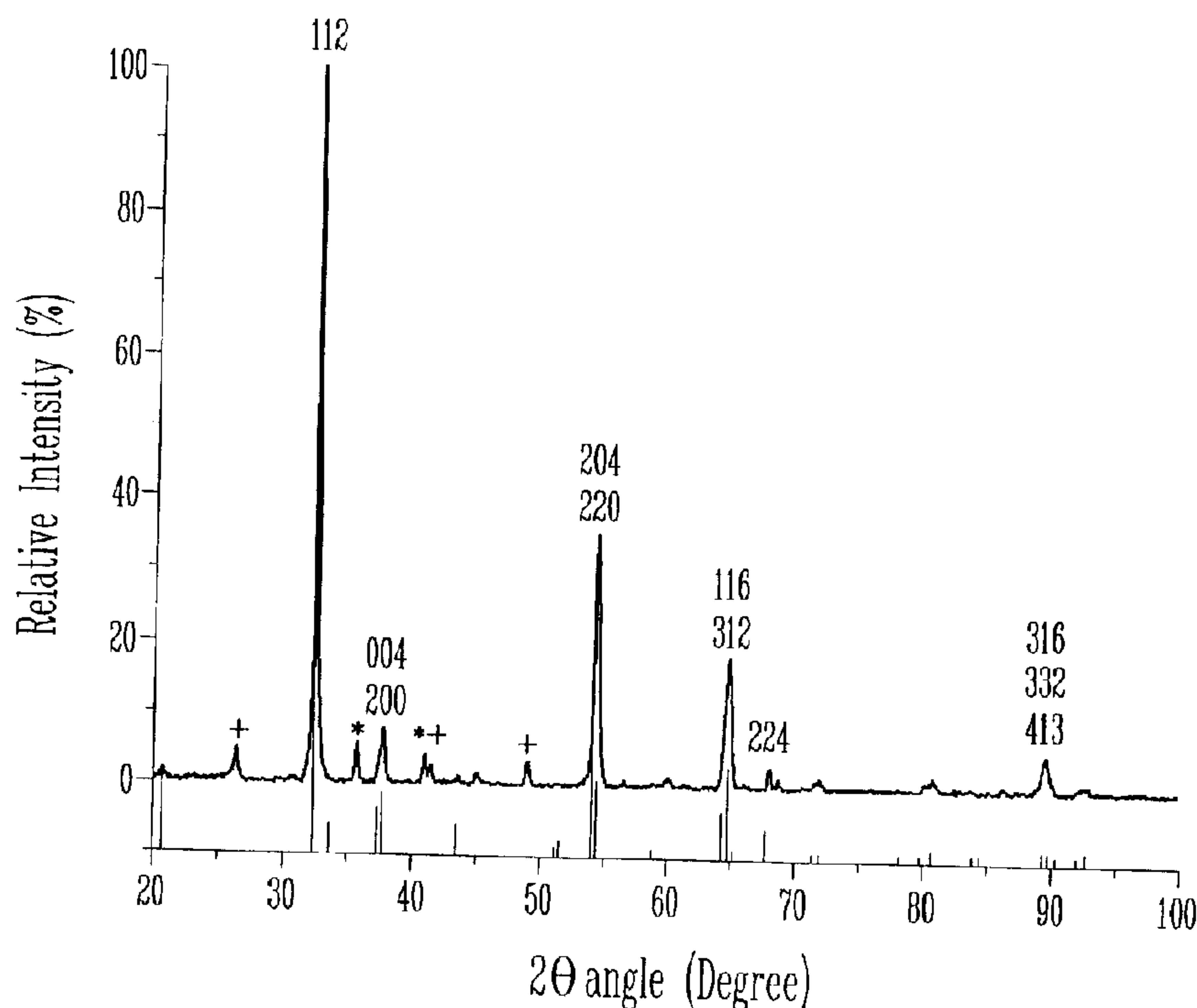




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(54) Title: PROCESSES FOR PREPARING CHALCOPYRITE-TYPE COMPOUNDS AND OTHER INORGANIC
COMPOUNDS



(57) **Abrégé/Abstract:**

There is provided a process for preparing compounds of formula $M^3M^1A_2$. The process comprises reacting a compound of formula $M^2M^1A_2$ with a compound of formula M^3X_2 , in the presence of at least one coordinating solvent. M^1 can be chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ; M^2 can be chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$; M^3 can be chosen from Cu^+ , Ag^+ , Li^+ , Na^+ , K^+ , Cs^+ , Rb^+ , Fr^+ , Au^+ , and Hg^+ ; A can be chosen from S and Se; and X_2 can be chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , and CN^- . Such compounds can be used for various purposes in the field of electrochemistry.

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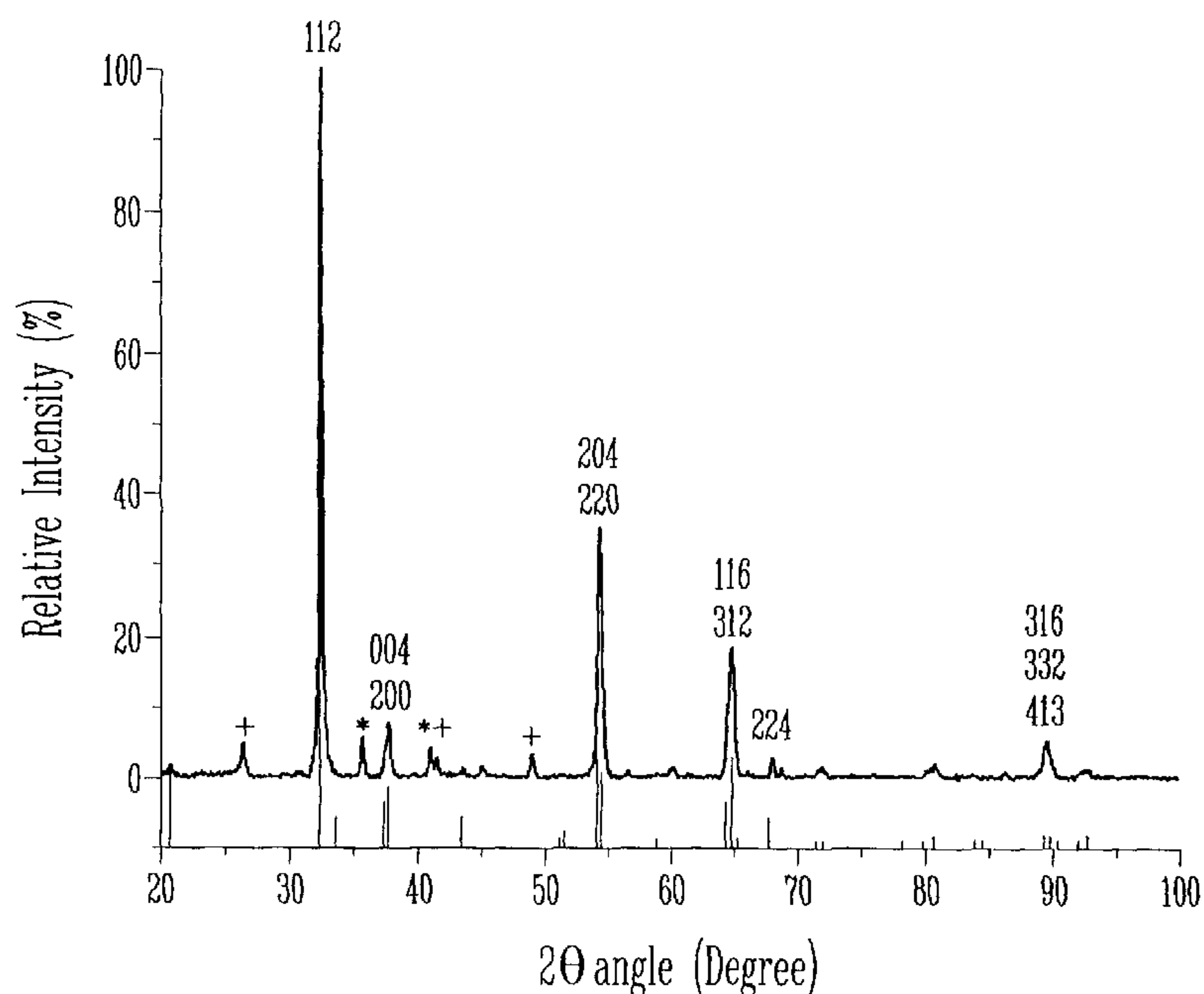
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(54) Title: PROCESSES FOR PREPARING CHALCOPYRITE-TYPE COMPOUNDS AND OTHER INORGANIC COMPOUNDS



(57) Abstract: There is provided a process for preparing compounds of formula $M^3M^1A_2$. The process comprises reacting a compound of formula $M^2M^1A_2$ with a compound of formula M^3X^2 , in the presence of at least one coordinating solvent. M^1 can be chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ; M^2 can be chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$; M^3 can be chosen from Cu^+ , Ag^+ , Li^+ , Na^+ , K^+ , Cs^+ , Rb^+ , Fr^+ , Au^+ , and Hg^+ ; A can be chosen from S and Se; and X^2 can be chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , and CN^- . Such compounds can be used for various purposes in the field of electrochemistry.

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PROCESSES FOR PREPARING CHALCOPYRITE-TYPE COMPOUNDS AND OTHER INORGANIC COMPOUNDS

TECHNICAL FIELD

The present invention relates to improvements in the field of preparation of inorganic compounds. In particular, this invention relates to the preparation of chalcopyrite-type compounds and other inorganic compounds such as compounds of families III-V or II-VI.

BACKGROUND OF THE INVENTION

So far, several attempts have been made so as to provide an efficient process for preparing chalcopyrite-type compounds (such as CuInS_2 , CuInSe_2 , AgInS_2 , etc.) and other inorganic compounds such as compounds of families III-V or II-VI (for example InP , GaN , CdS , CdSe , etc.). Many of these proposed processes were related to the preparation of nanocrystalline compounds. However, several of the proposed solutions were related to costly and tedious processes. These processes often required costly reagents or comprised several steps. Some of these steps were also carried out under toxic conditions. Some colloidal processes have also been proposed but they often lead to compounds which are not highly crystalline.

Czekelius *et al.* in *Advanced Materials*, 1999, vol. 11(8), 643-646, describe a process for preparing nanocrystalline CuInS_2 . This two-step process, however, requires the use of costly reagents. Also, this process uses phosphites which may form a resistive layer at the surface of the obtained CuInS_2 . Such a resistive layer may eventually cause a diminution of absorption of the visible light and a significant ohmic drop in a device incorporating such a material.

It would therefore be highly desirable to be provided with a process that would overcome the above-mentioned drawbacks.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide a process that would overcome the prior art drawbacks.

It is also another object of the present invention to provide a process for preparing chalcopryrite-type compounds, such as nanocrystalline chalcopryrite-type compounds, easily and at low costs.

It is also another object of the present invention to provide a process for preparing chalcopryrite-type compounds, such as nanocrystalline chalcopryrite-type compounds, which are highly crystalline.

It is also another object of the present invention to provide a process for preparing compounds of families III-V or II-VI easily and at low costs.

It is also another object of the present invention to provide a process for preparing nanocrystalline compounds of families III-V or II-VI easily and at low costs.

According to one aspect of the invention, there is provided a process for preparing a compound of formula $M^3M^1A_2$. The process comprises reacting a compound of formula $M^2M^1A_2$ with a compound of formula M^3X^2 , in the presence of at least one coordinating solvent, in order to obtain the compound of formula $M^3M^1A_2$,

wherein

M^1 is chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ;

M^2 is chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, wherein each T^1 independently represents a C_1 - C_6 alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a C_1 - C_6 alkyl which is linear or branched;

M^3 is chosen from Cu^+ , Ag^+ , Li^+ , Na^+ , K^+ , Cs^+ , Rb^+ , Fr^+ , Au^+ , and Hg^+ ;

A is chosen from S, Se, and, Te; and

X^2 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- .

According to another aspect of the invention, there is provided a process for preparing a compound of formula $M^3M^1A_2$. The process comprises:

- reacting a compound of formula $M^1(X^1)_3$ with a compound of formula $(M^2)_2A$, in the presence of at least one coordinating solvent, in order to obtain a compound of formula $M^2M^1A_2$;

- reacting the compound of formula $M^2M^1A_2$ with a compound of formula M^3X^2 , in the presence of the at least one coordinating solvent, at least one another coordinating solvent, or mixtures thereof, in order to obtain the compound of formula $M^3M^1A_2$,

wherein

M^1 is chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ;

M^2 is chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, wherein each T^1 independently represents a C_1 - C_6 alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a C_1 - C_6 alkyl which is linear or branched;

M^3 is chosen from Cu^+ , Ag^+ , Li^+ , Na^+ , K^+ , Cs^+ , Rb^+ , Fr^+ , Au^+ , and Hg^+ ;

A is chosen from S, Se, and Te;

X^1 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- ; and

X^2 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- .

It was found that the above-mentioned processes are very effective for preparing, at low costs, compounds defined by the formula $M^3M^1A_2$. In fact, this process is simple and can be rapidly carried out without requiring complicated steps. In fact, this process can be carried out without the use of costly reagents. Moreover, this process can permit to avoid carrying steps under toxic conditions such as a H_2S atmosphere. Such a process can also permit to obtain compounds of high purity and highly crystalline such as nanocrystalline compounds. It was also found that such a process is environment friendly and can be carried out rapidly. Moreover, it can be carried out in anhydrous conditions and considerably reduce the risks of formation of metal oxides.

According to another aspect of the invention, there is provided a process for preparing $CuInS_2$. The process comprises:

- reacting a compound of formula M^2InS_2 with a compound of formula CuX^2 , in the presence of at least one coordinating solvent, in order to obtain $CuInS_2$,

wherein

M^2 is chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, wherein each T^1 independently represents a C_1 - C_6 alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a C_1 - C_6 alkyl which is linear or branched; and

X^2 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- .

According to another aspect of the invention, there is provided a process for preparing $CuInS_2$. The process comprises:

- reacting $\text{In}(\text{X}^1)_3$ with a compound of formula $(\text{M}^2)_2\text{S}$, in the presence of at least one coordinating solvent, in order to obtain a compound of formula M^2InS_2 ; and

- reacting the compound of formula M^2InS_2 with a compound of formula CuX^2 , in the presence of the at least one coordinating solvent, at least one another coordinating solvent, or mixtures thereof, in order to obtain CuInS_2

wherein

M^2 is chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(\text{T}^1)_3\text{Si}^-$, and $\text{N}(\text{T}^2)_4^+$, wherein each T^1 independently represents a $\text{C}_1\text{-C}_6$ alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a $\text{C}_1\text{-C}_6$ alkyl which is linear or branched;

X^1 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- ; and

X^2 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- .

According to another aspect of the present invention, there is provided a process for preparing a compound of formula $\text{M}^3(\text{M}^5, \text{M}^1)\text{A}_2$. The process comprises reacting a compound of formula $\text{M}^2(\text{M}^5, \text{M}^1)\text{A}_2$ with a compound of formula M^3X^2 , in the presence of at least one coordinating solvent, in order to obtain the compound of formula $\text{M}^3(\text{M}^5, \text{M}^1)\text{A}_2$,

wherein

M^1 is chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ;

M^2 is chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(\text{T}^1)_3\text{Si}^-$, and $\text{N}(\text{T}^2)_4^+$, wherein each T^1 independently represents a $\text{C}_1\text{-C}_6$ alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a $\text{C}_1\text{-C}_6$ alkyl which is linear or branched;

M^3 is chosen from Cu^+ , Ag^+ , Li^+ , Na^+ , K^+ , Cs^+ , Rb^+ , Fr^+ , Au^+ , and Hg^+ ;

M^5 is chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ;

A is chosen from S, Se, and, Te; and

X^2 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- .

According to another aspect of the invention, there is provided a process for preparing a compound of formula $M^3(M^5, M^1)A_2$. The process comprises:

- reacting together a compound of formula $M^1(X^1)_3$, a compound of formula $M^5(X^3)_3$, and a compound of formula $(M^2)_2A$, in the presence of at least one coordinating solvent, in order to obtain a compound of formula $M^2(M^5, M^1)A_2$;

- reacting the compound of formula $M^2(M^5, M^1)A_2$ with a compound of formula M^3X^2 , in the presence of the at least one coordinating solvent, at least one another coordinating solvent, or mixtures thereof, in order to obtain the compound of formula $M^3(M^5, M^1)A_2$,

wherein

M^1 is chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ;

M^2 is chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, wherein each T^1 independently represents a C_1 - C_6 alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a C_1 - C_6 alkyl which is linear or branched;

M^3 is chosen from Cu^+ , Ag^+ , Li^+ , Na^+ , K^+ , Cs^+ , Rb^+ , Fr^+ , Au^+ , and Hg^+ ;

M^5 is chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ;

A is chosen from S, Se, and Te;

X^1 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- ;

X^2 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- ; and

X^3 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- .

According to another aspect of the invention, there is provided a process for preparing a compound of formula M^4A . The process comprises reacting a compound of formula M^4X_2 with a compound of formula $(M^2)_2A$, in the presence of at least one coordinating solvent, in order to obtain the compound of formula M^4A ,

wherein

M^2 is chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, wherein each T^1 independently represents a C_1 - C_6 alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a C_1 - C_6 alkyl which is linear or branched;

M^4 is chosen from Cd^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Hg^{2+} , Mg^{2+} , Mn^{2+} , Fe^{2+} , and Pb^{2+} ;

A is chosen from S, Se, and Te; and

X is chosen Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- .

It was found that the above-mentioned process is very effective to prepare, at low costs, compounds represented by formula M^4A . In fact, this process is simple and can be rapidly carried out without requiring complicated steps. In fact, this process can be carried out without the use of costly reagents. Moreover, this process can permit to avoid carrying steps under toxic

conditions such as a H₂S atmosphere. Such a process can also permit to obtain compounds of high purity and highly crystalline such as nanocrystalline compounds. It was also found that such a process is environment friendly and can be carried out rapidly. Moreover, it can be carried out in anhydrous conditions and considerably reduce the risks of formation of metal oxides.

According another aspect of the invention, there is provided a process for preparing a compound of formula M¹A. The process comprises reacting together a compound of formula M¹X₃ and a compound of formula (M²)₃A in the presence of at least one coordinating solvent, so as to obtain the compound of formula M¹A,

wherein

M¹ is chosen from B³⁺, Al³⁺, Ga³⁺, In³⁺, Tl³⁺, Fe³⁺, and Au³⁺;

M² is chosen from Li⁺, Na⁺, K⁺, Cs⁺, (T¹)₃Si⁻, and N(T²)₄⁺, wherein each T¹ independently represents a C₁-C₆ alkyl which is linear or branched, and each T² independently represents a hydrogen atom, or a C₁-C₆ alkyl which is linear or branched;

A is chosen from N, P, and As; and

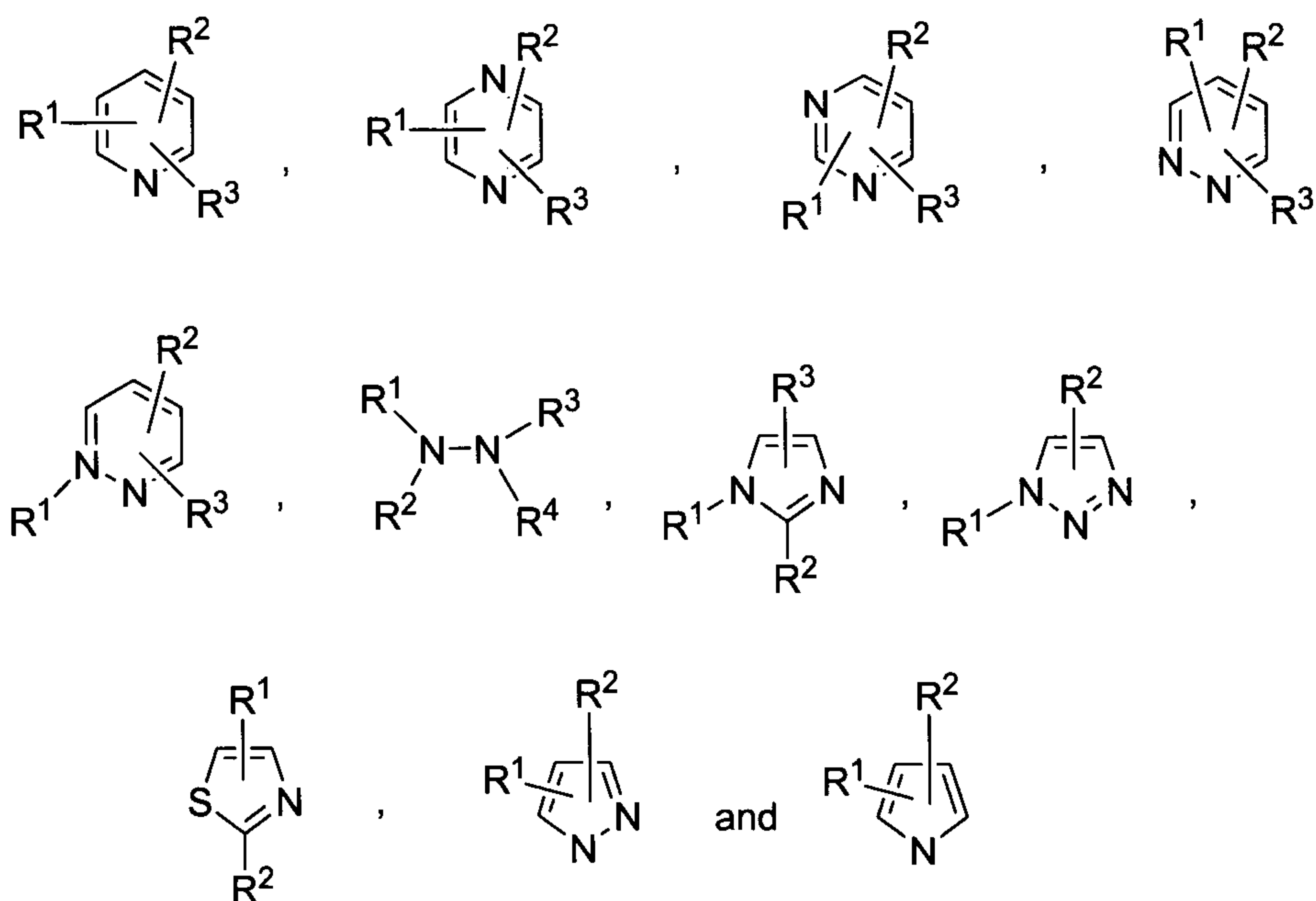
X is chosen from Cl⁻, Br⁻, I⁻, F⁻, CH₃COO⁻, NO₃⁻, OCN⁻, SCN⁻, and CN⁻.

It has been found that the above-mentioned process is very effective to prepare, at low costs, compound represented by formula M¹A. In fact, this process is simple and can be rapidly carried out without requiring complicated steps. In fact, this process can be carried out without the use of costly reagents. Such a process can also permit to obtain compounds of high purity and highly crystalline such as nanocrystalline compounds. It was also found that such a process is environment friendly and can be carried out rapidly. Moreover, it can be carried out in anhydrous conditions and considerably reduce the risks of formation of metal oxides.

The coordinating solvent can be chosen from N-methylimidazole, pyrazole, triazole, tetrazole, and mixtures thereof. As example, the coordinating solvent can be N-methylimidazole. A further solvent can be added to the coordinating solvent. The further solvent can be chosen from acetonitrile, dichloromethane, C₁-C₆ alcohols (such as ethanol, isopropanol), dimethylsulfoxide, C₂-C₁₀ amides (such as dimethylformamide), C₃-C₁₀ linear carbonates (such as dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate), C₃-C₁₀ cyclic carbonates (such as ethylene carbonate, propylene carbonate), C₁-C₆ alkylurea (such as tetramethylurea), ionic liquids, a room temperature molten salt, and mixtures thereof.

The another coordinating solvent can be chosen from N-methylimidazole, pyrazole, triazole, tetrazole, and mixtures thereof. As example, the another coordinating solvent can be N-methylimidazole. A further solvent can be added to the another coordinating solvent. The further solvent can be chosen from acetonitrile, dichloromethane, C₁-C₆ alcohols (such as ethanol, isopropanol), dimethylsulfoxide, C₂-C₁₀ amides (such as dimethylformamide), C₃-C₁₀ linear carbonates (such as dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate), C₃-C₁₀ cyclic carbonates (such as ethylene carbonate, propylene carbonate), C₁-C₆ alkylurea (such as tetramethylurea), ionic liquids, a room temperature molten salt, and mixtures thereof.

Alternatively, the coordinating solvent and/or the another coordinating solvent can be chosen from:



wherein

R¹, R², R³ and R⁴ are the same or different and are chosen from a hydrogen atom, C₁-C₁₂ alkyl which is linear or branched, C₃-C₁₂ cycloalkyl, C₁-C₁₂ heterocyclyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₆-C₁₂ aryl, C₆-C₂₀ aralkyl, C₆-C₂₀ alkylaryl, and C₁-C₁₂ heteroaryl,

R¹ and R² may be joined together to form a 5 to 14 membered heterocyclyl or is a part of polymer chain or network.

Some of these compounds represented by these structures may be in a solid form at room temperature and may be heated so as to be in liquid form or they can alternatively be mixed with another organic solvent which is liquid at room temperature.

The compounds of formula M³M¹A₂ can be, for example, chosen from CuInS₂, CuInSe₂, CuInTe₂, AuInS₂, AuInSe₂, AuInTe₂, AgInS₂, AgInSe₂, AgInTe₂, HgInS₂, HgInSe₂, HgInTe₂, LiInS₂, LiInSe₂, LiInTe₂, CuGaS₂, CuGaSe₂, CuGaTe₂, AuGaS₂, AuGaSe₂, AuGaTe₂, AgGaS₂, AgGaSe₂, AgGaTe₂, HgGaS₂, HgGaSe₂, HgGaTe₂, CuAlS₂, CuAlSe₂, CuAlTe₂, AuAlS₂, AuAlSe₂, AuAlTe₂, AgAlS₂, AgAlSe₂, AgAlTe₂, HgAlS₂, HgAlSe₂, HgAlTe₂, CuAuS₂, CuAuSe₂, CuAuTe₂, AuAuS₂, AuAuSe₂, AuAuTe₂, AgAuS₂, AgAuSe₂,

AgAuTe₂, HgAuS₂, HgAuSe₂, HgAuTe₂, LiFeS₂, LiFeSe₂, LiFeTe₂, AgFeS₂, AgFeSe₂, AgFeTe₂, LiGaS₂, LiGaSe₂, and LiGaTe₂. They can also be chosen from CuInS₂, AuInS₂, AgInS₂, AgInSe₂, CuGaS₂, AuGaS₂, CuAlS₂, and LiFeS₂. In one particular embodiment, they may be, as example, CuInS₂ or AgInS₂.

In the processes for preparing compounds of formula M³M¹A₂, M² can be, as example, chosen from Li⁺, Na⁺, and K⁺; and X² can be chosen from Cl⁻, Br⁻, I⁻, F⁻, and CN⁻. In another embodiment, M² can be Li⁺ and X² can be Cl⁻. In another embodiment, M² can be Li⁺ and X² can be I⁻. In another embodiment, M² can be Li⁺ and X² can be CN⁻.

In one example, M¹ can be In³⁺; M² can be chosen from Li⁺, Na⁺, and K⁺; M³ can be chosen from Cu⁺, and Ag⁺; A can be chosen from S and Se; and X² can be chosen from Cl⁻, Br⁻, I⁻, F⁻, and CN⁻.

In another example, M¹ can be In³⁺; M² can be chosen from Li⁺, Na⁺, and K⁺; M³ can be chosen from Cu⁺, and Ag⁺; A can be S; and X² can be chosen from Cl⁻, and CN⁻.

In another example, M¹ can be chosen from B³⁺, Al³⁺, Ga³⁺, In³⁺, Tl³⁺, Fe³⁺, and Au³⁺; M² can be chosen from Li⁺, Na⁺, K⁺, Cs⁺, (T¹)₃Si⁻, and N(T²)₄⁺, wherein each T¹ independently represents a C₁-C₆ alkyl which is linear or branched, and each T² independently represents a hydrogen atom, or a C₁-C₆ alkyl which is linear or branched; M³ can be chosen from Ag⁺, Li⁺, Na⁺, K⁺, Cs⁺, Rb⁺, Fr⁺, Au⁺, and Hg⁺; A can be chosen from S and Se; and X² can be chosen from Cl⁻, Br⁻, I⁻, F⁻, CH₃COO⁻, NO₃⁻, and CN⁻.

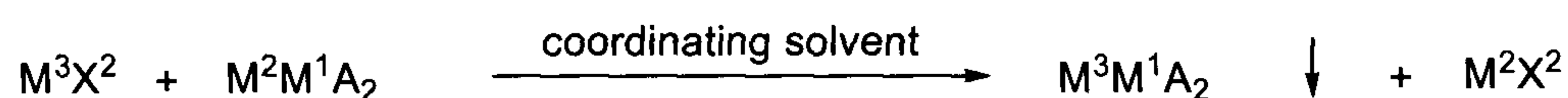
In another example, M¹ can be chosen from B³⁺, Al³⁺, Ga³⁺, In³⁺, Tl³⁺, Fe³⁺, and Au³⁺; M² can be chosen from Li⁺, Na⁺, K⁺, Cs⁺, (T¹)₃Si⁻, and N(T²)₄⁺, wherein each T¹ independently represents a C₁-C₆ alkyl which is linear or branched, and each T² independently represents a hydrogen atom, or a C₁-C₆ alkyl which is linear or branched; M³ can be chosen from Cu⁺, Ag⁺, Li⁺, Na⁺,

K^+ , Cs^+ , Rb^+ , Fr^+ , Au^+ , and Hg^+ ; A can be Se; and X^2 can be chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , and CN^- .

In another example, M^1 can be chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ; M^2 can be chosen from Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, wherein each T^1 independently represents a C_1 - C_6 alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a C_1 - C_6 alkyl which is linear or branched; M^3 can be chosen from Cu^+ , Ag^+ , Li^+ , Na^+ , K^+ , Cs^+ , Rb^+ , Fr^+ , Au^+ , and Hg^+ ; A can be chosen from S and Se; and X^2 can be chosen from Br^- , I^- , F^- , CH_3COO^- , NO_3^- , and CN^- .

In another example, when $M^3M^1A_2$ is $CuInS_2$, M^2 can be chosen from Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$. In a further example when $M^3M^1A_2$ is $CuInS_2$, X^2 can be chosen from Br^- , I^- , F^- , CH_3COO^- , NO_3^- , and CN^- . In still a further example, when $M^3M^1A_2$ is $CuInS_2$, M^2 can be chosen from Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, and X^2 can be chosen from Br^- , I^- , F^- , CH_3COO^- , NO_3^- , and CN^- .

When preparing a compound of formula $M^3M^1A_2$, the reaction between M^3X^2 and $M^2M^1A_2$ can be carried out as follows:



For example, M^3X^2 and $M^2M^1A_2$ can be reacted together at a temperature of about $-10\text{ }^\circ\text{C}$ to about $180\text{ }^\circ\text{C}$. They can also be reacted together at other ranges of temperature such as about $-5\text{ }^\circ\text{C}$ to about $50\text{ }^\circ\text{C}$, about $0\text{ }^\circ\text{C}$ to about $40\text{ }^\circ\text{C}$, about 5 to about $35\text{ }^\circ\text{C}$, or about 15 to about $30\text{ }^\circ\text{C}$. Alternatively, M^3X^2 and $M^2M^1A_2$ can be reacted together at room temperature.

For example, $M^3M^1A_2$ can be precipitated, and separated from a mixture comprising the coordinating solvent and a by-product solubilized therein, by means of a filtration. Such a by-product can be M^2X^2 . Alternatively, $M^3M^1A_2$ can be, for example, precipitated, and separated from the coordinating solvent and the compound of formula M^2X^2 , by means of a filtration.

In one embodiment, the compound of formula $M^2M^1A_2$ can be reacted with the compound of formula M^3X^2 by adding the compound of formula M^3X^2 to a composition comprising the compound of formula $M^2M^1A_2$ and the coordinating solvent.

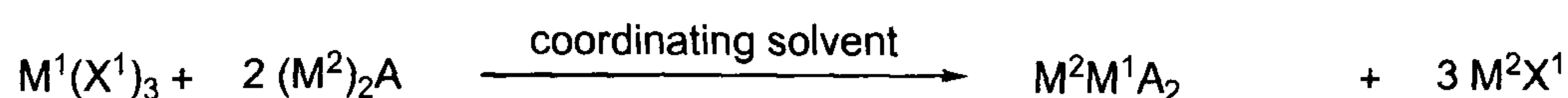
In another embodiment, the compound of formula $M^2M^1A_2$ can be reacted with the compound of formula M^3X^2 by adding a composition comprising the compound of formula M^3X^2 and the coordinating solvent to a composition comprising the compound of formula $M^2M^1A_2$ and the coordinating solvent. For example, the composition comprising the compound of formula M^3X^2 and the coordinating solvent can be added dropwise to the composition comprising the compound of formula $M^2M^1A_2$ and the coordinating solvent.

In another embodiment, the compound of formula $M^2M^1A_2$ can be reacted with the compound of formula M^3X^2 by adding the compound of formula M^3X^2 to a composition comprising the compound of formula $M^2M^1A_2$ and the another coordinating solvent.

In another embodiment, the compound of formula $M^2M^1A_2$ can be reacted with the compound of formula M^3X^2 by adding a composition comprising the compound of formula M^3X^2 and the another coordinating solvent to a composition comprising the compound of formula $M^2M^1A_2$ and the another coordinating solvent. For example, the composition comprising the compound of formula M^3X^2 and the another coordinating solvent can be added dropwise to the composition comprising the compound of formula $M^2M^1A_2$ and the another coordinating solvent.

For example, the compound of formula $M^2M^1A_2$ can be reacted with the compound of formula M^3X^2 in the presence of the coordinating solvent.

The reaction between $M^1(X^1)_3$ and $(M^2)_2A$ can be, as example, carried out as follows:



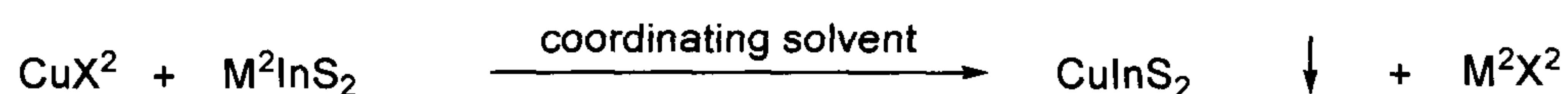
For example, $M^1(X^1)_3$ and $(M^2)_2A$ can be reacted together at a temperature of about $-10\text{ }^{\circ}\text{C}$ to about $180\text{ }^{\circ}\text{C}$. They can also be reacted together at other ranges of temperature such as about $-5\text{ }^{\circ}\text{C}$ to about $50\text{ }^{\circ}\text{C}$, about $0\text{ }^{\circ}\text{C}$ to about $40\text{ }^{\circ}\text{C}$, about 5 to about $35\text{ }^{\circ}\text{C}$, or about 15 to about $30\text{ }^{\circ}\text{C}$. Alternatively, $M^1(X^1)_3$ and $(M^2)_2A$ can be reacted together at room temperature.

In one embodiment, the compound of formula $M^1(X^1)_3$, the compound of formula $(M^2)_2A$, and the coordinating solvent can be mixed together and agitated in order to obtain the compound of formula $M^2M^1A_2$. Agitation can be provided by various techniques known to the person skilled in the art such as sonic bath, stirring with various agitation means, etc.

In another embodiment, a composition comprising the compound of formula $M^1(X^1)_3$ and the coordinating solvent can be mixed with a composition comprising the compound of formula $(M^2)_2A$ and the coordinating solvent.

When preparing a compound of formula $M^3M^1A_2$, X^1 and X^2 can be different. Alternatively, they can be the same. For example, X^1 can be chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , and NO_3^- . Alternatively, it can be chosen from Cl^- , and I^- or it can be Cl^- .

In one embodiment, the compound of formula $M^3M^1A_2$ can be CuInS_2 . When preparing such a compound by using compounds of formulas CuX^2 and M^2InS_2 , the latter two can be reacted together as follows:



For example, CuX^2 and M^2InS_2 can be reacted together at a temperature of about $-10\text{ }^{\circ}\text{C}$ to about $180\text{ }^{\circ}\text{C}$. They can also be reacted together at other ranges of temperature such as about $-5\text{ }^{\circ}\text{C}$ to about $50\text{ }^{\circ}\text{C}$, about $0\text{ }^{\circ}\text{C}$ to about $40\text{ }^{\circ}\text{C}$, about 5 to about $35\text{ }^{\circ}\text{C}$, or about 15 to about $30\text{ }^{\circ}\text{C}$. Alternatively, CuX^2 and M^2InS_2 can be reacted together at room temperature.

For example, CuInS_2 can be precipitated, and separated from a mixture comprising the coordinating solvent and a by-product solubilized therein, by

means of a filtration. Such a by-product can be M^2X^2 . Alternatively, $CuInS_2$ can be, for example, precipitated, and separated from the coordinating solvent and the compound of formula M^2X^2 , by means of a filtration.

In one embodiment, the compound of formula M^2InS_2 can be reacted with the compound of formula CuX^2 by adding the compound of formula CuX^2 to a composition comprising the compound of formula M^2InS_2 and the coordinating solvent.

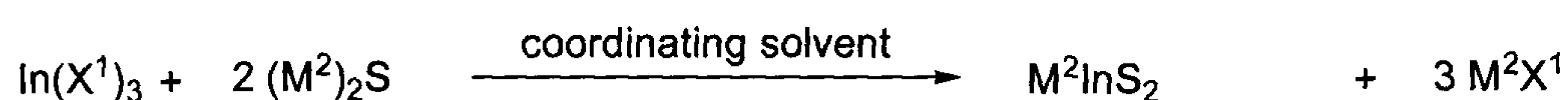
In another embodiment, the compound of formula M^2InS_2 can be reacted with the compound of formula CuX^2 by adding a composition comprising the compound of formula CuX^2 and the coordinating solvent to a composition comprising the compound of formula M^2InS_2 and the coordinating solvent. For example, the composition comprising the compound of formula CuX^2 and the coordinating solvent can be added dropwise to the composition comprising the compound of formula M^2InS_2 and the coordinating solvent. X^2 can be, as example, chosen from Cl^- and I^- or it can be Cl^- . For example, the compound of formula M^2InS_2 can be reacted with the compound of formula CuX^2 in the presence of the coordinating solvent. The $CuInS_2$ obtained can be nanocrystalline.

In one embodiment, the compound of formula M^2InS_2 can be reacted with the compound of formula CuX^2 by adding the compound of formula CuX^2 to a composition comprising the compound of formula M^2InS_2 and the another coordinating solvent.

In another embodiment, the compound of formula M^2InS_2 can be reacted with the compound of formula CuX^2 by adding a composition comprising the compound of formula CuX^2 and the another coordinating solvent to a composition comprising the compound of formula M^2InS_2 and the another coordinating solvent. For example, the composition comprising the compound of formula CuX^2 and the another coordinating solvent can be added dropwise to the composition comprising the compound of formula M^2InS_2 and the another coordinating solvent.

X^2 can be, as example, chosen from Cl^- and I^- or it can be Cl^- . For example, the compound of formula M^2InS_2 can be reacted with the compound of formula CuX^2 in the presence of the coordinating solvent. The $CuInS_2$ obtained can be nanocrystalline.

When preparing $CuInS_2$, $In(X^1)_3$ can be reacted with the compound of formula $(M^2)_2S$, in the presence of the coordinating solvent. Such a reaction can be carried out as follows:



For example, $In(X^1)_3$ and $(M^2)_2S$ can be reacted together at a temperature of about $-10\text{ }^\circ\text{C}$ to about $180\text{ }^\circ\text{C}$. They can also be reacted together at other ranges of temperature such as about $-5\text{ }^\circ\text{C}$ to about $50\text{ }^\circ\text{C}$, about $0\text{ }^\circ\text{C}$ to about $40\text{ }^\circ\text{C}$, about 5 to about $35\text{ }^\circ\text{C}$, or about 15 to about $30\text{ }^\circ\text{C}$. Alternatively, $In(X^1)_3$ and $(M^2)_2S$ can be reacted together at room temperature.

In one embodiment, the compound of formula $In(X^1)_3$, the compound of formula $(M^2)_2S$, and the coordinating solvent can be mixed together and agitated in order to obtain $CuInS_2$. Agitation can be provided by various techniques known to the person skilled in the art such as sonic bath, stirring with various agitation means, etc.

In another embodiment, a composition comprising the compound of formula $In(X^1)_3$ and the coordinating solvent can be mixed with a composition comprising the compound of formula $(M^2)_2S$ and the coordinating solvent.

When preparing $CuInS_2$, X^1 and X^2 can be different. Alternatively, they can be the same. For example, X^1 can be chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , and NO_3^- . Alternatively, it can be chosen from Cl^- , and I^- or it can be Cl^- . For example, X^2 can be chosen from Cl^- , and I^- or it can be I^- .

The compounds of formula $M^3(M^5, M^1)A_2$ can be, for example, chosen from $Cu(Al, In)S_2$, $Ag(Al, In)S_2$, $Cu(Ga, In)S_2$, $Cu(Al, In)Se_2$, $Ag(Al, In)Se_2$, and $Cu(Ga, In)Se_2$. They can also be chosen from $Cu(Al, In)S_2$, $Ag(Al, In)S_2$, and

Cu(Ga,In)S₂, or from Cu(Al,In)Se₂, Ag(Al,In)Se₂, and Cu(Ga,In)Se₂. For example, the molar ratio M⁵/M¹ can have various values such as less than about 1, less than about 0.75, less than about 0.5, less than about 0.25, less than about 0.1, less than about 0.05, less than about 0.04, less than about 0.02, less than about 0.01, less than about 0.002, or less than about 0.001.

For example, when preparing a compound of formula M³(M⁵,M¹)A₂, the compound of formula M²(M⁵,M¹)A₂ can be reacted with the compound of formula M³X² in the presence of the coordinating solvent. For example, M³X² and M²(M⁵,M¹)A₂ can be reacted together at a temperature of about -10 °C to about 180 °C. They can also be reacted together at other temperatures such as about -5 °C to about 50 °C, about 0 °C to about 40 °C, about 5 to about 35 °C, or about 15 to about 30 °C. Alternatively, M³X² and M²(M⁵,M¹)A₂ can be reacted together at room temperature. In one embodiment, M¹ can be different than M⁵. M¹ can also be the same than M⁵. In another embodiment, M² can be chosen from Li⁺, Na⁺, and K⁺; and X² can be chosen from Cl⁻, Br⁻, I⁻, F⁻, and CN⁻. In another embodiment, M² can be Li⁺ and X² can be Cl⁻. In a further embodiment, M² can be Li⁺ and X² can be I⁻. In still a further embodiment, M² can be Li⁺ and X² can be CN⁻. In another embodiment, M² can be chosen from Li⁺, Na⁺, and (CH₃)₃Si⁻. Alternatively, M² can be Li⁺.

When preparing a compound of formula M³(M⁵,M¹)A₂, M¹(X¹)₃, M⁵(X³)₃, and (M²)₂A can be, as example, reacted together at a temperature of about -10 °C to about 180 °C. They can also be reacted together at other ranges of temperature such as about -5 °C to about 50 °C, about 0 °C to about 40 °C, about 5 to about 35 °C, or about 15 to about 30 °C. Alternatively, M¹(X¹)₃, M⁵(X³)₃, and (M²)₂A can be reacted together at room temperature.

For example, when preparing a compound of formula M³(M⁵,M¹)A₂, X¹ and X² can be different. Alternatively, they can be the same. X¹, X², and X³ can also be the same. In one embodiment, X¹ can be chosen from Cl⁻, Br⁻, I⁻, F⁻, CH₃COO⁻, and NO₃⁻. In another embodiment, X¹ can be Cl⁻. In another embodiment, M¹ can be different than M⁵.

The compounds of formula M^4A can be, for example, chosen from CdS, CdSe, CdTe, CoS, CoSe, CoTe, NiS, NiSe, NiTe, MgS, MgSe, MgTe, MnS, MnSe, MnTe, FeS, FeSe, FeTe, ZnS, ZnSe, ZnTe, PbS, PbSe, PbTe, ZnS, ZnSe, and ZnTe. Alternatively, they can be chosen from CdS, CdSe, CdTe, CoS, and ZnSe.

When preparing a compound of formula M^4A by reacting a compound of formula M^4X_2 with a compound of formula $(M^2)_2A$, the reaction can be carried out as follows:



For example, M^4X_2 and $(M^2)_2A$ can be reacted together at a temperature of about -10 °C to about 180 °C. They can also be reacted together at other ranges of temperature such as about -5 °C to about 50 °C, about 0 °C to about 40 °C, about 5 to about 35 °C, or about 15 to about 30 °C. Alternatively, M^4X_2 and $(M^2)_2A$ can be reacted together at room temperature.

The compound of formula M^4A can be precipitated, and separated from a mixture comprising the coordinating solvent and a by-product solubilized therein, by means of a filtration. The by-product can be M^2X . The compound of formula M^4A can be precipitated, and separated from the coordinating solvent and the compound of formula M^2X , by means of a filtration.

In one embodiment, when preparing a compound of formula M^4A , X can be chosen from Cl^- , Br^- , I^- , and CN^- . Alternatively, it can be chosen from Cl^- , I^- , and CN^- . M^2 can be chosen from Li^+ , Na^+ , and $(CH_3)_3Si^-$.

The compounds of formula M^1A can be, for example, chosen from GaP, GaAs, GaN, InP, InAs, and InN. Alternatively, they can be chosen from GaAs and InP. When preparing a compound of formula M^1A by reacting a compound of formula M^1X_3 with a compound of formula $(M^2)_3A$, the reaction can be carried out as follows:



For example, M^1X_3 and $(M^2)_3A$ can be reacted together at a temperature of about $-10\text{ }^{\circ}\text{C}$ to about $180\text{ }^{\circ}\text{C}$. They can also be reacted together at other ranges of temperature such as about $-5\text{ }^{\circ}\text{C}$ to about $50\text{ }^{\circ}\text{C}$, about $0\text{ }^{\circ}\text{C}$ to about $40\text{ }^{\circ}\text{C}$, about 5 to about $35\text{ }^{\circ}\text{C}$, or about 15 to about $30\text{ }^{\circ}\text{C}$. Alternatively, M^1X_3 and $(M^2)_3A$ can be reacted together at room temperature.

The compound of formula M^1A can be precipitated, and separated from a mixture comprising the coordinating solvent and a by-product solubilized therein, by means of a filtration. The by-product can be M^2X . The compound of formula M^1A can be precipitated, and separated from the coordinating solvent and the compound of formula M^2X , by means of a filtration.

In one embodiment, when preparing a compound of formula M^1A , X can be chosen from Cl^- , Br^- , I^- , and CN^- . Alternatively, it can be chosen from Cl^- , I^- , and CN^- . M^2 can be chosen from Li^+ , Na^+ , and $(\text{CH}_3)_3\text{Si}^-$.

The processes of the present invention can further comprise drying the so-obtained compound or composition. They can be dried as example by centrifugation, heating, vacuum, or combinations thereof. The processes of the present invention can also further comprise annealing the so-obtained compound or composition. For example, they can be annealed at a temperature of at least about $75\text{ }^{\circ}\text{C}$. Alternatively, they can be annealed at various other temperatures such as at least about $100\text{ }^{\circ}\text{C}$, at least about $150\text{ }^{\circ}\text{C}$, at least about $200\text{ }^{\circ}\text{C}$, at least about $250\text{ }^{\circ}\text{C}$, at least about $300\text{ }^{\circ}\text{C}$, at least about $400\text{ }^{\circ}\text{C}$, or at least about $500\text{ }^{\circ}\text{C}$. The temperature can also be about $100\text{ }^{\circ}\text{C}$ to about $500\text{ }^{\circ}\text{C}$ or about $200\text{ }^{\circ}\text{C}$ to about $400\text{ }^{\circ}\text{C}$.

For example, the annealing treatment can be carried out over a period of at least about 30 minutes. Alternatively, the annealing treatment can be carried out over various periods of time such as at least about 45 minutes, at least about 60 minutes, at least about 90 minutes, at least about 120 minutes, or at

least about 180 minutes. The duration of the annealing treatment can also be about 60 minutes to about 180 minutes.

The annealing treatment can be, as example, carried out under vacuum. The vacuum can be at least about 50 mTorr or alternatively at least about 100 mTorr.

The compounds and compositions obtained via the various processes of the present invention can be nanocrystalline. The compounds obtained may also be in the form of particles having a diameter of less than 500 nm or alternatively of other values such as less than 250 nm or less than 100 nm. The compounds and compositions obtained are, as example, semiconducting material.

The processes of the present invention can further comprise preparing an electrode comprising the obtained compound or composition. These processes can also comprise mixing the obtained compound or composition with a binder so as to obtain a mixture suitable for the preparation of an electrode or mixing the obtained compound or composition with a binder so as to obtain a suitable precursor for the preparation of an electrode.

Alternatively, the processes of the present invention can comprise mixing the obtained compound or composition with a binder so as to obtain a mixture comprising the compound or composition and the binder, and preparing an electrode with the mixture. The mixture optionally comprises a solvent such as N-methylpyridinone. As example, a thin film of the mixture can be coated on a substrate in order to prepare the electrode. Suitable substrate can comprise a metal such as Mo, Au, Al, Cu, or mixtures thereof. The mixture can further comprise a conductivity enhancer such as carbon black, graphite, carbon nanotubes, or mixtures thereof. The binder can be any suitable polymers adapted to make such a preparation and suitable for the preparation an electrode. The person skilled in the art would clearly recognize that a plurality of various polymers can be used as binder. In a non-limitative manner, the

binder can be polyvinylidene fluoride (PVDF), poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), or mixtures thereof.

According to another aspect of the invention, there is provided a composition comprising at least two compounds, a first compound obtained by a process as previously defined, and a second compound obtained by a process as previously defined.

According to another aspect of the invention, there is provided a compound prepared according to a process previously defined for preparing $M^3M^1A_2$, wherein two different compounds of formula $M^1(X^1)_3$ are reacted with the compound of formula $(M^2)_2A$. As example, the two compounds of formula $M^1(X^1)_3$ can be $InCl_3$ or $GaCl_3$. They can be used in various proportions such as $InCl_3$ (90 %) and $GaCl_3$ (10 %), $InCl_3$ (95 %) and $GaCl_3$ (5%), based on the molar ratio. Such a compound can be chosen from $Cu(Al,In)S_2$, $Ag(Al,In)S_2$, $Cu(Ga,In)S_2$, $Cu(Al,In)Se_2$, $Ag(Al,In)Se_2$, $Cu(Ga,In)Se_2$, and mixtures thereof. It was found that the obtained compounds can have a high purity and can be prepared at low costs. Moreover, it was found that the obtained compounds can be highly crystalline.

According to another aspect of the invention, there is provided the use of a process as defined in the present invention, for the preparation of a nanocrystalline compound or composition. Such a compound or composition can be used in a solar cell.

According to another aspect of the invention, there is provided the use of a process as defined in the present invention, for the preparation of a compound or composition, suitable for use in the field of optoelectronic.

According to another aspect of the invention, there is provided the use of a process as defined in the present invention, for the preparation of a compound or composition, suitable for use in the preparation of a photodiode, a transistor, a sensor, a laser diode, or a digital light projector.

According to another aspect of the invention, there is provided a method for preparing a nanocrystalline compound or composition, suitable for use in a solar cell. The method comprises carrying out a process as defined in the present invention

According to another aspect of the invention, there is provided a method for preparing a compound or composition suitable for use in the field of optoelectronic, the method comprising carrying out a process as defined in the present invention.

According to another aspect of the invention, there is provided a method for preparing a compound or composition suitable for use in the preparation of a photodiode, a transistor, a sensor, a laser diode, or a digital light projector. The method comprises carrying out a process as defined in the present invention.

According to another aspect of the invention, there is provided a composition comprising at least one compound obtained by a process as defined in the present invention and a binder.

According to another aspect of the invention, there is provided a composition comprising at least two compounds, a first compound obtained by a process as defined in the present invention, and a second compound obtained by a process as defined in the present invention.

According to another aspect of the invention, there is provided the use of a compound or composition as defined in the present invention, in the manufacture of an optoelectronic device, a photoluminescent device or a wireless communication device.

According to another aspect of the invention, there is provided a method for preparing a solar cell, a photodiode, a transistor, a sensor, a laser diode or a digital light projector, comprising using a compound or composition as defined in the present invention, as a component or precursor in the preparation thereof.

According to another aspect of the invention, there is provided a method for preparing an optoelectronic device, a photoluminescent device or a wireless communication device, comprising using a compound or composition in the present invention, as a component or precursor in the preparation thereof.

According to another aspect of the invention, there is provided a nanocrystalline compound suitable for use in a solar cell. The compound is prepared by a process as defined in the present invention.

According to another aspect of the invention, there is provided a nanocrystalline compound suitable for use in the field of optoelectronic. The compound is prepared by a process as defined in the present invention.

According to another aspect of the invention, there is provided a nanocrystalline compound suitable for use in the preparation of a photodiode, a transistor, a sensor, a laser diode, or a digital light projector. The compound is prepared by a process as defined in the present invention.

According to another aspect of the invention, there is provided a solar cell, a photodiode, a transistor, a sensor, a laser diode or a digital light projector, comprising a compound or composition as defined in the present invention.

According to another aspect of the invention, there is provided an optoelectronic device, a photoluminescent device or a wireless communication device comprising a compound or composition as defined in the present invention.

According to another aspect of the invention, there is provided a compound or composition obtained by a process as defined in the present invention.

The compounds or compositions of the present invention can convert light to an electrical signal. They can also act as detectors in CDROM drives, DVD players and barcode scanners and represent the key functional element in solar panels, scanners and digital cameras. These compounds or compositions can also be useful in photovoltaic devices such as thin film solar

cells. They can also be used in transistors that can be found in all electronic devices and systems. They can be used as the primary active element that acts as a switch, logic element or amplifier. The compounds or compositions of the present invention can also be used in laser diodes that can be found in CDROM drives, DVD players and barcode scanners. They can provide a compact and efficient source of coherent light. In optoelectronic devices, the compounds or compositions of the present invention can be used as transmitters and receivers so as to provide the infrared signals that can propagate over large distances along optical fibers. These transmitters can enable rapid transmission of large amount of digital information across the world through the Internet.

According to another aspect of the invention, there is provided a composition comprising InCl_3 and a coordinating solvent as defined in the present invention. The solvent can be N-methylimidazole.

According to another aspect of the invention, there is provided the use of the composition comprising InCl_3 and a coordinating solvent as defined in the present invention, as an anhydrous source of InCl_3 .

According to another aspect of the present invention, there is provided the use of a coordinating solvent as defined in the present invention, for preparing a InCl_3 -based composition, wherein the composition comprises the coordinating solvent and InCl_3 stabilized and dissolved by the latter.

According to another aspect of the present invention, there is provided the use of a coordinating solvent as defined in the present invention, for solubilizing and stabilizing InCl_3 . For example, InCl_3 can be solubilized and stabilized under anhydrous conditions such as under an inert gas atmosphere as for example nitrogen or argon.

According to another aspect of the present invention, there is provided a method for preparing an InCl_3 -based composition, comprising dissolving and stabilizing InCl_3 in a coordinating solvent as defined in the present invention.

For example, InCl_3 can be solubilized and stabilized under anhydrous conditions such as under an inert gas atmosphere as for example nitrogen or argon.

According to another aspect of the present invention, there is provided in a method of using InCl_3 as a catalyst, the improvement wherein the InCl_3 is provided in the form of a composition comprising InCl_3 and a coordinating solvent as defined in the present invention.

BRIEF DESCRIPTION OF DRAWINGS

In the following drawings, which represent by way of examples only particular embodiments of the present invention.

Fig. 1 shows a UV-visible absorption spectrum of a CuInS_2 sample obtained by a process according to one embodiment of the present invention, wherein the sample has not been annealed;

Fig. 2 shows a X-ray diffraction (XRD) pattern of the CuInS_2 sample analyzed in Fig. 1;

Fig. 3 shows a X-ray diffraction (XRD) pattern of a CuInS_2 sample obtained by a process according to another embodiment of the present invention, wherein the sample was annealed at 300 °C, under a vacuum of 100 mTorr, for a period of 2 hours;

Fig. 4 shows a X-ray diffraction (XRD) pattern of a CuInS_2 sample obtained by a process according to another embodiment of the present invention, wherein the sample was annealed at 500 °C, under a vacuum of 100 mTorr, for a period of 2 hours;

Fig. 5 shows a Scanning Electron Microscope (SEM) image of the sample analyzed in Fig. 1, wherein the scale is 1 μm ;

Fig. 6 shows a Scanning Electron Microscope (SEM) image of the sample analyzed in Fig. 1, wherein the scale is 200 nm;

Fig. 7 shows a Scanning Electron Microscope (SEM) image of the sample analyzed in Fig. 3, wherein the scale is 1 μm ;

Fig. 8 shows a Scanning Electron Microscope (SEM) image of the sample analyzed in Fig. 3, wherein the scale is 200 nm;

Fig. 9 shows a Scanning Electron Microscope (SEM) image of the sample analyzed in Fig. 4, wherein the scale is 1 μm ;

Fig. 10 shows a Scanning Electron Microscope (SEM) image of the sample analyzed in Fig. 4, wherein the scale is 500 nm;

Fig. 11 shows a UV-visible absorption spectrum of a AgInS_2 sample obtained by a process according to another embodiment of the present invention, wherein the sample has not been annealed;

Fig. 12 shows a X-ray diffraction (XRD) pattern of an AgInS_2 sample obtained by a process according to another embodiment of the present invention, wherein the sample has been annealed at 100 $^{\circ}\text{C}$, under a vacuum of 100 mTorr, for a period of 1 hour;

Fig. 13 shows a X-ray diffraction (XRD) pattern of an AgInS_2 sample obtained by a process according to another embodiment of the present invention, wherein the sample has been annealed at 400 $^{\circ}\text{C}$, under a vacuum of 100 mTorr, for a period of 2 hours;

Fig. 14 shows a UV-visible absorption spectrum of a CdS sample obtained by a process according to another embodiment of the present invention, wherein the sample has been annealed at 300 $^{\circ}\text{C}$, under a vacuum of 100 mTorr, for a period of 2 hours;

Fig. 15 shows a X-ray diffraction (XRD) pattern of the CdS sample analyzed in Fig. 14; and

Fig. 16 shows a X-ray diffraction (XRD) pattern of an InP sample obtained by a process according to another embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Further features and advantages of the invention will become more readily apparent from the following description of various particular embodiments as illustrated by way of examples.

Examples

Example 1 : Synthesis of CuInS₂

InCl₃ (165.9 mg, 0.75 mmol) was dissolved in 17 mL of anhydrous N-methylimidazole (NMI) in a 250 mL two-neck flask under argon at room temperature. Lithium sulfide (137.8 mg, 1.5 mmol) was suspended in 15 mL NMI at room temperature. Both compositions or solutions were mixed together and after one hour of ultrasonic bath treatment, a transparent yellowish solution (solution A) was obtained.

In a separate 250 mL two-neck flask, CuCl (74.2 mg, 0.75 mmol) was dissolved in 9 mL NMI under argon (solution B).

After both solutions A and B were cooled to 5°C, solution B was added dropwise over 15 minutes to solution A under argon. The resulting dark orange suspension was stable against aggregation. The mixture was stirred during 12 hours at 5°C. Then, the particles were centrifuged, filtered and dried at room temperature under vacuum overnight. The CuInS₂ particles can eventually be annealed.

The sample obtained in Example 1 was analyzed by UV-visible spectroscopy (Fig. 1) and by XRD (Fig. 2). The sample was also analyzed by Scanning Electron Microscopy and the results are shown in Fig. 5 (scale of 1 μm) and in Fig. 6 (scale of 200 nm).

Further samples have been prepared in a similar manner as previously defined, but in these cases, the samples have been annealed. A sample was annealed at 300 °C, under a vacuum of 100 mTorr, for a period of 2 hours, and various analyses have been carried out on it including the X-ray diffraction (XRD) pattern of Fig. 3, the Scanning Electron Microscope (SEM) image of Fig. 7 (scale of 1 μm), and the Scanning Electron Microscope (SEM) image of Fig. 8 (scale of 200 nm).

Another sample was annealed at 500 °C, under a vacuum of 100 mTorr, for a period of 2 hours, and various analyses have been carried out on it including the X-ray diffraction (XRD) pattern of Fig. 4, the Scanning Electron Microscope (SEM) image of Fig. 9 (scale of 1 μm), and the Scanning Electron Microscope (SEM) image of Fig. 10 (scale of 500 nm). In Fig. 4, the peaks labeled with "*" correspond to an In_2O_3 phase and the peaks labeled with "+" correspond to a Cu_2S phase.

The trend that can be seen from Figs. 2 to 4 is that a better crystallinity is observed for higher annealing temperatures. The general trend that can be seen from Figs. 5 to 10 is that particles coalescence is more significant at higher annealing temperatures.

The UV-visible spectrum was obtained from particles of the sample suspended in acetonitrile; the spectrum is characteristic of semiconducting particles with a bandgap energy of 1.55 eV, very close to the theoretical value of 1.5 eV for CuInS_2 . The XRD data of Figs. 2 to 4 were obtained from a D5000 Siemens diffractometer, using a cobalt tube (wavelength λ_1 : 1.78897 Å and λ_2 : 1.79285 Å) and a silicon detector. Diffractograms were recorded

between 2θ ranging from 20° to 100° . Intensities were recorded in counts per second (CPS) and normalized in percentage of intensities. The peak assignment was done with the DiffractAT software. The samples of Example 1 were also analyzed by atomic emission spectroscopy using an Inductive Coupled Plasma (ICP) and the stoichiometry obtained before and after annealing is 0.98 Cu for 1 In. Another ICP analysis was carried out on a sample prepared according to a similar manner as previously described (solutions A and B were mixed together at room temperature) and the stoichiometry obtained before and after annealing is 0.93 Cu for 1 In. The results from ICP as well as Figs. 1 to 10 thus clearly show that the obtained product was semiconducting CuInS_2 having a good crystallinity, with a particle diameter of less than 100 nm.

Example 2 : Synthesis of AgInS_2

InCl_3 (165.9 mg, 0.75 mmol) was dissolved in 17 mL anhydrous N-methylimidazole (NMI) in a 250 mL two-neck flask under argon at room temperature. Lithium sulfide (137.8 mg, 1.5 mmol) was suspended in 15 mL NMI at room temperature. Both solutions were mixed together and after one hour in an ultrasonic bath, a transparent yellowish solution (solution A) was obtained.

In a separate 250 mL two-neck flask, AgCN (100.4 mg, 0.75 mmol) was dissolved in 9 mL NMI under argon (solution B).

Then, solution B was added dropwise over 15 minutes to solution A under argon at 25°C . The resulting dark orange suspension was stable against aggregation. The mixture was heated during 1 hour at 80°C . Then, the particles were centrifuged, filtered and dried at room temperature under vacuum overnight. The sample obtained in Example 2 was then analyzed by UV-visible spectroscopy (Fig. 11). The UV-visible spectrum was obtained from particles of the sample suspended in acetonitrile; the spectrum is

characteristic of semiconducting particles with a bandgap energy of 1.85eV, very close to the theoretical value of 1.8 eV for AgInS_2 .

Further samples have been prepared in a similar manner as previously defined, but in these cases, the samples have been annealed. A sample was annealed at 100 °C, under a vacuum of 100 mTorr, for a period of 1 hour, and it was characterized by the X-ray diffraction (XRD) pattern of Fig. 12. Another sample was annealed at 400 °C, under a vacuum of 100 mTorr, for a period of 2 hours, and it was characterized by the X-ray diffraction (XRD) pattern of Fig. 13. In Fig. 13, the peaks labeled with "*" correspond to an Ag_2S phase and the peaks labeled with "+" correspond to an In_2O_3 phase.

The trend that can be seen from Figs. 12 and 13 is that a better crystallinity is observed for higher annealing temperatures.

The XRD data of Figs. 12 and 13 were obtained from a diffractometer, using a copper tube (wavelength λ_1 : 1.5418 Å) and a silicon detector. Diffractograms were recorded between 2θ ranging from 10° to 80°. Intensities were recorded in counts per second (CPS) and normalized in percentage of intensities. The peak assignment was done with the DiffractAT software. The samples of Example 2 were also analyzed by atomic emission spectroscopy using an Inductive Coupled Plasma (ICP) and the stoichiometry obtained before annealing is 1.07 Ag for 1 In. The results from ICP as well as Figs. 11 to 13 thus clearly show that the obtained product was crystalline semiconducting AgInS_2 .

Example 3 : Preparation of thin film layer high performance electrodes

In order to prepare thin film layer high performance electrodes using the compounds obtained by the process of the present invention, a polymeric binder and conductivity enhancer are used. The binder and the conductivity enhancer are mixed together with an organic solvent and a chalcopyrite-type compound so to obtain a suspension. Then, the suspension is coated on a

substrate (used as a current collector) using a blade applicator and then dried under vacuum at 50°C during 12 hours.

An example of a composition for such a suspension can be 95 % wt chalcopyrite-type compound such as CuInS_2 , 3% wt polyvinylidene fluoride (PVDF) and / or poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) as binder, 2% carbon black powder as conductivity enhancer and N-methylpyridinone (NMP) as solvent.

Example 4 : Synthesis of CdS

CdCl_2 (74.5 mg, 0.406 mmol) was dissolved in 5 mL of anhydrous N-methylimidazole (NMI) in a 250 mL two-neck flask under argon at room temperature. Lithium sulfide (22 mg, 0.47 mmol) was suspended in 40 mL of NMI at room temperature. Both solutions were mixed together. The resulting yellowish suspension was stirred during 2 hour at 25°C and then heated at 80°C for one hour. Then, the particles were centrifuged, filtered and dried at room temperature under vacuum overnight. The CdS particles obtained were then annealed for at least 2 hour at 300°C at 100 mTorr.

The sample obtained in Example 4 was analyzed by UV-visible spectroscopy (Fig. 14) and by XRD (Fig. 15). The UV-visible spectrum was obtained from particles of the sample suspended in N-methylimidazole; the spectrum is characteristic of semiconducting particles. The XRD data of Fig. 15 were obtained from a D5000 Siemens diffractometer, using a cobalt tube (wavelength λ_1 : 1.78897 Å and λ_2 : 1.79285 Å) and a silicon detector. Diffractograms were recorded between 2θ ranging from 20° to 90°. Intensities were recorded in counts per second (CPS) and normalized in percentage of intensities. The peak assignment was done with the DiffractAT software. In Fig. 15, the peaks labeled with "*" correspond to a crystalline cubic central face phase of CdS, the peaks labeled with "+" correspond to another crystalline phase of hexagonal α -CdS and the peaks labeled with "#" correspond to a hexagonal phase of metallic Cd.

The sample of Example 4 was also analyzed by Inductive Coupled Plasma (ICP) and the stoichiometry obtained before and after annealing is 1 Cd for 1 S. The results from ICP as well as Figs. 14 and 15 thus clearly show that the obtained product was semiconducting CdS having a good crystallinity.

Example 5 : Synthesis of InP

InCl₃ (183.7 mg, 83.4 mmol) was dissolved in 20 mL of anhydrous N-methylimidazole (NMI) in a 250 mL two-neck flask under argon at room temperature. (Me₃Si)₃P (200.4 mg, 80 mmol) was dissolved in 50 mL of anhydrous acetonitrile at room temperature. Both solutions were mixed together. The resulting dark red suspension was stirred during 12 hours at 25°C. Then, the particles were centrifuged, filtered and dried at room temperature under vacuum overnight. The InP particles obtained were annealed for at least 3 hour at 150°C at 100 mTorr.

The sample obtained in Example 5 was analyzed by XRD (Fig. 16). The XRD data of Fig. 16 were obtained from a D5000 Siemens diffractometer, using a cobalt tube (wavelength λ_1 : 1.78897 Å and λ_2 : 1.79285 Å) and a silicon detector. Diffractograms were recorded between 2 θ ranging from 20° to 90°. Intensities were recorded in counts per second (CPS) and normalized in percentage of intensities. The peak assignment was done with the DiffractAT software. The sample of Example 5 was also analyzed by Energy dispersive X-ray spectroscopy (EDX) and the stoichiometry obtained before and after annealing is 1 In for 1.12 P. The results from EDX as well as Fig. 16 thus show that the obtained product was InP. Moreover, XPS (X-Ray Photoelectron Spectroscopy) measurements have shown that InP is present at the material surface.

While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modifications and this application is intended to cover any variations, uses, or adaptations of the invention following, in general, the principles of the

invention and including such departures from the present disclosure as come within known or customary practice within the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth, and as follows in the scope of the appended claims.

WHAT IS CLAIMED IS:

1. A process for preparing a compound of formula $M^3M^1A_2$, said process comprising:

- reacting a compound of formula $M^1(X^1)_3$ with a compound of formula $(M^2)_2A$, in the presence of at least one coordinating solvent, in order to obtain a compound of formula $M^2M^1A_2$;

- reacting said compound of formula $M^2M^1A_2$ with a compound of formula M^3X^2 , in the presence of said at least one coordinating solvent, at least one another coordinating solvent, or mixtures thereof, in order to obtain said compound of formula $M^3M^1A_2$,

wherein

M^1 is chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ;

M^2 is chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, wherein each T^1 independently represents a C_1 - C_6 alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a C_1 - C_6 alkyl which is linear or branched;

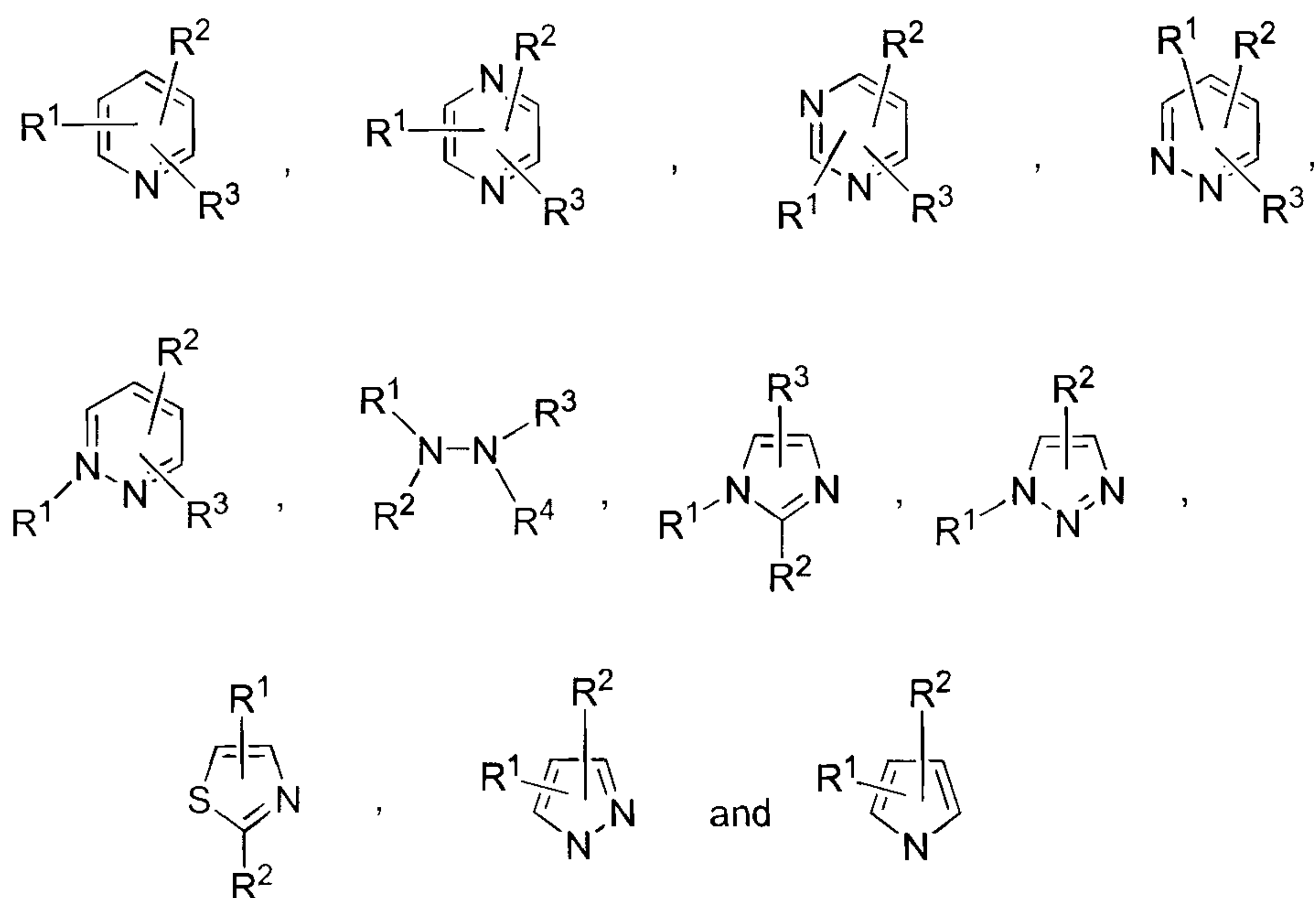
M^3 is chosen from Cu^+ , Ag^+ , Li^+ , Na^+ , K^+ , Cs^+ , Rb^+ , Fr^+ , Au^+ , and Hg^+ ;

A is chosen from S, Se, and Te;

X^1 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- ;

X^2 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- ; and

said at least one coordinating solvent is chosen from



wherein

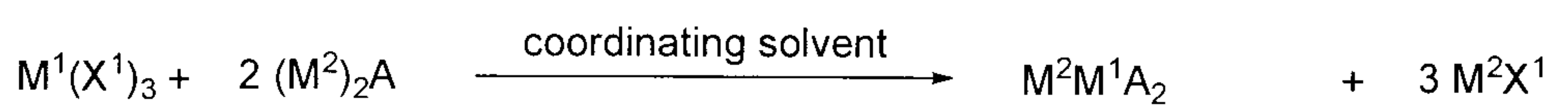
R^1 , R^2 , R^3 and R^4 are the same or different and are chosen from a hydrogen atom, C_1 - C_{12} alkyl which is linear or branched, C_3 - C_{12} cycloalkyl, C_1 - C_{12} heterocyclyl, C_2 - C_8 alkenyl, C_2 - C_8 alkynyl, C_6 - C_{12} aryl, C_6 - C_{20} aralkyl, C_6 - C_{20} alkylaryl, and C_1 - C_{12} heteroaryl,

R^1 and R^2 may be joined together to form a 5 to 14 membered heterocyclyl or is a part of polymer chain or network.

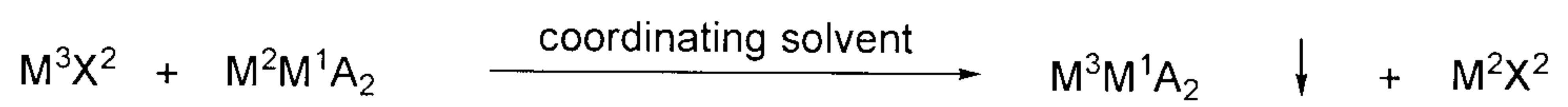
2. The process of claim 1, wherein said compound of formula $M^2M^1A_2$ is reacted with said compound of formula M^3X^2 in the presence of said at least one coordinating solvent.
3. The process of claim 1 or 2, wherein said at least one coordinating solvent is chosen from N-methylimidazole, N-vinylimidazole, pyrazole, triazole, and mixtures thereof.

4. The process of claim 1 or 2, wherein said at least one coordinating solvent is N-methylimidazole.
5. The process of any one of claims 1 to 4, wherein a further solvent is added to said at least one coordinating solvent, said further solvent being chosen from acetonitrile, dichloromethane, C₁-C₆ alcohols, dimethylsulfoxide, C₂-C₁₀ amides, C₃-C₁₀ linear carbonates, C₃-C₁₀ cyclic carbonates, C₁-C₆ alkylurea, ionic liquids, a room temperature molten salt, and mixtures thereof.
6. The process of any one of claims 1 to 4, wherein a further solvent is added to said at least one coordinating solvent, said further solvent being chosen from ethanol, isopropanol, dimethylformamide, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, ethylene carbonate, propylene carbonate, tetramethylurea, and mixtures thereof.
7. The process of claim 1, wherein M²M¹A₂ is reacted with M³X² in the presence of said at least one another coordinating solvent, which is chosen from N-methylimidazole, N-vinylimidazole, pyrazole, triazole, and mixtures thereof.
8. The process of claim 1, wherein M²M¹A₂ is reacted with M³X² in the presence of said at least one another coordinating solvent, which is N-methylimidazole.
9. The process of any one of claims 1, 7, and 8, wherein a further solvent is added to said at least one another coordinating solvent, said further solvent being chosen from acetonitrile, dichloromethane, C₁-C₆ alcohols, dimethylsulfoxide, C₂-C₁₀ amides, C₃-C₁₀ linear carbonates, C₃-C₁₀ cyclic carbonates, C₁-C₆ alkylurea, ionic liquids, a room temperature molten salt, and mixtures thereof.

10. The process of any one of claims 1, 7, and 8, wherein a further solvent is added to said at least one another coordinating solvent, said further solvent being chosen from ethanol, isopropanol, dimethylformamide, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, ethylene carbonate, propylene carbonate, tetramethylurea, and mixtures thereof.
11. The process of claim 5 or 9, wherein said further solvent is said room temperature molten salt and comprises a cation chosen from dialkylimidazolium, trialkylsulfonium, quaternary amine and quaternary phosphonium, and an anion chosen from $(\text{FSO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_3\text{C}^-$, CF_3SO_3^- , CF_3COO^- , AsF_6^- , CH_3COO^- , $(\text{CN})_2\text{N}^-$, NO_3^- , 2.3HF , Cl^- , Br^- , I^- , PF_6^- , BF_4^- , and ClO_4^- .
12. The process of claim 11, wherein said quaternary amine is a $\text{C}_1\text{-C}_{20}$ tetraalkylammonium and said quaternary phosphonium is a $\text{C}_1\text{-C}_{20}$ tetraalkylphosphonium or a $\text{C}_6\text{-C}_{12}$ tetraarylphosphonium.
13. The process of any one of claims 1 to 12, wherein the reaction between $\text{M}^1(\text{X}^1)_3$ and $(\text{M}^2)_2\text{A}$ is carried out as follows:



14. The process of any one of claims 1 to 13, wherein the reaction between M^3X^2 and $\text{M}^2\text{M}^1\text{A}_2$ is carried out as follows:



15. The process of any one of claims 1 to 14, wherein $\text{M}^1(\text{X}^1)_3$ and $(\text{M}^2)_2\text{A}$ are reacted together at a temperature of about $-10\text{ }^\circ\text{C}$ to about $180\text{ }^\circ\text{C}$.

16. The process of claim 15, wherein said temperature is about -5 °C to about 50 °C.
17. The process of any one of claims 1 to 14, wherein $M^1(X^1)_3$ and $(M^2)_2A$ are reacted together at room temperature.
18. The process of any one of claims 1 to 17, wherein M^3X^2 and $M^2M^1A_2$ are reacted together at a temperature of about -10 °C to about 180 °C.
19. The process of claim 18, wherein said temperature is about -5 °C to about 50 °C.
20. The process of any one of claims 1 to 17, wherein M^3X^2 and $M^2M^1A_2$ are reacted together at room temperature.
21. The process of any one of claims 1 to 20, wherein said compound of formula $M^3M^1A_2$ is precipitated, and separated from a mixture comprising said at least one coordinating solvent and a by-product solubilized therein, by means of a filtration.
22. The process of claim 21, wherein said by-product is M^2X^2 .
23. The process of claim 14, wherein said compound of formula $M^3M^1A_2$ is precipitated, and separated from said at least one coordinating solvent and said compound of formula M^2X^2 , by means of a filtration.
24. The process of any one of claims 1 to 23, wherein said compound of formula $M^1(X^1)_3$, said compound of formula $(M^2)_2A$, and said at least one coordinating solvent are mixed together and agitated in order to obtain said compound of formula $M^2M^1A_2$.
25. The process of any one of claims 1 to 23, wherein said compound of formula $M^1(X^1)_3$, said compound of formula $(M^2)_2A$, and said at least

one coordinating solvent are mixed together and agitated in a sonic bath in order to obtain said compound of formula $M^2M^1A_2$.

26. The process of claim 24 or 25, wherein a composition comprising said compound of formula $M^1(X^1)_3$ and said at least one coordinating solvent is mixed with a composition comprising said compound of formula $(M^2)_2A$ and said at least one coordinating solvent.
27. The process of claim 1, 7, or 8 wherein said compound of formula $M^2M^1A_2$ is reacted with said compound of formula M^3X^2 by adding said compound of formula M^3X^2 to a composition comprising said compound of formula $M^2M^1A_2$ and said at least one coordinating solvent, said at least one another coordinating solvent, or mixtures thereof.
28. The process of claim 1, 7, or 8 wherein said compound of formula $M^2M^1A_2$ is reacted with said compound of formula M^3X^2 by adding a composition comprising said compound of formula M^3X^2 and said at least one another coordinating solvent to a composition comprising said compound of formula $M^2M^1A_2$ and said at least one another coordinating solvent.
29. The process of claim 28, wherein the composition comprising said compound of formula M^3X^2 and said at least one another coordinating solvent is added dropwise to the composition comprising said compound of formula $M^2M^1A_2$ and said at least one another coordinating solvent.
30. The process of any one of claims 1 to 29, wherein X^1 and X^2 are different.
31. The process of any one of claims 1 to 29, wherein X^1 and X^2 are the same.

32. The process of any one of claims 1 to 28, wherein X^1 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , and NO_3^- .
33. The process of any one of claims 1 to 28, wherein X^1 is Cl^- .
34. A process for preparing a compound of formula $M^3M^1A_2$, said process comprising reacting a compound of formula $M^2M^1A_2$ with a compound of formula M^3X^2 , in the presence of at least one coordinating solvent, in order to obtain said compound of formula $M^3M^1A_2$,

wherein

M^1 is chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ;

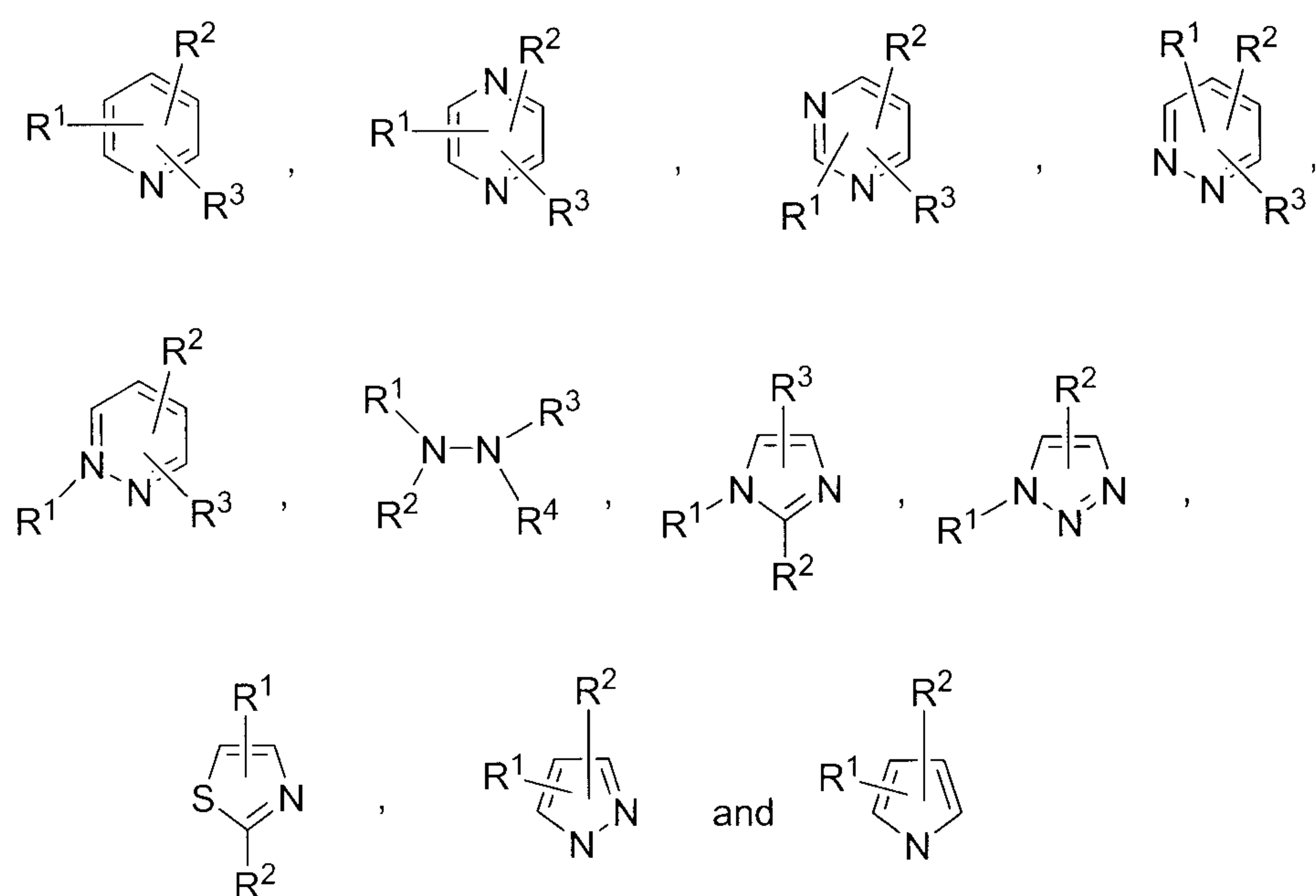
M^2 is chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, wherein each T^1 independently represents a C_1 - C_6 alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a C_1 - C_6 alkyl which is linear or branched;

M^3 is chosen from Cu^+ , Ag^+ , Li^+ , Na^+ , K^+ , Cs^+ , Rb^+ , Fr^+ , Au^+ , and Hg^+ ;

A is chosen from S, Se, and, Te;

X^2 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- ; and

said at least one coordinating solvent is chosen from

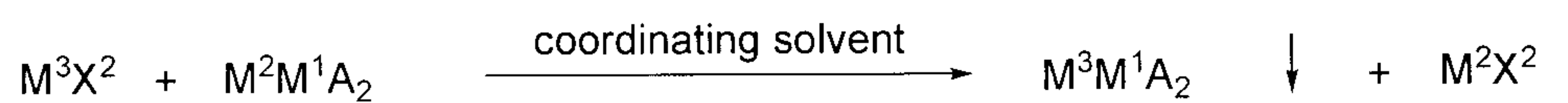


wherein

R¹, R², R³ and R⁴ are the same or different and are chosen from a hydrogen atom, C₁-C₁₂ alkyl which is linear or branched, C₃-C₁₂ cycloalkyl, C₁-C₁₂ heterocyclyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₆-C₁₂ aryl, C₆-C₂₀ aralkyl, C₆-C₂₀ alkylaryl, and C₁-C₁₂ heteroaryl,

R¹ and R² may be joined together to form a 5 to 14 membered heterocyclyl or is a part of polymer chain or network.

35. The process of claim 34, wherein said at least one coordinating solvent is chosen from N-methylimidazole, N-vinylimidazole, pyrazole, triazole, and mixtures thereof.
36. The process of claim 34, wherein said at least one coordinating solvent is N-methylimidazole.
37. The process of any one of claims 34 to 36, wherein the reaction between M³X² and M²M¹A₂ is carried out as follows:



38. The process of any one of claims 34 to 37, wherein a further solvent is added to said at least one coordinating solvent, said further solvent being chosen from acetonitrile, dichloromethane, C₁-C₆ alcohols, dimethylsulfoxide, C₂-C₁₀ amides, C₃-C₁₀ linear carbonates, C₃-C₁₀ cyclic carbonates, C₁-C₆ alkylurea, ionic liquids, a room temperature molten salt, and mixtures thereof.
39. The process of any one of claims 34 to 37, wherein a further solvent is added to said at least one another coordinating solvent, said further solvent being chosen from ethanol, isopropanol, dimethylformamide, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, ethylene carbonate, propylene carbonate, tetramethylurea, and mixtures thereof.
40. The process of claim 38, wherein said further solvent is said room temperature molten salt and comprises a cation chosen from dialkylimidazolium, trialkylsulfonium, quaternary amine and quaternary phosphonium, and an anion chosen from (FSO₂)₂N⁻, (CF₃SO₂)₂N⁻, (C₂F₅SO₂)₂N⁻, (CF₃SO₂)₃C⁻, CF₃SO₃⁻, CF₃COO⁻, AsF₆⁻, CH₃COO⁻, (CN)₂N⁻, NO₃⁻, 2.3HF, Cl⁻, Br⁻, I⁻, PF₆⁻, BF₄⁻, and ClO₄⁻.
41. The process of claim 40, wherein said quaternary amine is a C₁-C₂₀ tetraalkylammonium and said quaternary phosphonium is a C₁-C₂₀ tetraalkylphosphonium or a C₆-C₁₂ tetraarylphosphonium.
42. The process of any one of claims 34 to 41, wherein M³X² and M²M¹A₂ are reacted together at a temperature of about -10 °C to about 180 °C.
43. The process of claim 42, wherein said temperature is about -5 °C to about 50 °C.

44. The process of any one of claims 34 to 41, wherein M^3X^2 and $M^2M^1A_2$ are reacted together at room temperature.
45. The process of any one of claims 34 to 44, wherein said compound of formula $M^3M^1A_2$ is precipitated, and separated from a mixture comprising said at least one coordinating solvent and a by-product solubilized therein, by means of a filtration.
46. The process of claim 45, wherein said by-product is M^2X^2 .
47. The process of claim 37, wherein said compound of formula $M^3M^1A_2$ is precipitated, and separated from said at least one coordinating solvent and said compound of formula M^2X^2 , by means of a filtration.
48. The process of any one of claims 34 to 47, wherein said compound of formula $M^2M^1A_2$ is reacted with said compound of formula M^3X^2 by adding said compound of formula M^3X^2 to a composition comprising said compound of formula $M^2M^1A_2$ and said at least one coordinating solvent.
49. The process of any one of claims 34 to 47, wherein said compound of formula $M^2M^1A_2$ is reacted with said compound of formula M^3X^2 by adding a composition comprising said compound of formula M^3X^2 and said at least one coordinating solvent to a composition comprising said compound of formula $M^2M^1A_2$ and said at least one coordinating solvent.
50. The process of claim 49, wherein the composition comprising said compound of formula M^3X^2 and said at least one coordinating solvent is added dropwise to the composition comprising said compound of formula $M^2M^1A_2$ and said at least one coordinating solvent.

51. The process of any one of claims 1 to 50, wherein said compound of formula $M^3M^1A_2$ is chosen from $CuInS_2$, $CuInSe_2$, $CuInTe_2$, $AuInS_2$, $AuInSe_2$, $AuInTe_2$, $AgInS_2$, $AgInSe_2$, $AgInTe_2$, $HgInS_2$, $HgInSe_2$, $HgInTe_2$, $LiInS_2$, $LiInSe_2$, $LiInTe_2$, $CuGaS_2$, $CuGaSe_2$, $CuGaTe_2$, $AuGaS_2$, $AuGaSe_2$, $AuGaTe_2$, $AgGaS_2$, $AgGaSe_2$, $AgGaTe_2$, $HgGaS_2$, $HgGaSe_2$, $HgGaTe_2$, $CuAlS_2$, $CuAlSe_2$, $CuAlTe_2$, $AuAlS_2$, $AuAlSe_2$, $AuAlTe_2$, $AgAlS_2$, $AgAlSe_2$, $AgAlTe_2$, $HgAlS_2$, $HgAlSe_2$, $HgAlTe_2$, $CuAuS_2$, $CuAuSe_2$, $CuAuTe_2$, $AuAuS_2$, $AuAuSe_2$, $AuAuTe_2$, $AgAuS_2$, $AgAuSe_2$, $AgAuTe_2$, $HgAuS_2$, $HgAuSe_2$, $HgAuTe_2$, $LiFeS_2$, $LiFeSe_2$, $LiFeTe_2$, $AgFeS_2$, $AgFeSe_2$, $AgFeTe_2$, $LiGaS_2$, $LiGaSe_2$, and $LiGaTe_2$.
52. The process of any one of claims 1 to 50, wherein said compound of formula $M^3M^1A_2$ is chosen from $CuInS_2$, $AuInS_2$, $AgInS_2$, $AgInSe_2$, $CuGaS_2$, $AuGaS_2$, $CuAlS_2$, and $LiFeS_2$.
53. The process of any one of claims 1 to 50, wherein said compound of formula $M^3M^1A_2$ is chosen from $CuInS_2$, and $AgInS_2$.
54. The process of any one of claims 1 to 53, wherein M^2 is chosen from Li^+ , Na^+ , and K^+ ; and X^2 is chosen from Cl^- , Br^- , I^- , F^- , and CN^- .
55. The process of any one of claims 1 to 53, wherein M^2 is Li^+ and X^2 is Cl^- .
56. The process of any one of claims 1 to 53, wherein M^2 is Li^+ and X^2 is I^- .
57. The process of any one of claims 1 to 53, wherein M^2 is Li^+ and X^2 is CN^- .
58. The process of any one of claims 1 to 53, wherein

M^1 is In^{3+} ;

M^2 is chosen from Li^+ , Na^+ , and K^+ ;

M^3 is chosen from Cu^+ , and Ag^+ ;

A is chosen from S and Se; and

X^2 is chosen from Cl^- , Br^- , I^- , F^- , and CN^- .

59. The process of any one of claims 1 to 53, wherein

M^1 is In^{3+} ;

M^2 is chosen from Li^+ , Na^+ , and K^+ ;

M^3 is chosen from Cu^+ , and Ag^+ ;

A is S; and

X^2 is chosen from Cl^- , and CN^- .

60. The process of any one of claims 1 to 50, wherein

M^1 is chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ;

M^2 is chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, wherein each T^1 independently represents a C_1 - C_6 alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a C_1 - C_6 alkyl which is linear or branched;

M^3 is chosen from Ag^+ , Li^+ , Na^+ , K^+ , Cs^+ , Rb^+ , Fr^+ , Au^+ , and Hg^+ ;

A is chosen from S and Se; and

X^2 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , and CN^- .

61. The process of any one of claims 1 to 50, wherein

M^1 is chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ;

M^2 is chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, wherein each T^1 independently represents a C_1 - C_6 alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a C_1 - C_6 alkyl which is linear or branched;

M^3 is chosen from Cu^+ , Ag^+ , Li^+ , Na^+ , K^+ , Cs^+ , Rb^+ , Fr^+ , Au^+ , and Hg^+ ;

A is Se; and

X^2 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , and CN^- .

62. The process of any one of claims 1 to 50, wherein

M^1 is chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ;

M^2 is chosen from Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, wherein each T^1 independently represents a C_1 - C_6 alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a C_1 - C_6 alkyl which is linear or branched;

M^3 is chosen from Cu^+ , Ag^+ , Li^+ , Na^+ , K^+ , Cs^+ , Rb^+ , Fr^+ , Au^+ , and Hg^+ ;

A is chosen from S and Se; and

X^2 is chosen from Br^- , I^- , F^- , CH_3COO^- , NO_3^- , and CN^- .

63. The process of any one of claims 1 to 50, wherein when $M^3M^1A_2$ is $CuInS_2$, M^2 is chosen from Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$.

64. The process of any one of claims 1 to 50, wherein when $M^3M^1A_2$ is $CuInS_2$, X^2 is chosen from Br^- , I^- , F^- , CH_3COO^- , NO_3^- , and CN^- .
65. The process of any one of claims 1 to 50, wherein when $M^3M^1A_2$ is $CuInS_2$, M^2 is chosen from Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, and X^2 is chosen from Br^- , I^- , F^- , CH_3COO^- , NO_3^- , and CN^- .
66. The process of any one of claims 1 to 65, wherein said obtained compound of formula $M^3M^1A_2$ is nanocrystalline.
67. A process for preparing $CuInS_2$, said process comprising:
- reacting $In(X^1)_3$ with a compound of formula $(M^2)_2S$, in the presence of at least one coordinating solvent, in order to obtain a compound of formula M^2InS_2 ; and
 - reacting said compound of formula M^2InS_2 with a compound of formula CuX^2 , in the presence of said at least one coordinating solvent, at least one another coordinating solvent, or mixtures thereof, in order to obtain said $CuInS_2$

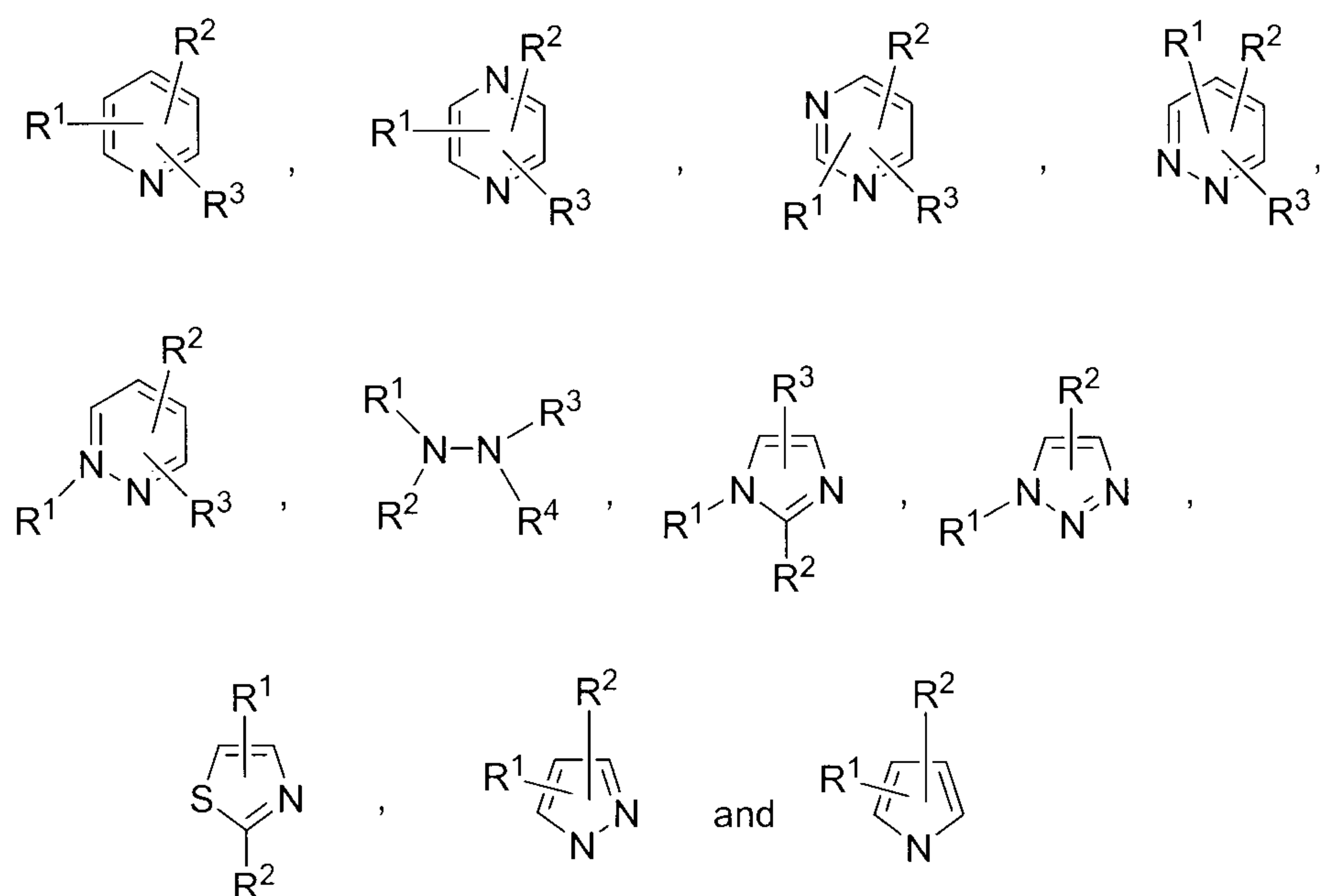
wherein

M^2 is chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, wherein each T^1 independently represents a C_1 - C_6 alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a C_1 - C_6 alkyl which is linear or branched;

X^1 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- ; and

X^2 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- ;

said at least one coordinating solvent is chosen from



wherein

R¹, R², R³ and R⁴ are the same or different and are chosen from a hydrogen atom, C₁-C₁₂ alkyl which is linear or branched, C₃-C₁₂ cycloalkyl, C₁-C₁₂ heterocyclyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₆-C₁₂ aryl, C₆-C₂₀ aralkyl, C₆-C₂₀ alkylaryl, and C₁-C₁₂ heteroaryl,

R¹ and R² may be joined together to form a 5 to 14 membered heterocyclyl or is a part of polymer chain or network.

68. The process of claim 67, wherein $\text{In}(\text{X}^1)_3$ is reacted with said compound of formula $(\text{M}^2)_2\text{S}$, in the presence of said at least one coordinating solvent.
69. The process of claim 67 or 68, wherein said at least one coordinating solvent is chosen from N-methylimidazole, N-vinylimidazole, pyrazole, triazole, and mixtures thereof.

70. The process of claim 67 or 68, wherein said at least one coordinating solvent is N-methylimidazole.
71. The process of any one of claims 67 to 70, wherein a further solvent is added to said at least one coordinating solvent, said further solvent being chosen from acetonitrile, dichloromethane, C₁-C₆ alcohols, dimethylsulfoxide, C₂-C₁₀ amides, C₃-C₁₀ linear carbonates, C₃-C₁₀ cyclic carbonates, C₁-C₆ alkylurea, ionic liquids, a room temperature molten salt, and mixtures thereof.
72. The process of any one of claims 67 to 70, wherein a further solvent is added to said at least one coordinating solvent, said further solvent being chosen from ethanol, isopropanol, dimethylformamide, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, ethylene carbonate, propylene carbonate, tetramethylurea, and mixtures thereof.
73. The process of claim 67, wherein M²InS₂ is reacted with CuX² in the presence of said at least one another coordinating solvent which is chosen from N-methylimidazole, N-vinylimidazole, pyrazole, triazole, and mixtures thereof.
74. The process of claim 67, wherein M²InS₂ is reacted with CuX² in the presence of said at least one another coordinating solvent which is N-methylimidazole.
75. The process of claim 73 or 74, wherein a further solvent is added to said at least one another coordinating solvent, said further solvent being chosen from acetonitrile, dichloromethane, C₁-C₆ alcohols, dimethylsulfoxide, C₂-C₁₀ amides, C₃-C₁₀ linear carbonates, C₃-C₁₀ cyclic carbonates, C₁-C₆ alkylurea, ionic liquids, a room temperature molten salt, and mixtures thereof.

76. The process of claim 73 or 74, wherein a further solvent is added to said at least one another coordinating solvent, said further solvent being chosen from ethanol, isopropanol, dimethylformamide, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, ethylene carbonate, propylene carbonate, tetramethylurea, and mixtures thereof.
77. The process of claim 75, wherein said further solvent is said room temperature molten salt and comprises a cation chosen from dialkylimidazolium, trialkylsulfonium, quaternary amine and quaternary phosphonium, and an anion chosen from $(\text{FSO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_3\text{C}^-$, CF_3SO_3^- , CF_3COO^- , AsF_6^- , CH_3COO^- , $(\text{CN})_2\text{N}^-$, NO_3^- , 2.3HF , Cl^- , Br^- , I^- , PF_6^- , BF_4^- , and ClO_4^- .
78. The process of claim 77, wherein said quaternary amine is a C_1 - C_{20} tetraalkylammonium and said quaternary phosphonium is a C_1 - C_{20} tetraalkylphosphonium or a C_6 - C_{12} tetraarylphosphonium.
79. The process of any one of claims 67 to 78, wherein the reaction between $\text{In}(\text{X}^1)_3$ and $(\text{M}^2)_2\text{S}$ is carried out as follows:
- $$\text{In}(\text{X}^1)_3 + 2 (\text{M}^2)_2\text{S} \xrightarrow{\text{coordinating solvent}} \text{M}^2\text{InS}_2 + 3 \text{M}^2\text{X}^1.$$
80. The process of any one of claims 67 to 79, wherein the reaction between CuX^2 and M^2InS_2 is carried out as follows:
- $$\text{CuX}^2 + \text{M}^2\text{InS}_2 \xrightarrow{\text{coordinating solvent}} \text{CuInS}_2 \downarrow + \text{M}^2\text{X}^2.$$
81. The process of any one of claims 67 to 80, wherein $\text{In}(\text{X}^1)_3$ and $(\text{M}^2)_2\text{S}$ are reacted together at a temperature of about -10°C to about 180°C .

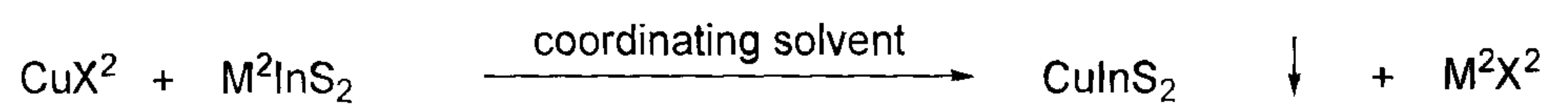
82. The process of claim 81, wherein said temperature is about -5 °C to about 50 °C.
83. The process of any one of claims 67 to 80, wherein $\text{In}(\text{X}^1)_3$ and $(\text{M}^2)_2\text{S}$ are reacted together at room temperature.
84. The process of any one of claims 67 to 83, wherein CuX^2 and M^2InS_2 are reacted together at a temperature of about -10 to about 180 °C.
85. The process of claim 84, wherein said temperature is about -5 to about 50 °C.
86. The process of any one of claims 67 to 83, wherein CuX^2 and M^2InS_2 are reacted together at room temperature.
87. The process of any one of claims 67 to 86, wherein said compound of formula M^2InS_2 is precipitated, and separated from a mixture comprising said at least one coordinating solvent and a by-product solubilized therein, by means of a filtration.
88. The process of claim 87, wherein said by-product is M^2X^2 .
89. The process of claim 80, wherein CuInS_2 is precipitated, and separated from said at least one coordinating solvent and said compound of formula M^2X^2 , by means of a filtration.
90. The process of any one of claims 67 to 89, wherein said compound of formula $\text{In}(\text{X}^1)_3$, said compound of formula $(\text{M}^2)_2\text{S}$, and said at least one coordinating solvent are mixed together and agitated in order to obtain said compound of formula M^2InS_2 .
91. The process of any one of claims 67 to 89, wherein said compound of formula $\text{In}(\text{X}^1)_3$, said compound of formula $(\text{M}^2)_2\text{S}$, and said at least

one coordinating solvent are mixed together and agitated in a sonic bath in order to obtain said compound of formula M^2InS_2 .

92. The process of claim 90 or 91, wherein a composition comprising said compound of formula $In(X^1)_3$ and said at least one coordinating solvent is mixed with a composition comprising said compound of formula $(M^2)_2S$ and said at least one coordinating solvent.
93. The process of any one of claims 67 to 92, wherein said compound of formula M^2InS_2 is reacted with said compound of formula CuX^2 by adding said compound of formula CuX^2 to a composition comprising said compound of formula M^2InS_2 and said at least one another coordinating solvent.
94. The process of any one of claims 67 to 92, wherein said compound of formula M^2InS_2 is reacted with said compound of formula CuX^2 by adding a composition comprising said compound of formula CuX^2 and said at least one another coordinating solvent to a composition comprising said compound of formula M^2InS_2 and said at least one another coordinating solvent.
95. The process of claim 94, wherein the composition comprising said compound of formula CuX^2 and said at least one another coordinating solvent is added dropwise to the composition comprising said compound of formula M^2InS_2 and said at least one another coordinating solvent.
96. A process for preparing $CuInS_2$, said process comprising:
 - reacting a compound of formula M^2InS_2 with a compound of formula CuX^2 , in the presence of at least one coordinating solvent, in order to obtain said $CuInS_2$,

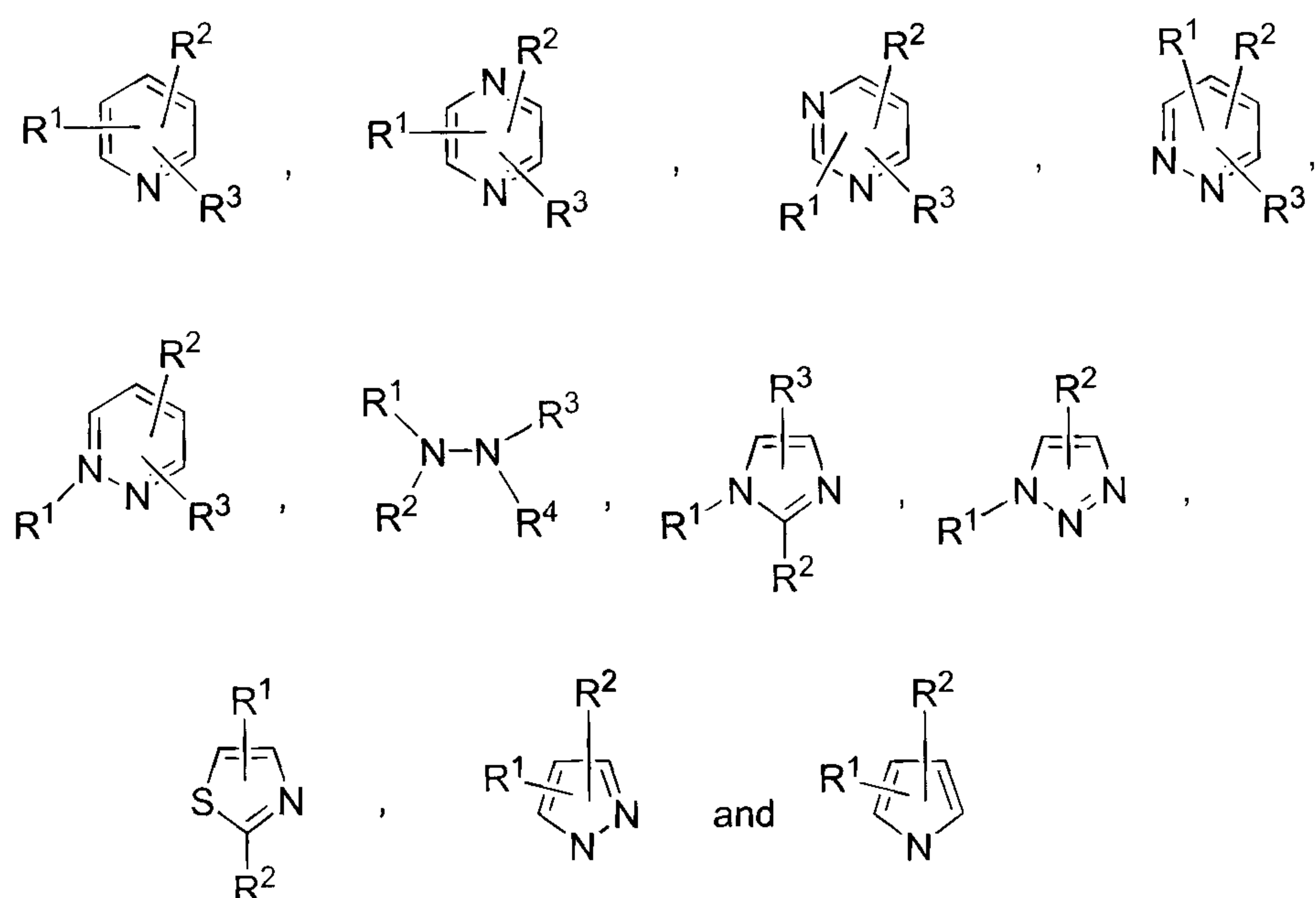
97. The process of claim 96, wherein said at least one coordinating solvent is chosen from N-methylimidazole, N-vinylimidazole, pyrazole, triazole, and mixtures thereof.
98. The process of claim 96, wherein said at least one coordinating solvent is N-methylimidazole.
99. The process of any one of claims 96 to 98, wherein a further solvent is added to said at least one coordinating solvent, said further solvent being chosen from acetonitrile, dichloromethane, C₁-C₆ alcohols, dimethylsulfoxide, C₂-C₁₀ amides, C₃-C₁₀ linear carbonates, C₃-C₁₀ cyclic carbonates, C₁-C₆ alkylurea, ionic liquids, a room temperature molten salt, and mixtures thereof.
100. The process of any one of claims 96 to 98, wherein a further solvent is added to said at least one coordinating solvent, said further solvent being chosen from ethanol, isopropanol, dimethylformamide, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, ethylene carbonate, propylene carbonate, tetramethylurea, and mixtures thereof.
101. The process of claim 99, wherein said further solvent is said room temperature molten salt and comprises a cation chosen from dialkylimidazolium, trialkylsulfonium, quaternary amine and quaternary phosphonium, and an anion chosen from (FSO₂)₂N⁻, (CF₃SO₂)₂N⁻, (C₂F₅SO₂)₂N⁻, (CF₃SO₂)₃C⁻, CF₃SO₃⁻, CF₃COO⁻, AsF₆⁻, CH₃COO⁻, (CN)₂N⁻, NO₃⁻, 2.3HF, Cl⁻, Br⁻, I⁻, PF₆⁻, BF₄⁻, and ClO₄⁻.
102. The process of claim 101, wherein said quaternary amine is a C₁-C₂₀ tetraalkylammonium and said quaternary phosphonium is a C₁-C₂₀ tetraalkylphosphonium or a C₆-C₁₂ tetraarylphosphonium.

103. The process of any one of claims 96 to 102, wherein the reaction between CuX^2 and M^2InS_2 is carried out as follows:



104. The process of any one of claims 96 to 103, wherein CuX^2 and M^2InS_2 are reacted together at a temperature of about -10 to about 180 °C.
105. The process of claim 104, wherein said temperature is about -5 to about 50 °C.
106. The process of any one of claims 96 to 103, wherein CuX^2 and M^2InS_2 are reacted together at room temperature.
107. The process of any one of claims 96 to 106, wherein said CuInS_2 is precipitated, and separated from a mixture comprising said at least one coordinating solvent and a by-product solubilized therein, by means of a filtration.
108. The process of claim 107, wherein said by-product is M^2X^2 .
109. The process of claim 103, wherein CuInS_2 is precipitated, and separated from said at least one coordinating solvent and said compound of formula M^2X^2 , by means of a filtration.
110. The process of any one of claims 96 to 109, wherein said compound of formula M^2InS_2 is reacted with said compound of formula CuX^2 by adding said compound of formula CuX^2 to a composition comprising said compound of formula M^2InS_2 and said at least one coordinating solvent.

111. The process of any one of claims 96 to 110, wherein said compound of formula M^2InS_2 is reacted with said compound of formula CuX^2 by adding a composition comprising said compound of formula CuX^2 and said at least one coordinating solvent to a composition comprising said compound of formula M^2InS_2 and said at least one coordinating solvent.
112. The process of claim 111, wherein the composition comprising said compound of formula CuX^2 and said at least one coordinating solvent is added dropwise to the composition comprising said compound of formula M^2InS_2 and said at least one coordinating solvent.
113. The process of any one of claims 67 to 112, wherein X^2 is chosen from Cl^- and I^- .
114. The process of any one of claims 67 to 112, wherein X^2 is Cl^- .
115. The process of any one of claims 67 to 114, wherein said $CuInS_2$ obtained is nanocrystalline.
116. The process of claim 1 or 67, wherein said at least one another coordinating solvent is chosen from



wherein

R¹, R², R³ and R⁴ are the same or different and are chosen from a hydrogen atom, C₁-C₁₂ alkyl which is linear or branched, C₃-C₁₂ cycloalkyl, C₁-C₁₂ heterocyclyl, C₂-C₈ alkenyl, C₂-C₈ alkynyl, C₆-C₁₂ aryl, C₆-C₂₀ aralkyl, C₆-C₂₀ alkylaryl, and C₁-C₁₂ heteroaryl,

R¹ and R² may be joined together to form a 5 to 14 membered heterocyclyl or is a part of polymer chain or network.

117. The process of claim 116, wherein a further solvent is added to said another coordinating solvent, said further solvent being chosen from acetonitrile, dichloromethane, C₁-C₆ alcohols, dimethylsulfoxide, C₂-C₁₀ amides, C₃-C₁₀ linear carbonates, C₃-C₁₀ cyclic carbonates, C₁-C₆ alkylurea, ionic liquids, a room temperature molten salt, and mixtures thereof.
118. The process of claim 116, wherein a further solvent is added to said at least one another coordinating solvent, said further solvent being chosen from ethanol, isopropanol, dimethylformamide, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, ethylene

carbonate, propylene carbonate, tetramethylurea, and mixtures thereof.

119. The process of claim 118, wherein said further solvent is said room temperature molten salt and comprises a cation chosen from dialkylimidazolium, trialkylsulfonium, quaternary amine and quaternary phosphonium, and an anion chosen from $(\text{FSO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_3\text{C}^-$, CF_3SO_3^- , CF_3COO^- , AsF_6^- , CH_3COO^- , $(\text{CN})_2\text{N}^-$, NO_3^- , 2.3HF , Cl^- , Br^- , I^- , PF_6^- , BF_4^- , and ClO_4^- .
120. The process of claim 119, wherein said quaternary amine is a $\text{C}_1\text{-C}_{20}$ tetraalkylammonium and said quaternary phosphonium is a $\text{C}_1\text{-C}_{20}$ tetraalkylphosphonium or a $\text{C}_6\text{-C}_{12}$ tetraarylphosphonium.
121. The process of any one of claims 1 to 53 and 67 to 112, wherein $(\text{T}^1)_3\text{Si-}$ is $(\text{CH}_3)_3\text{Si-}$.
122. The process of any one of claims 1 to 53 and 67 to 112, wherein $\text{N}(\text{T}^2)_4^+$ is NH_4^+ .
123. The process of any one of claims 1 to 122, further comprising drying the compound obtained at the end of said process.
124. The process of claim 123, wherein the compound is dried by centrifugation, heating, vacuum, or combinations thereof.
125. The process of any one of claims 1 to 124, further comprising annealing the compound obtained at the end of said process.
126. The process of any one of claims 1 to 125, further comprising preparing an electrode comprising the obtained compound.

127. The process of any one of claims 1 to 126, further comprising mixing the obtained compound with a binder so as to obtain a mixture suitable for the preparation of an electrode.
128. The process of any one of claims 1 to 126, further comprising mixing the obtained compound with a binder so as to obtain a suitable precursor for the preparation of an electrode.
129. The process of any one of claims 1 to 126, further comprising mixing the obtained compound with a binder so as to obtain a mixture comprising said compound and said binder, and preparing an electrode with said mixture.
130. The process of claim 129, wherein a thin film of said mixture is coated on a substrate in order to prepare said electrode.
131. The process of claim 130, wherein said substrate comprises a metal chosen from Mo, Au, Al, Cu, and mixtures thereof.
132. The process of any one of claims 127 to 131, wherein said mixture further comprises a conductivity enhancer.
133. The process of claim 132, wherein said conductivity enhancer is chosen from carbon black, graphite, carbon nanotubes, and mixtures thereof.
134. The process of any one of claims 127 to 133, wherein said binder is a polymer.
135. The process of claim 134, wherein said polymer is chosen from polyvinylidene fluoride (PVDF), vinylidene poly(fluoride-co-hexafluoropropylene), and mixtures thereof.

136. The process of any one of claims 127 to 135, wherein said mixture further comprises a solvent.
137. The process of claim 136, wherein said solvent is N-methylpyridinone.
138. Use of a process as defined in anyone of claims 1 to 125, for the preparation of a nanocrystalline compound suitable for use in a solar cell.
139. Use of a process as defined in anyone of claims 1 to 125, for the preparation of a compound suitable for use in the field of optoelectronic.
140. Use of a process as defined in anyone of claims 1 to 125, for the preparation of a compound suitable for use in the preparation of a photodiode, a transistor, a sensor, a laser diode, or a digital light projector.
141. A method for preparing a nanocrystalline compound suitable for use in a solar cell, said method comprising carrying out a process as defined in anyone of claims 1 to 125.
142. A method for preparing a compound suitable for use in the field of optoelectronic, said method comprising carrying out a process as defined in anyone of claims 1 to 125.
143. A method for preparing a compound suitable for use in the preparation of a photodiode, a transistor, a sensor, a laser diode, or a digital light projector, said method comprising carrying out a process as defined in anyone of claims 1 to 125.
144. A process for preparing a compound of formula $M^3(M^5, M^1)A_2$, said process comprising:

- reacting together a compound of formula $M^1(X^1)_3$, a compound of formula $M^5(X^3)_3$, and a compound of formula $(M^2)_2A$, in the presence of at least one coordinating solvent, in order to obtain a compound of formula $M^2(M^5, M^1)A_2$;

- reacting said compound of formula $M^2(M^5, M^1)A_2$ with a compound of formula M^3X^2 , in the presence of said at least one coordinating solvent, at least one another coordinating solvent, or mixtures thereof, in order to obtain said compound of formula $M^3(M^5, M^1)A_2$,

wherein

M^1 is chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ;

M^2 is chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, wherein each T^1 independently represents a C_1 - C_6 alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a C_1 - C_6 alkyl which is linear or branched;

M^3 is chosen from Cu^+ , Ag^+ , Li^+ , Na^+ , K^+ , Cs^+ , Rb^+ , Fr^+ , Au^+ , and Hg^+ ;

M^5 is chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ;

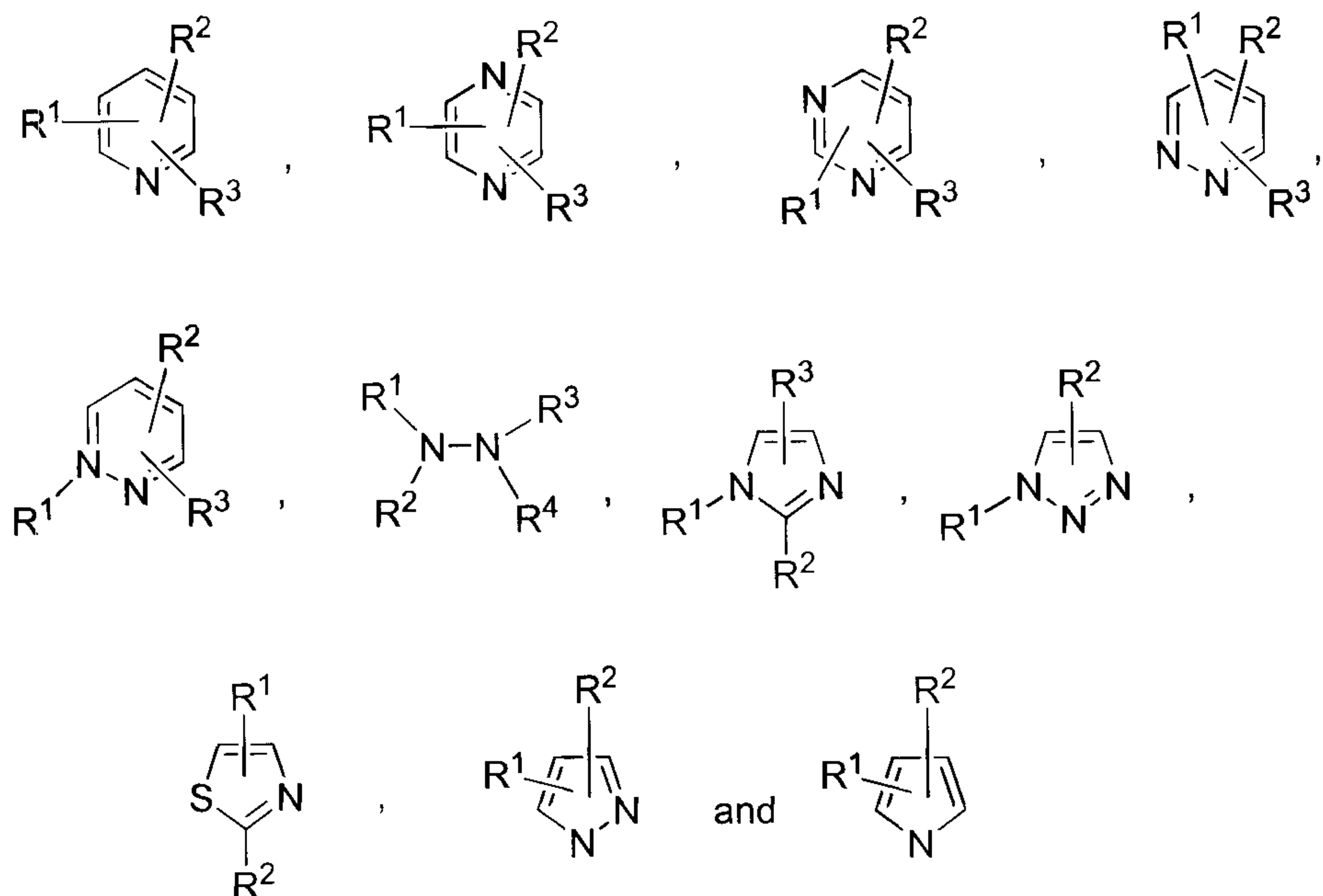
A is chosen from S, Se, and Te;

X^1 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- ;

X^2 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- ;

X^3 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- ;

said at least one coordinating solvent is chosen from



wherein

R^1 , R^2 , R^3 and R^4 are the same or different and are chosen from a hydrogen atom, C_1 - C_{12} alkyl which is linear or branched, C_3 - C_{12} cycloalkyl, C_1 - C_{12} heterocyclyl, C_2 - C_8 alkenyl, C_2 - C_8 alkynyl, C_6 - C_{12} aryl, C_6 - C_{20} aralkyl, C_6 - C_{20} alkylaryl, and C_1 - C_{12} heteroaryl,

R^1 and R^2 may be joined together to form a 5 to 14 membered heterocyclyl or is a part of polymer chain or network.

145. The process of claim 144, wherein said compound of formula $M^2(M^5, M^1)A_2$ is reacted with said compound of formula M^3X^2 in the presence of said at least one coordinating solvent.

146. The process of claim 144 or 145, wherein said at least one coordinating solvent is chosen from of N-methylimidazole, N-vinylimidazole, pyrazole, triazole, and mixtures thereof.
147. The process of claim 144 or 145, wherein said at least one coordinating solvent is N-methylimidazole.
148. The process of any one of claims 144 to 147, wherein a further solvent is added to said at least one coordinating solvent, said further solvent being chosen from acetonitrile, dichloromethane, C₁-C₆ alcohols, dimethylsulfoxide, C₂-C₁₀ amides, C₃-C₁₀ linear carbonates, C₃-C₁₀ cyclic carbonates, C₁-C₆ alkylurea, ionic liquids, a room temperature molten salt, and mixtures thereof.
149. The process of any one of claims 144 to 147, wherein a further solvent is added to said at least one coordinating solvent, said further solvent being chosen from ethanol, isopropanol, dimethylformamide, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, ethylene carbonate, propylene carbonate, tetramethylurea, and mixtures thereof.
150. The process of any one of claims 144 to 149, wherein $M^2(M^5, M^1)A_2$ is reacted with M^3X^2 , in the presence of said at least one another coordinating solvent, which is chosen from of N-methylimidazole, N-vinylimidazole, pyrazole, triazole, and mixtures thereof.
151. The process of any one of claims 144 to 149, wherein $M^2(M^5, M^1)A_2$ is reacted with M^3X^2 , in the presence of said at least one another coordinating solvent, which is N-methylimidazole.
152. The process of claims 150 or 151, wherein a further solvent is added to said at least one another coordinating solvent, said further solvent being chosen from acetonitrile, dichloromethane, C₁-C₆ alcohols,

dimethylsulfoxide, C₂-C₁₀ amides, C₃-C₁₀ linear carbonates, C₃-C₁₀ cyclic carbonates, C₁-C₆ alkylurea, ionic liquids, a room temperature molten salt, and mixtures thereof.

153. The process of claim 150 or 151, wherein a further solvent is added to said at least one another coordinating solvent, said further solvent being chosen from ethanol, isopropanol, dimethylformamide, dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, ethylene carbonate, propylene carbonate, tetramethylurea, and mixtures thereof.
154. The process of claim 148 or 152, wherein said further solvent is said room temperature molten salt and comprises a cation chosen from dialkylimidazolium, trialkylsulfonium, quaternary amine and quaternary phosphonium, and an anion chosen from (FSO₂)₂N⁻, (CF₃SO₂)₂N⁻, (C₂F₅SO₂)₂N⁻, (CF₃SO₂)₃C⁻, CF₃SO₃⁻, CF₃COO⁻, AsF₆⁻, CH₃COO⁻, (CN)₂N⁻, NO₃⁻, 2.3HF, Cl⁻, Br⁻, I⁻, PF₆⁻, BF₄⁻, and ClO₄⁻.
155. The process of claim 154, wherein said quaternary amine is a C₁-C₂₀ tetraalkylammonium and said quaternary phosphonium is a C₁-C₂₀ tetraalkylphosphonium or a C₆-C₁₂ tetraarylphosphonium.
156. The process of any one of claims 144 to 155, wherein M¹(X¹)₃, M⁵(X³)₃, and (M²)₂A are reacted together at a temperature of about -10 °C to about 180 °C.
157. The process of claim 156, wherein said temperature is about -5 °C to about 50 °C.
158. The process of any one of claims 144 to 157, wherein M¹(X¹)₃, M⁵(X³)₃, and (M²)₂A are reacted together at room temperature.

159. The process of any one of claims 144 to 157, wherein M^3X^2 and $M^2(M^5, M^1)A_2$ are reacted together at a temperature of about $-10\text{ }^{\circ}\text{C}$ to about $180\text{ }^{\circ}\text{C}$.
160. The process of claim 159, wherein said temperature is about $-5\text{ }^{\circ}\text{C}$ to about $50\text{ }^{\circ}\text{C}$.
161. The process of any one of claims 144 to 160, wherein M^3X^2 and $M^2(M^5, M^1)A_2$ are reacted together at room temperature.
162. The process of any one of claims 144 to 161, wherein X^1 and X^2 are different.
163. The process of any one of claims 144 to 161, wherein X^1 and X^2 are the same.
164. The process of any one of claims 144 to 161, wherein X^1 , X^2 and X^3 are the same.
165. The process of any one of claims 144 to 164, wherein X^1 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , and NO_3^- .
166. The process of any one of claims 144 to 165, wherein X^1 is Cl^- .
167. The process of any one of claims 144 to 166, wherein M^1 is different than M^5 .
168. A process for preparing a compound of formula $M^3(M^5, M^1)A_2$, said process comprising reacting a compound of formula $M^2(M^5, M^1)A_2$ with a compound of formula M^3X^2 , in the presence of at least one coordinating solvent, in order to obtain said compound of formula $M^3(M^5, M^1)A_2$,

wherein

M^1 is chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ;

M^2 is chosen from Li^+ , Na^+ , K^+ , Cs^+ , $(T^1)_3Si^-$, and $N(T^2)_4^+$, wherein each T^1 independently represents a C_1 - C_6 alkyl which is linear or branched, and each T^2 independently represents a hydrogen atom, or a C_1 - C_6 alkyl which is linear or branched;

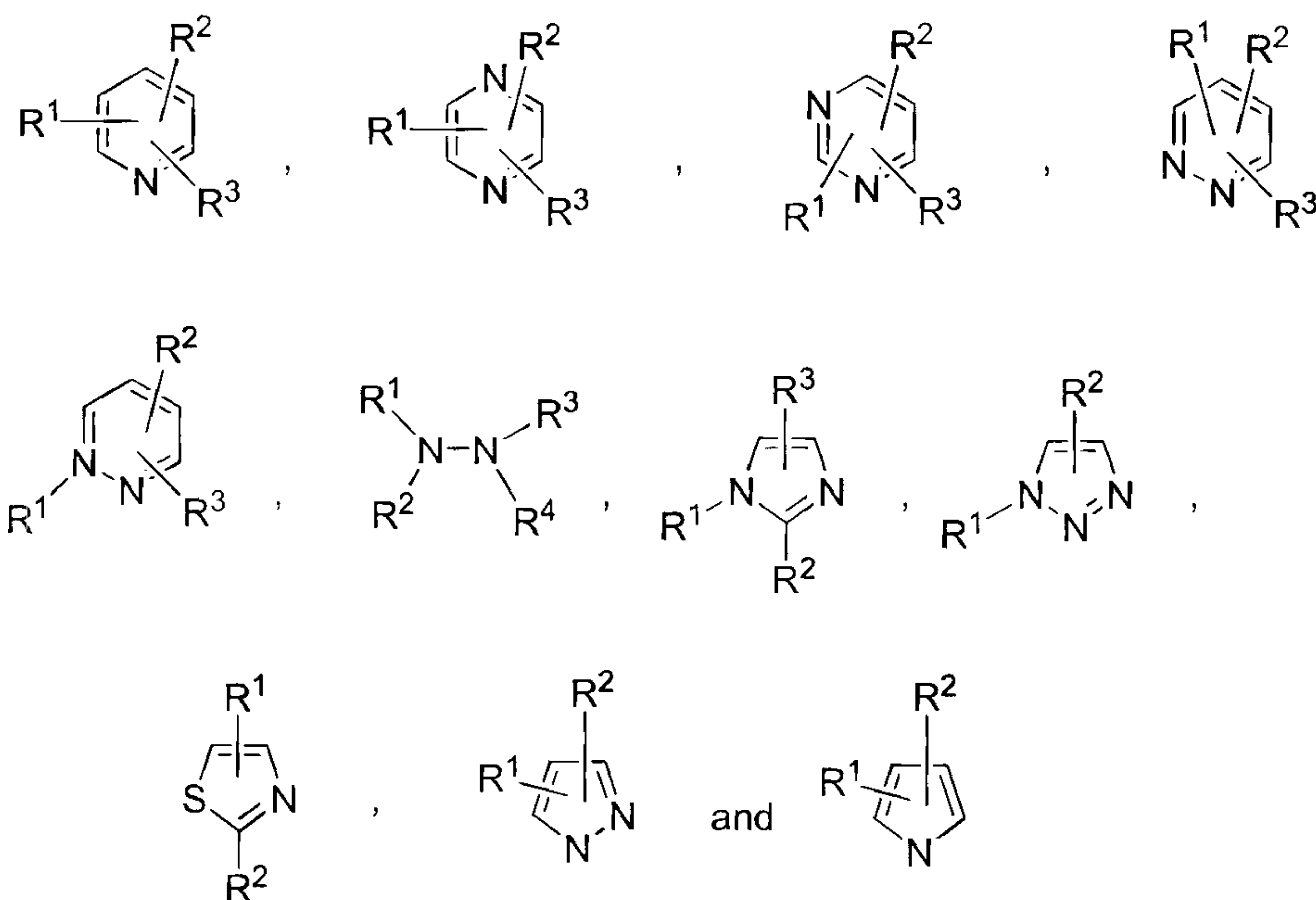
M^3 is chosen from Cu^+ , Ag^+ , Li^+ , Na^+ , K^+ , Cs^+ , Rb^+ , Fr^+ , Au^+ , and Hg^+ ;

M^5 is chosen from B^{3+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^{3+} , Fe^{3+} , and Au^{3+} ;

A is chosen from S, Se, and, Te; and

X^2 is chosen from Cl^- , Br^- , I^- , F^- , CH_3COO^- , NO_3^- , OCN^- , SCN^- , and CN^- ;

said at least one coordinating solvent is chosen from



wherein

R^1 , R^2 , R^3 and R^4 are the same or different and are chosen from a hydrogen atom, C_1 - C_{12} alkyl which is linear or branched, C_3 - C_{12} cycloalkyl, C_1 - C_{12} heterocyclyl, C_2 - C_8 alkenyl, C_2 - C_8 alkynyl, C_6 - C_{12} aryl, C_6 - C_{20} aralkyl, C_6 - C_{20} alkylaryl, and C_1 - C_{12} heteroaryl,

R^1 and R^2 may be joined together to form a 5 to 14 membered heterocyclyl or is a part of polymer chain or network.

169. The process of claim 168, wherein said at least one coordinating solvent is chosen from of N-methylimidazole, pyrazole, triazole, and mixtures thereof.
170. The process of claim 168, wherein said at least one coordinating solvent is N-methylimidazole.
171. The process of any one of claims 158 to 170, wherein a further solvent is added to said at least one coordinating solvent, said further solvent being chosen from acetonitrile, dichloromethane, C_1 - C_6 alcohols, dimethylsulfoxide, C_2 - C_{10} amides, C_3 - C_{10} linear carbonates, C_3 - C_{10} cyclic carbonates, C_1 - C_6 alkylurea, ionic liquids, a room temperature molten salt, and mixtures thereof.
172. The process of any one of claims 158 to 170, wherein a further solvent is added to said at least one coordinating solvent, said further solvent being chosen from ethanol, isopropanol dimethylformamide dimethylcarbonate, diethylcarbonate, ethylmethylcarbonate, ethylene carbonate, propylene carbonate tetramethylurea, and mixtures thereof.
173. The process of claim 171, wherein said further solvent is said room temperature molten salt and comprises a cation chosen from dialkylimidazolium, trialkylsulfonium, quaternary amine and quaternary phosphonium, and an anion chosen from $(FSO_2)_2N^-$,

$(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_3\text{C}^-$, CF_3SO_3^- , CF_3COO^- , AsF_6^- , CH_3COO^- , $(\text{CN})_2\text{N}^-$, NO_3^- , 2.3HF , Cl^- , Br^- , I^- , PF_6^- , BF_4^- , and ClO_4^- .

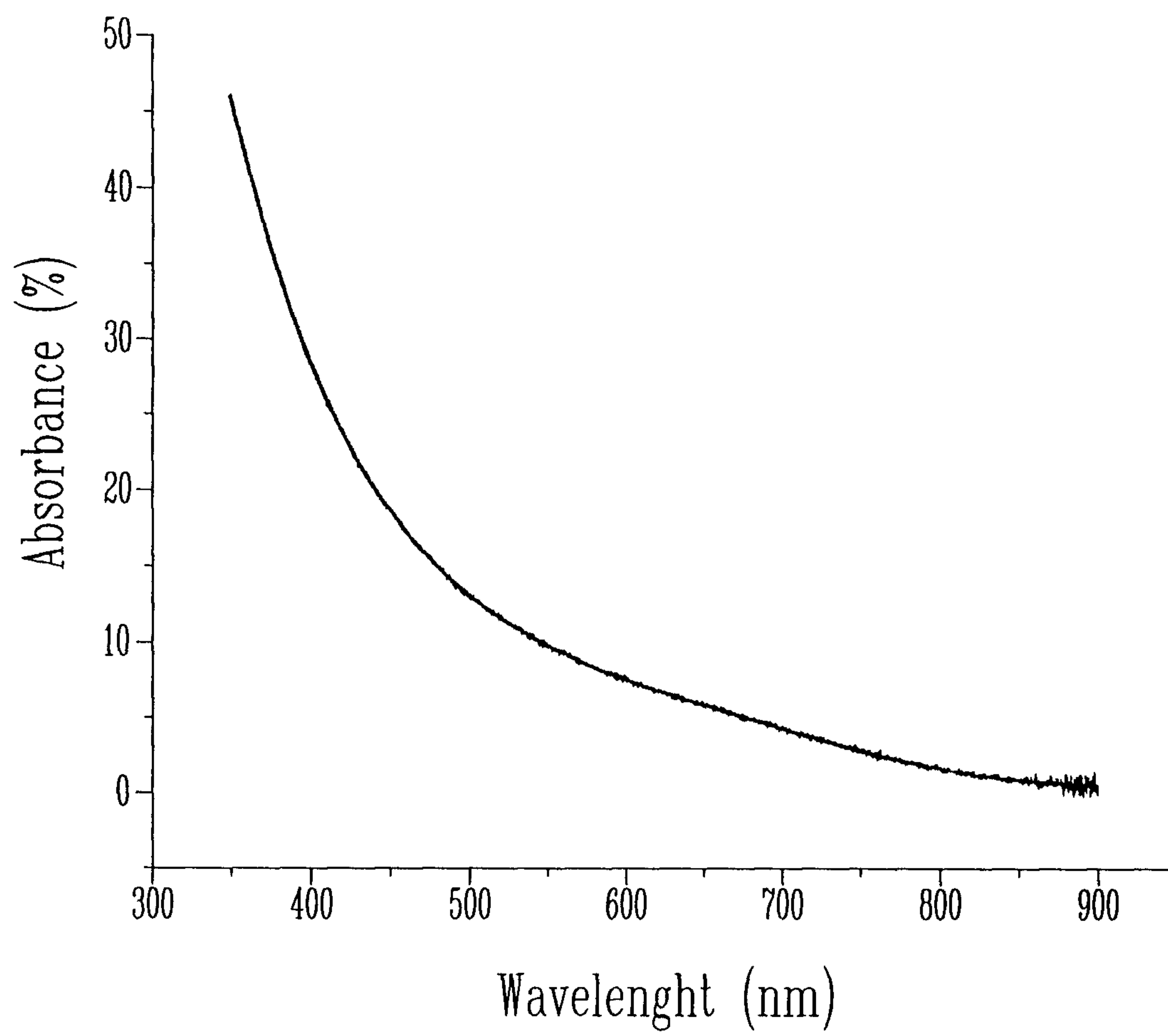
174. The process of claim 173, wherein said quaternary amine is a $\text{C}_1\text{-C}_{20}$ tetraalkylammonium and said quaternary phosphonium is a $\text{C}_1\text{-C}_{20}$ tetraalkylphosphonium or a $\text{C}_6\text{-C}_{12}$ tetraarylphosphonium.
175. The process of any one of claims 168 to 174, wherein M^3X^2 and $\text{M}^2(\text{M}^5, \text{M}^1)\text{A}_2$ are reacted together at a temperature of about $-10\text{ }^\circ\text{C}$ to about $180\text{ }^\circ\text{C}$.
176. The process of claim 175, wherein said temperature is about $-5\text{ }^\circ\text{C}$ to about $50\text{ }^\circ\text{C}$.
177. The process of any one of claims 168 to 174, wherein M^3X^2 and $\text{M}^2(\text{M}^5, \text{M}^1)\text{A}_2$ are reacted together at room temperature.
178. The process of any one of claims 168 to 177, wherein M^1 is different than M^5 .
179. The process of any one of claims 144 to 178, wherein M^2 is chosen from Li^+ , Na^+ , and K^+ ; and X^2 is chosen from Cl^- , Br^- , I^- , F^- , and CN^- .
180. The process of any one of claims 144 to 178, wherein M^2 is chosen from Li^+ and Na^+ ; and X^2 is chosen from Cl^- , and I^- .
181. The process of any one of claims 144 to 178, wherein M^2 is Li^+ and X^2 is Cl^- .
182. The process of any one of claims 144 to 178, wherein M^2 is Li^+ and X^2 is I^- .
183. The process of any one of claims 144 to 178, wherein M^2 is Li^+ and X^2 is CN^- .

184. The process of any one of claims 144 to 178, wherein M^2 is chosen from Li^+ , Na^+ , and $(CH_3)_3Si^-$.
185. The process of any one of claims 144 to 178, wherein M^2 is Li^+ .
186. The process of any one of claims 144 to 178, wherein said compound of formula $M^3(M^5, M^1)A_2$ is chosen from $Cu(Al, In)S_2$, $Ag(Al, In)S_2$, $Cu(Ga, In)S_2$, $Cu(Al, In)Se_2$, $Ag(Al, In)Se_2$, and $Cu(Ga, In)Se_2$.
187. The process of any one of claims 144 to 178, wherein said compound of formula $M^3(M^5, M^1)A_2$ is chosen from $Cu(Al, In)S_2$, $Ag(Al, In)S_2$, $Cu(Ga, In)S_2$, $Cu(Al, In)Se_2$, $Ag(Al, In)Se_2$, and $Cu(Ga, In)Se_2$.
188. The process of any one of claims 144 to 187, wherein said compound of formula $M^3(M^5, M^1)A_2$ is a compound in which the molar ratio M^5/M^1 is less than about 1.
189. The process of any one of claims 144 to 187, wherein said compound of formula $M^3(M^5, M^1)A_2$ is a compound in which the molar ratio M^5/M^1 is less than about 0.5.
190. The process of any one of claims 144 to 187, wherein said compound of formula $M^3(M^5, M^1)A_2$ is a compound in which the molar ratio M^5/M^1 is less than about 0.25.
191. The process of any one of claims 144 to 187, wherein said compound of formula $M^3(M^5, M^1)A_2$ is a compound in which the molar ratio M^5/M^1 is less than about 0.1.
192. The process of any one of claims 144 to 187, wherein said compound of formula $M^3(M^5, M^1)A_2$ is a compound in which the molar ratio M^5/M^1 is less than about 0.02.

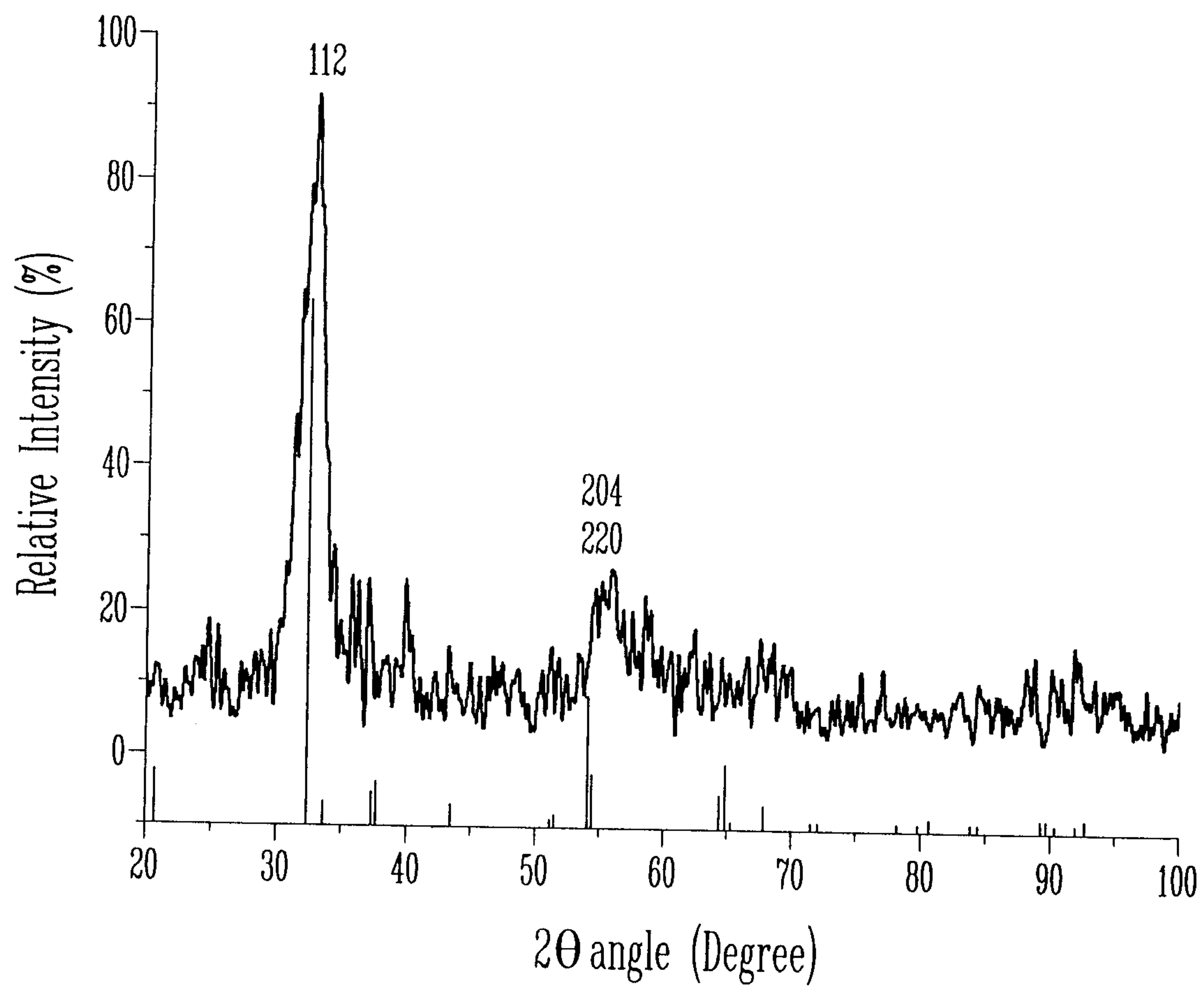
193. The process of any one of claims 144 to 187, wherein said compound of formula $M^3(M^5, M^1)A_2$ is a compound in which the molar ratio M^5/M^1 is less than about 0.01.
194. The process of any one of claims 144 to 187, wherein said compound of formula $M^3(M^5, M^1)A_2$ is a compound in which the molar ratio M^5/M^1 is less than about 0.002.
195. The process of any one of claims 144 to 187, wherein said compound of formula $M^3(M^5, M^1)A_2$ is a compound in which the molar ratio M^5/M^1 is less than about 0.001.
196. The process of any one of claims 144 to 187, further comprising annealing the so-obtained compound.
197. The process of claim 125 or 196, wherein the compound obtained at the end of said process is annealed for a period of at least about 30 minutes at a temperature of at least about 75 °C.
198. The process of claim 125 or 196, wherein the compound obtained at the end of said process is annealed for a period of at least about 60 minutes at a temperature of at least about 100 °C.
199. The process of claim 125 or 196, wherein the compound obtained at the end of said process is annealed for a period of at least about 120 minutes at a temperature of at least about 200 °C.
200. The process of claim 125 or 196, wherein the compound obtained at the end of said process is annealed for a period of at least about 180 minutes at a temperature of at least about 100 °C.

201. The process of claim 125 or 196, wherein the compound obtained at the end of said process is annealed for a period of at least about 180 minutes at a temperature of at least about 200 °C.
202. The process of any one of claims 197 to 201, wherein said temperature is at least about 250 °C.
203. The process of any one of claims 197 to 201, wherein said temperature is at least about 300 °C.
204. The process of any one of claims 197 to 201, wherein said temperature is at least about 400 °C.
205. The process of any one of claims 197 to 201, wherein said temperature is at least about 500 °C.
206. The process of any one of claims 197 to 201, wherein said temperature is about 100 °C to about 500 °C.
207. The process of any one of claims 197 to 201, wherein said temperature is about 200 °C to about 400 °C.
208. The process of any one of claims 197 to 207, wherein said compound is annealed under vacuum.
209. The process of any one of claims 197 to 207, wherein said compound is annealed under a vacuum of at least about 50 mTorr.
210. The process of any one of claims 197 to 207, wherein said compound is annealed under a vacuum of at least about 100 mTorr.

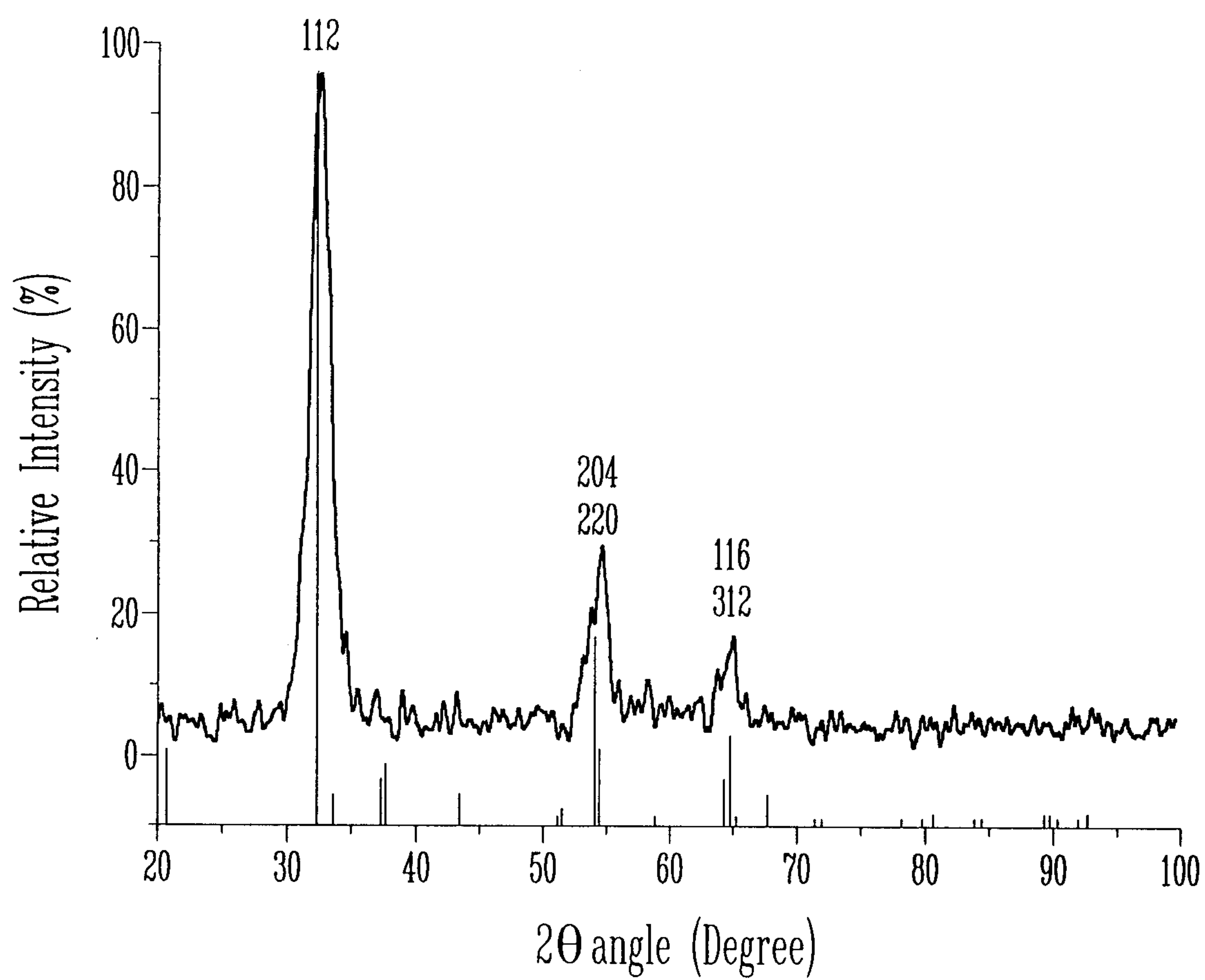
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FIG. 1

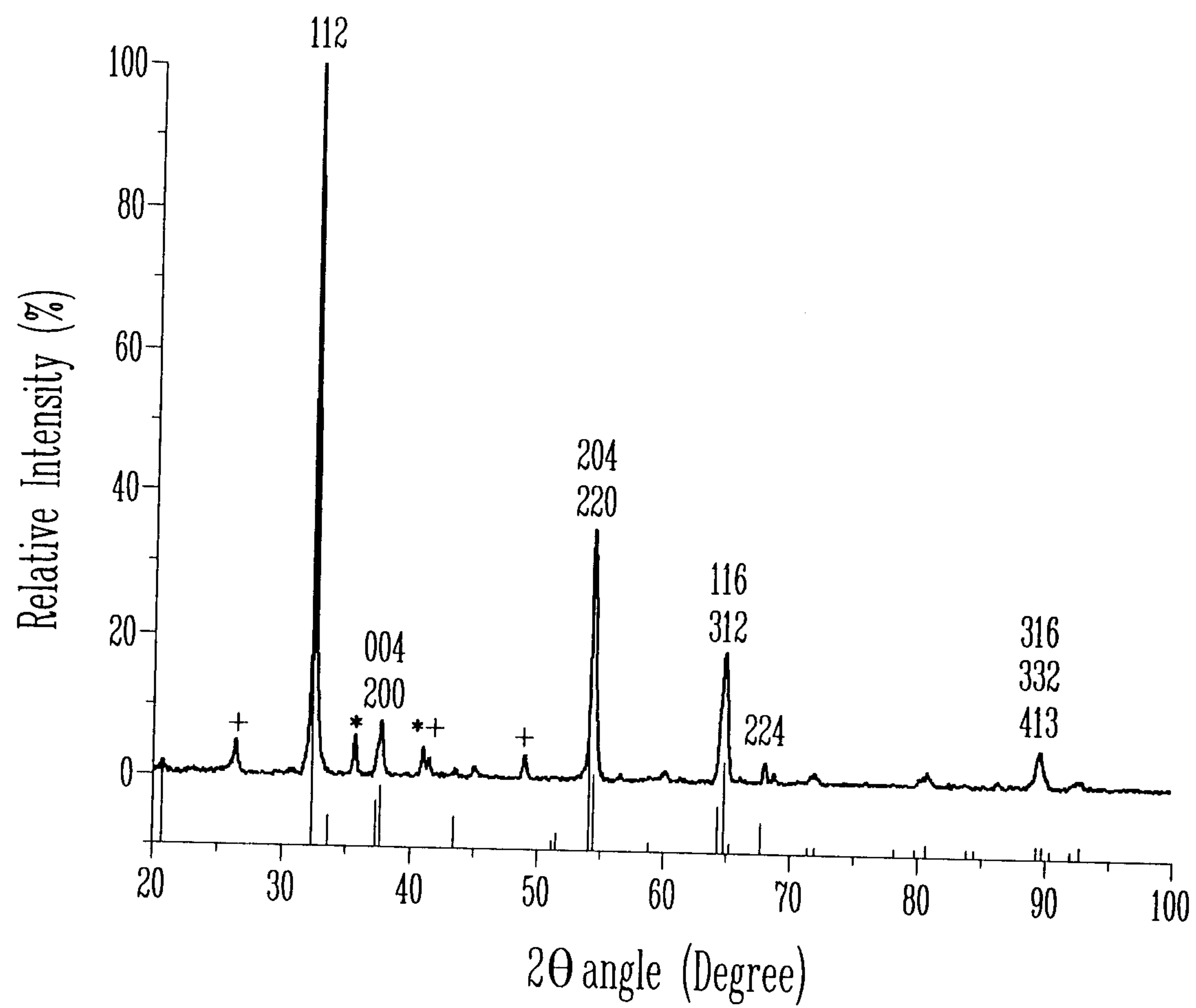
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FIG. 2

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FIG. 3

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FIG - 4

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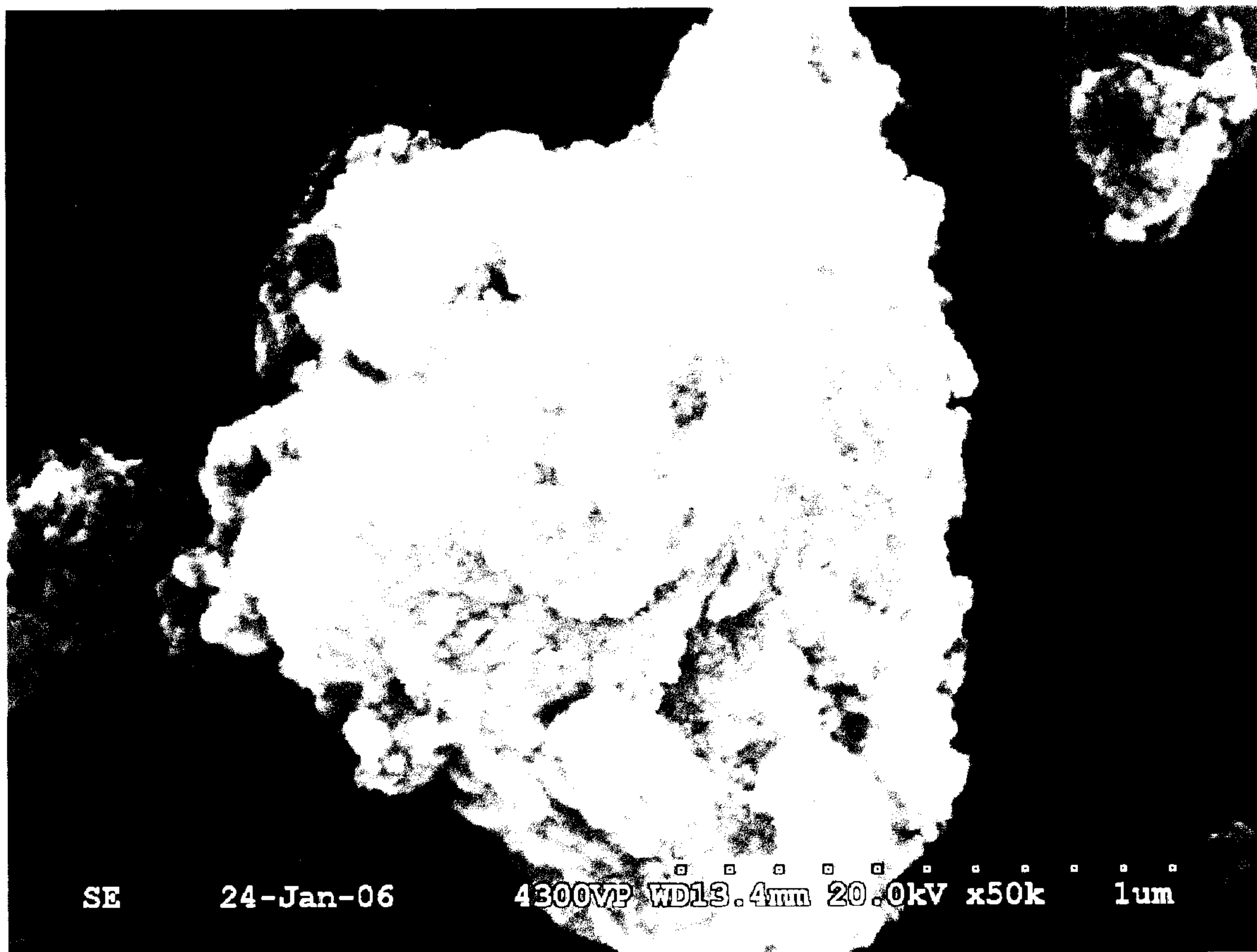


FIG. 5

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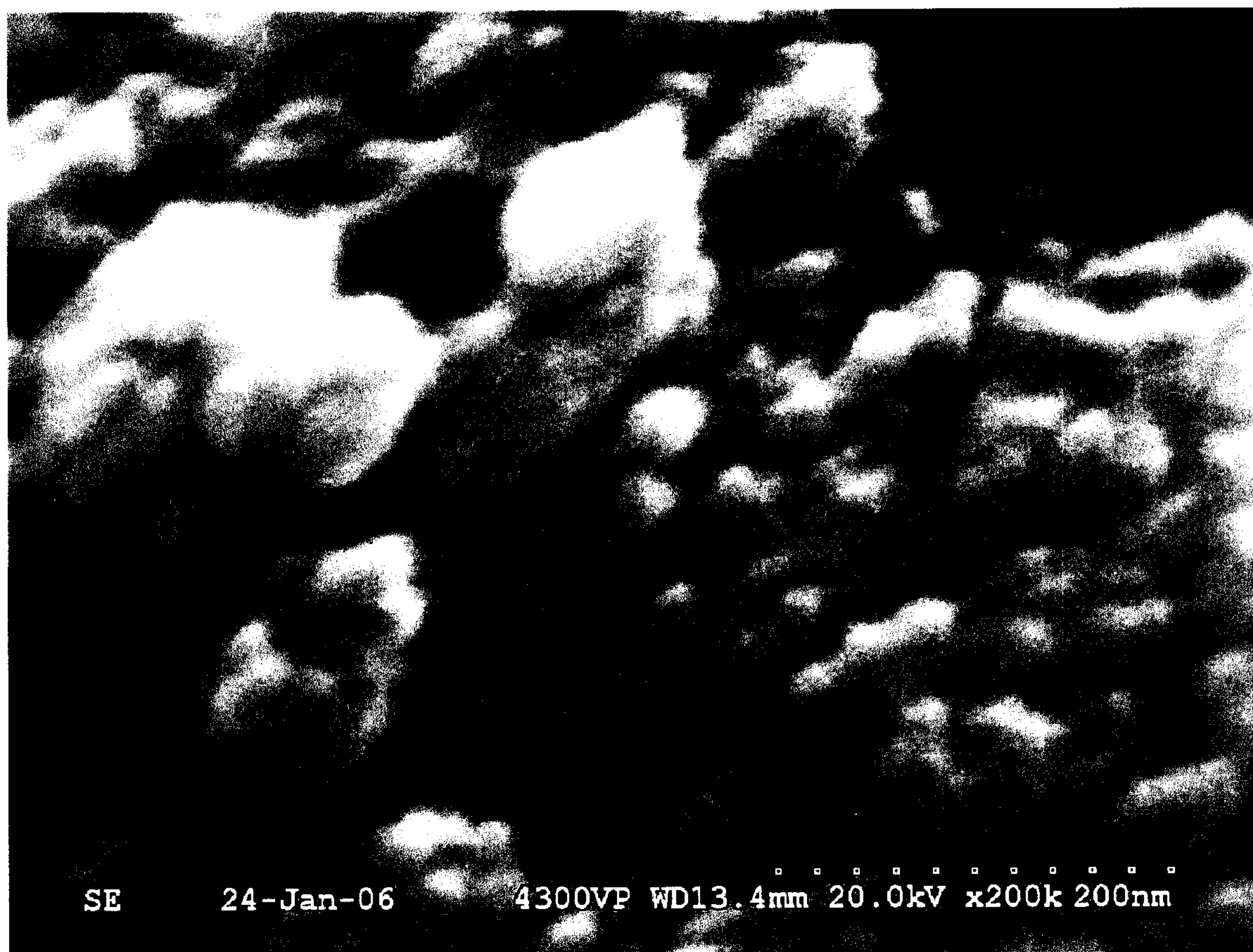


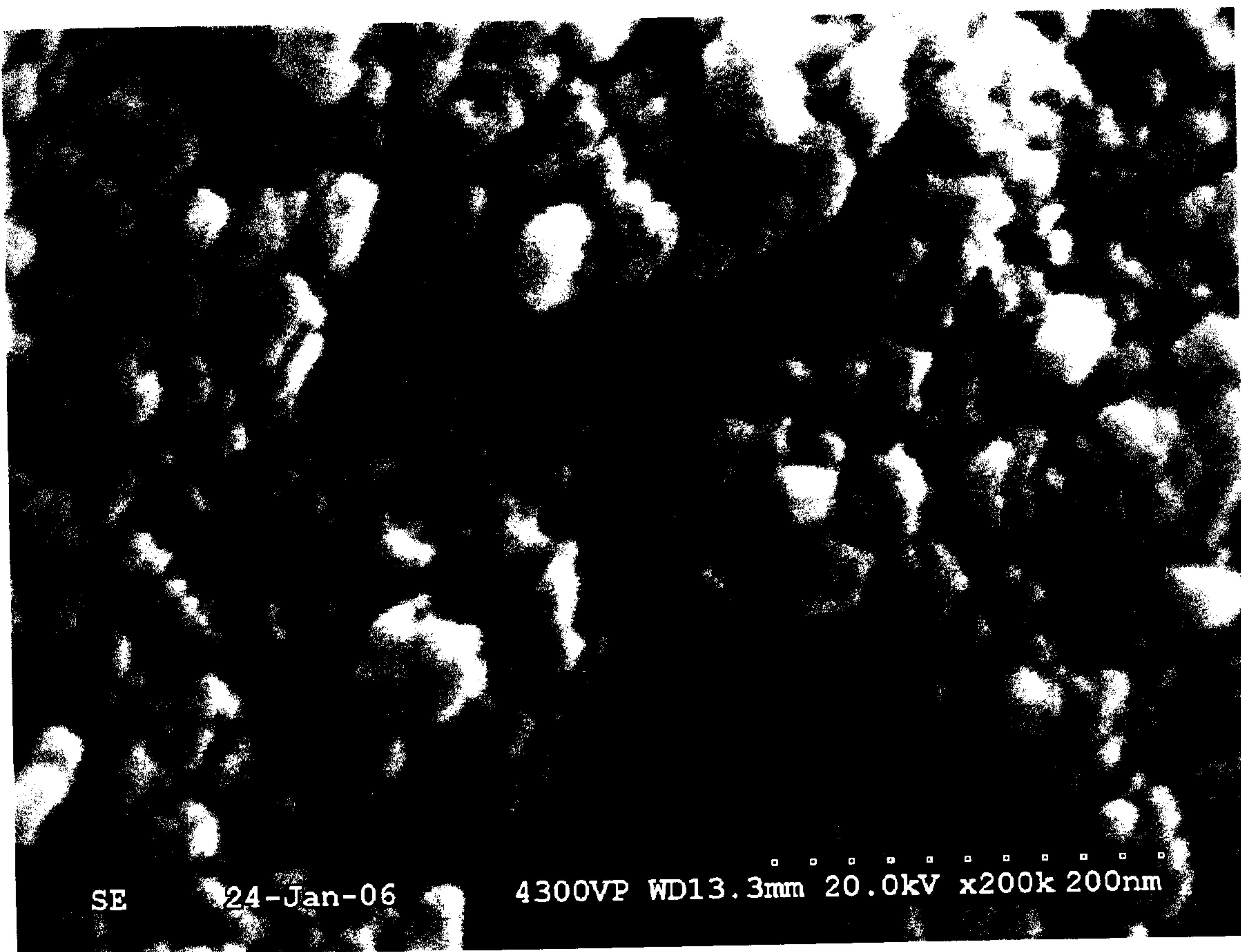
FIG. 6

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FIG. 7

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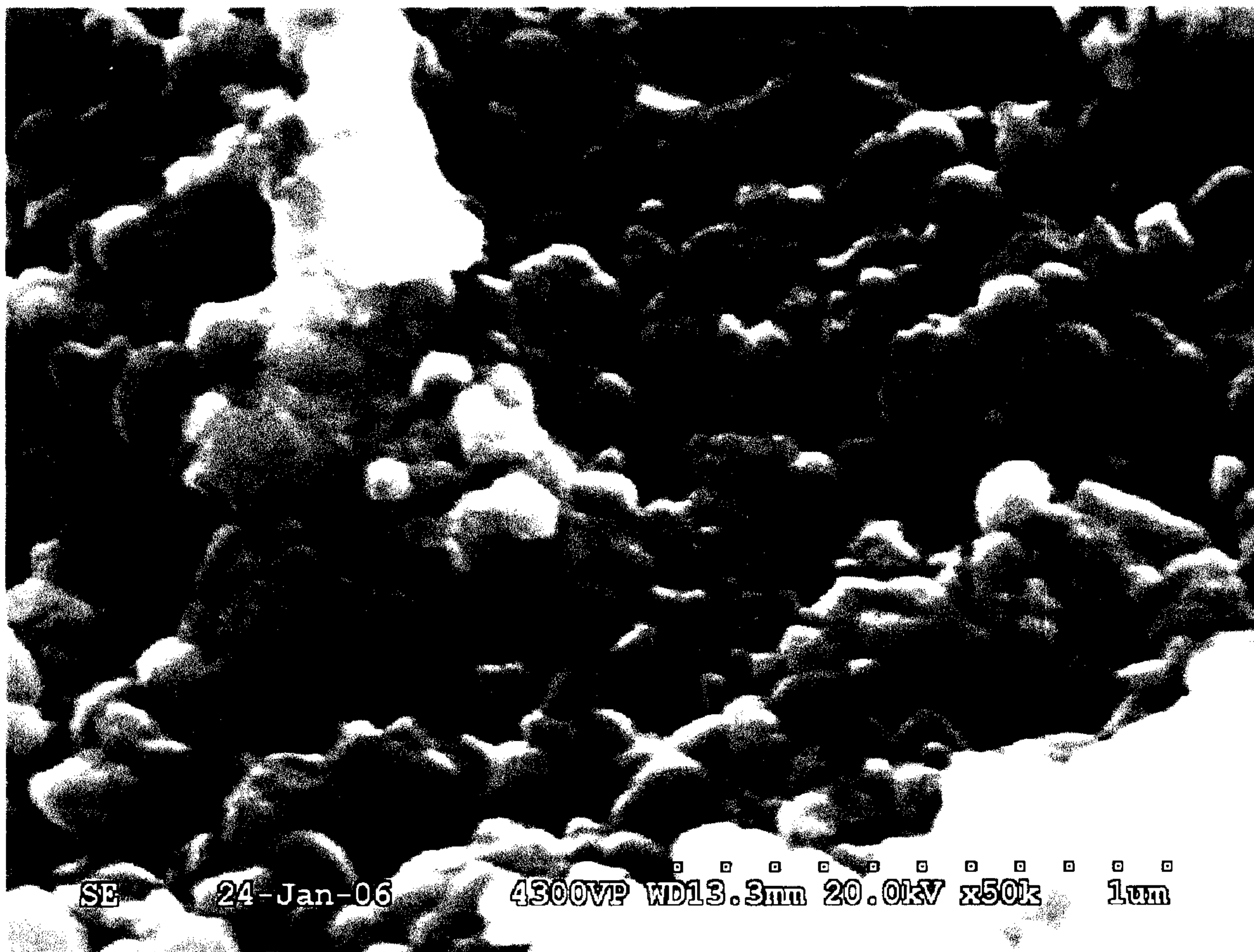


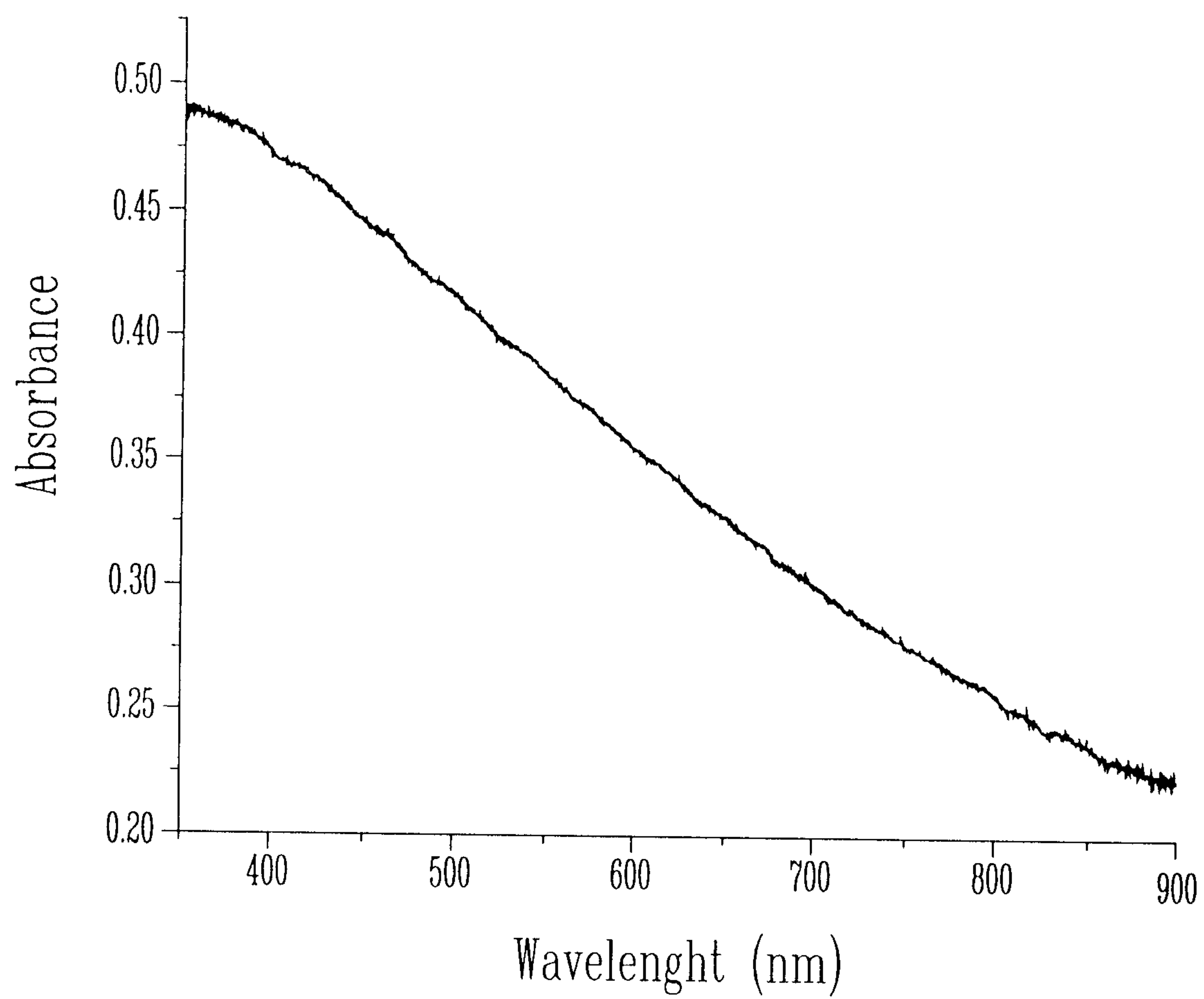
FIG. 9

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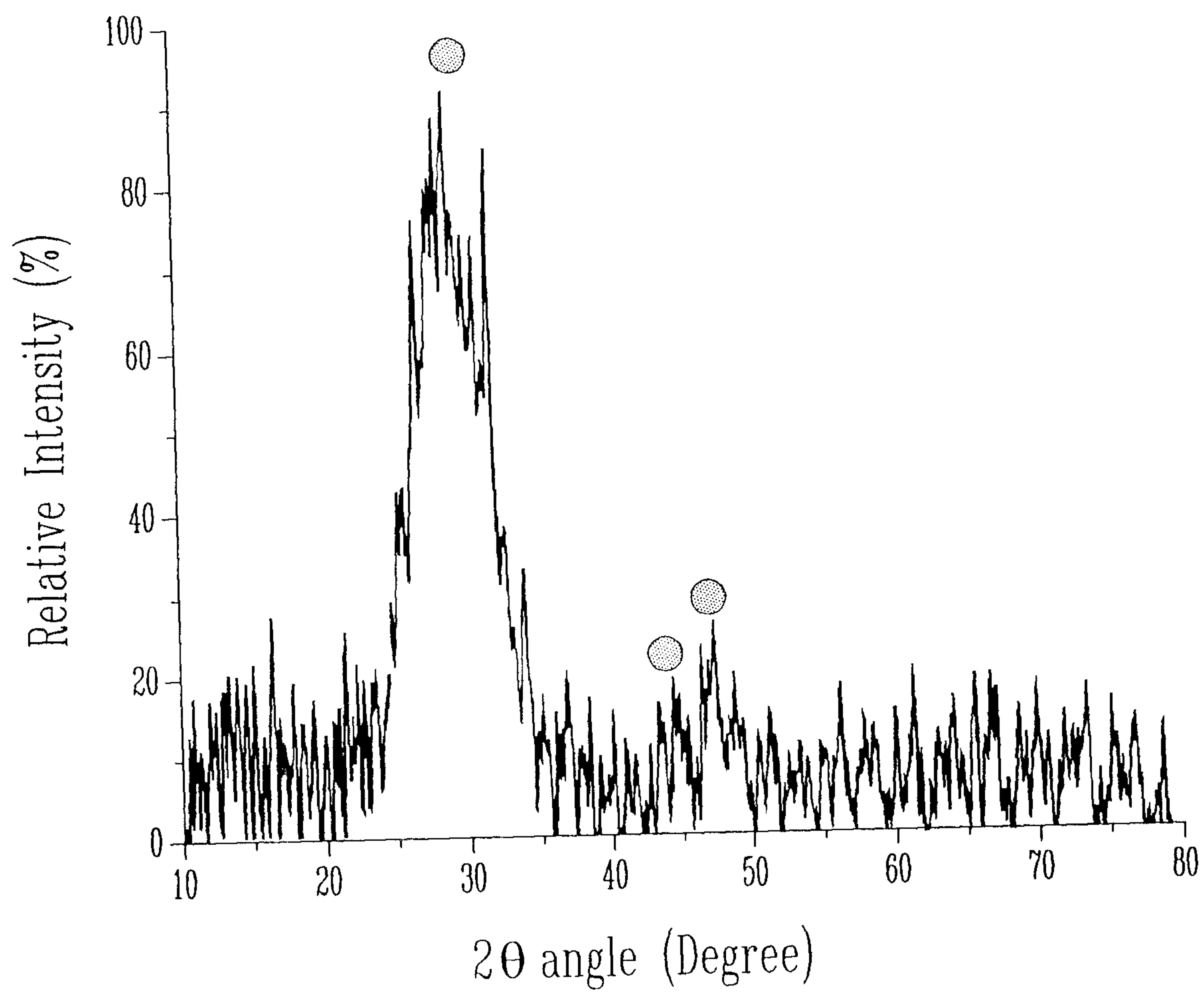


FIG. 10

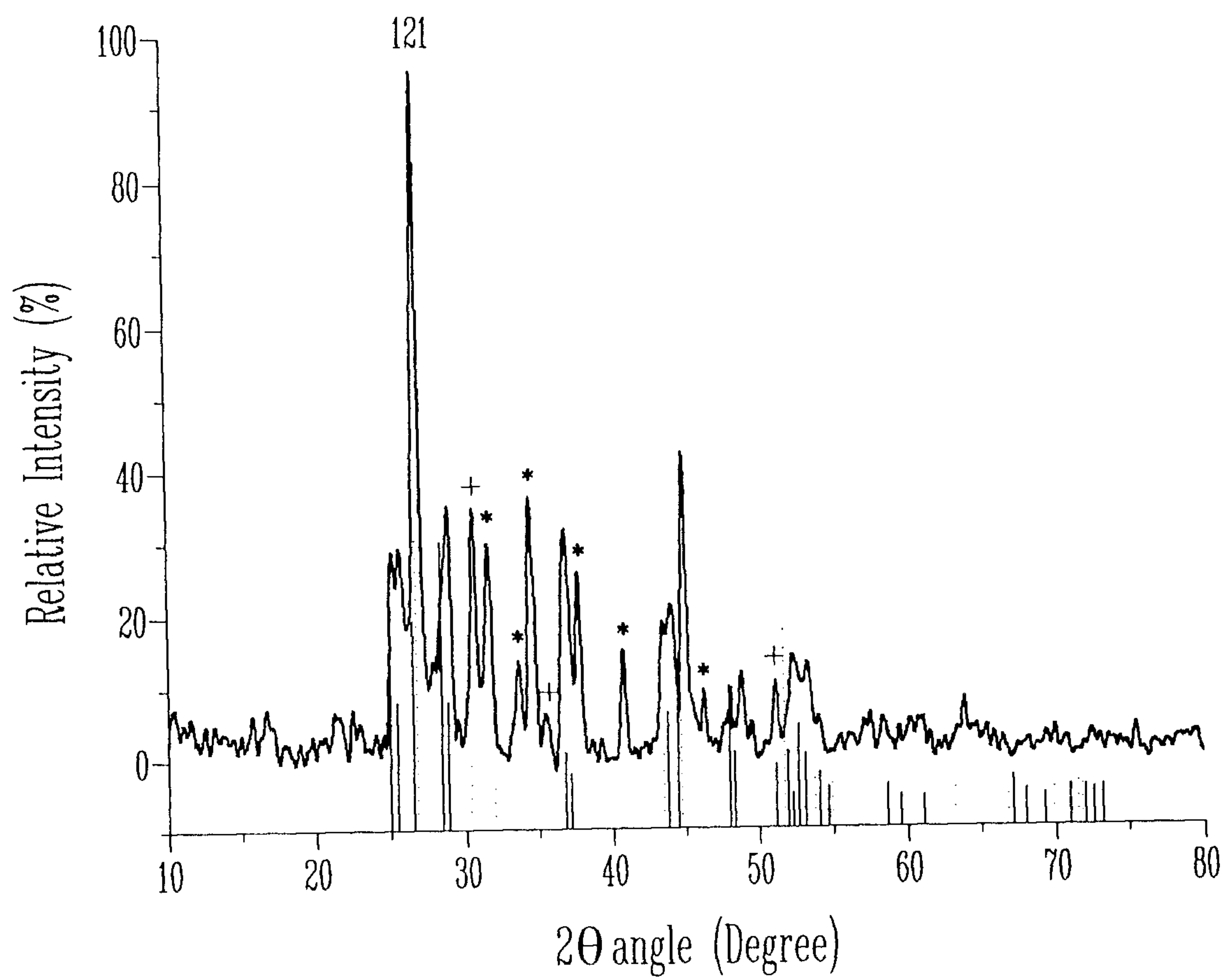
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FIG. 11

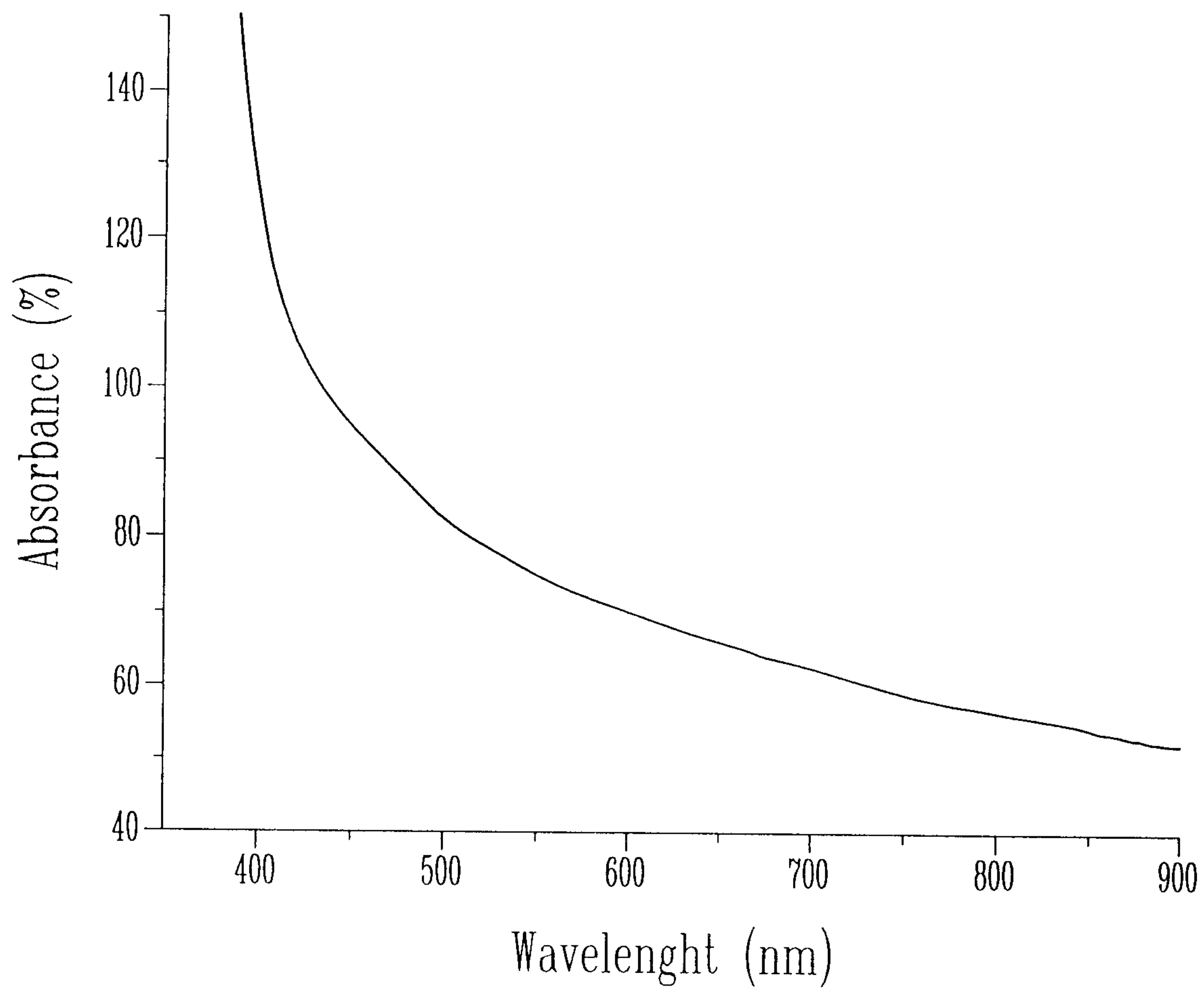
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FIG. 12

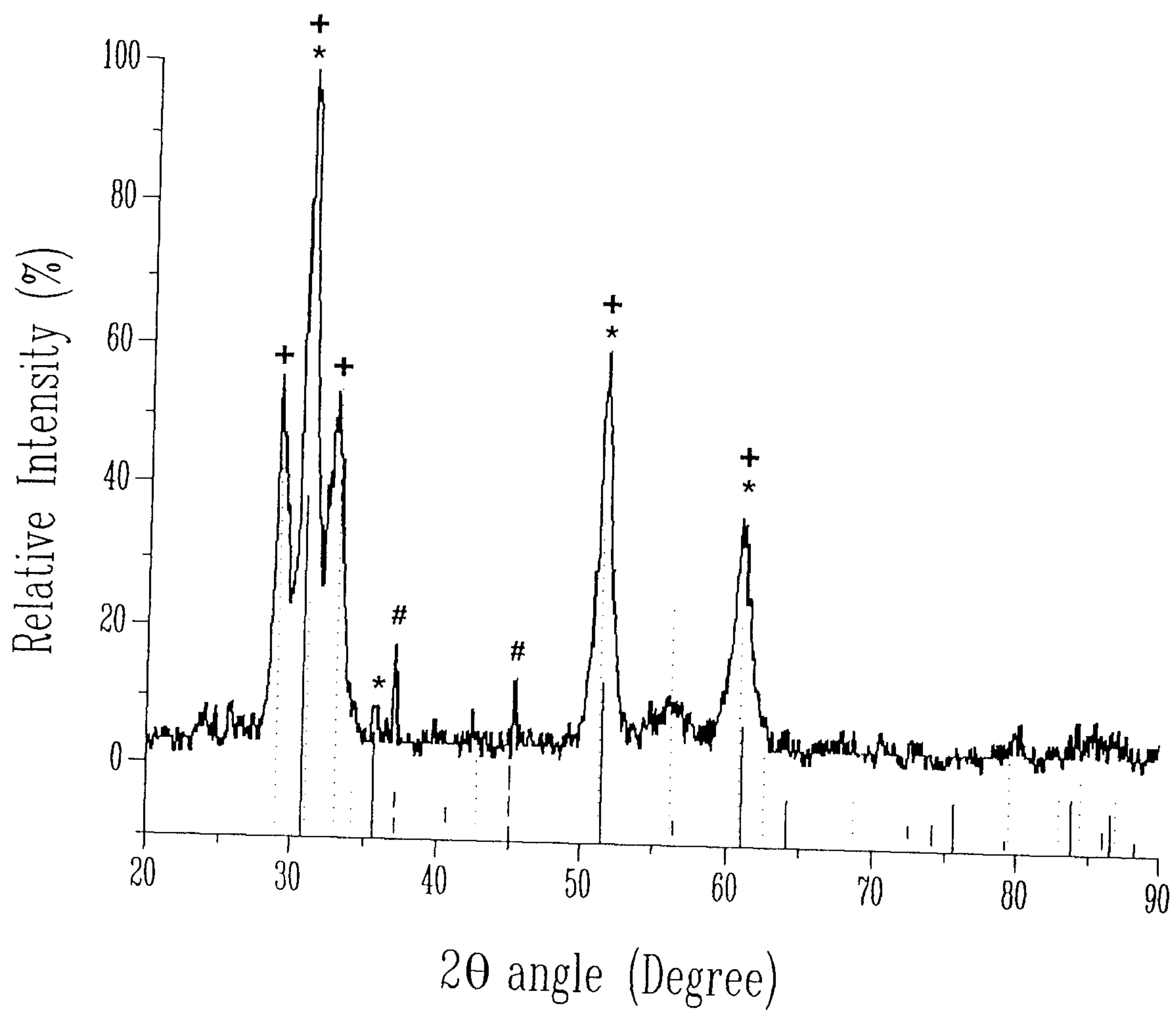
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FIG. 13

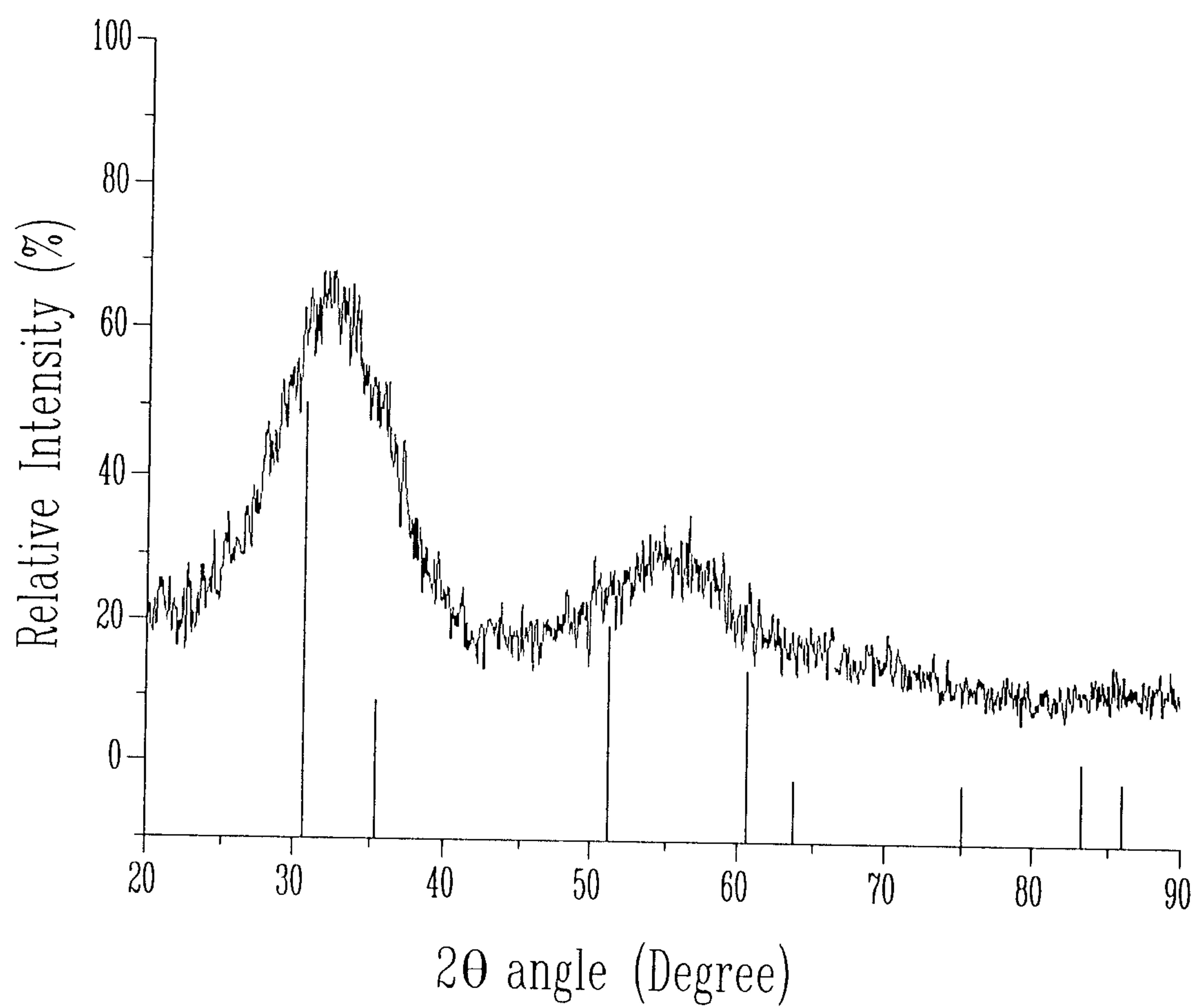
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FIG. 14

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FIG. 15

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FIG. 16

