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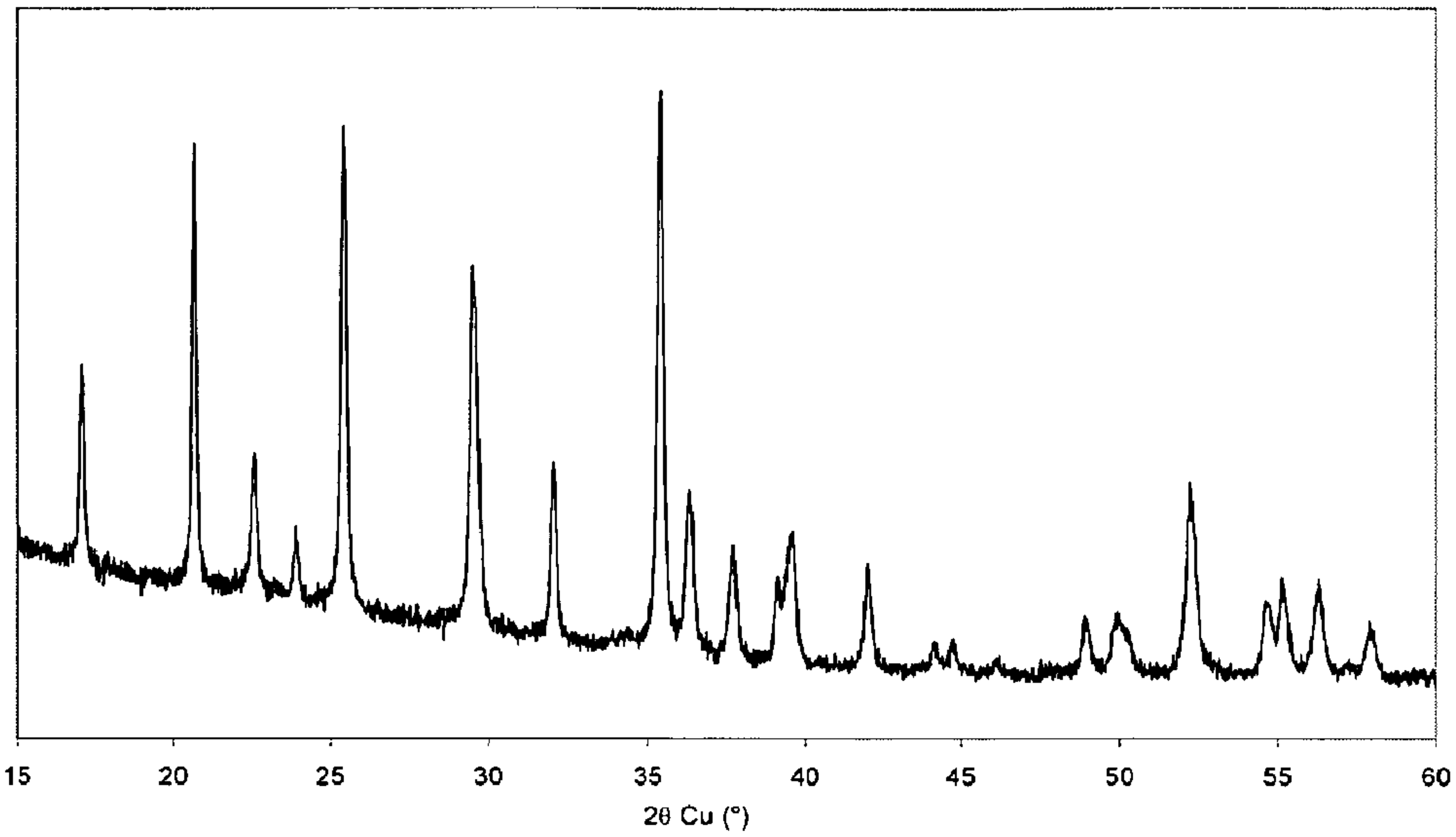
(54) **Titre :** SYNTHESE DE $LiFeMPO_4$....NANOMETRIQUE CRISTALLINE
(54) **Title:** SYNTHESIS OF CRYSTALLINE NANOMETRIC $LiFeMPO_4$



(57) **Abrégé/Abstract:**
The present invention relates to lithium secondary batteries and more specifically to positive electrode materials operating at potentials greater than 2.8 V vs. Li^+/Li in non-aqueous electrochemical cells. In particular, the invention relates to crystalline

(57) **Abrégé(suite)/Abstract(continued):**
nanometric olivine-type $LiFe_{I-x}M_xPO_4$ powder with M is Co and/or Mn, and 0<x<1, with small particle size and narrow particle size distribution. A direct precipitation process is described, comprising the steps of: - providing a water-based mixture having at a pH between 6 and 10, containing a dipolar aprotic additive, and $Li^{(I)}$, $Fe^{(II)}$, $P^{(V)}$, and $Co^{(II)}$ and/or $Mn^{(II)}$ as precursor components; - heating said water-based mixture to a temperature less than or equal to its boiling point at atmospheric pressure, thereby precipitating crystalline $LiFe_{I-x}M_xPO_4$ powder. An extremely fine particle size is obtained of about 80 nm for Mn and 275 nm for Co, both with a narrow distribution. The fine particle size is believed to accounts for excellent high-drain properties, while minimizing the need for conductive additives. The narrow distribution facilitates the electrode manufacturing process and ensures a homogeneous current distribution within the battery.

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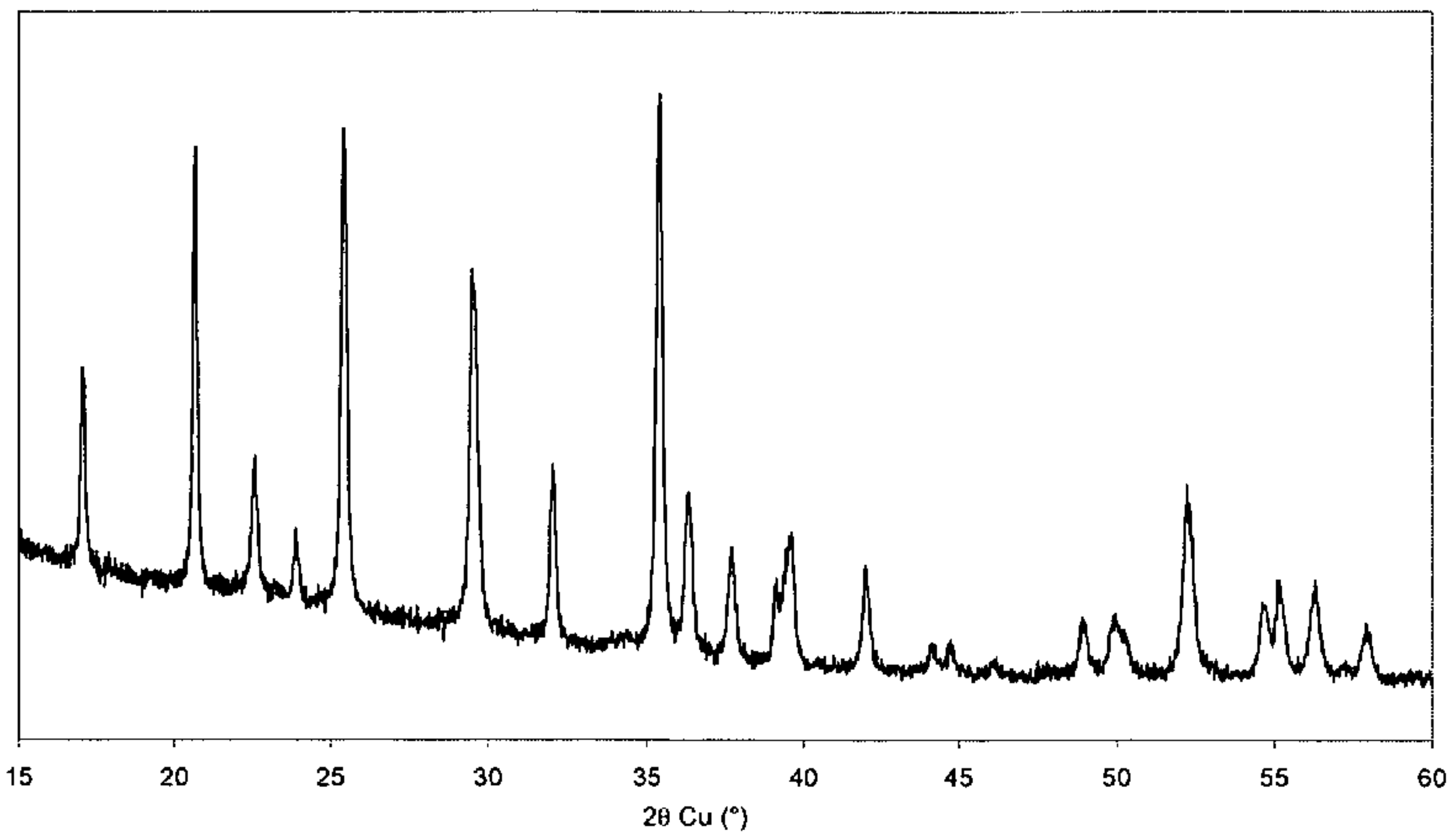
(54) Title: SYNTHESIS OF CRYSTALLINE NANOMETRIC $LiFeMPO_4$



(57) Abstract: The present invention relates to lithium secondary batteries and more specifically to positive electrode materials operating at potentials greater than 2.8 V *vs.* Li^+/Li in non-aqueous electrochemical cells. In particular, the invention relates to crystalline nanometric olivine-type $LiFe_{1-x}M_xPO_4$ powder with M is Co and/or Mn, and $0<x<1$, with small particle size and narrow particle size distribution. A direct precipitation process is described, comprising the steps of: - providing a water-based mixture having at a pH between 6 and 10, containing a dipolar aprotic additive, and $Li^{(I)}$, $Fe^{(II)}$, $P^{(V)}$, and $Co^{(II)}$ and/or $Mn^{(II)}$ as precursor components; - heating said water-based mixture to a temperature less than or equal to its boiling point at atmospheric pressure, thereby precipitating crystalline $LiFe_{1-x}M_xPO_4$ powder. An extremely fine particle size is obtained of about 80 nm for Mn and 275 nm for Co, both with a narrow distribution. The fine particle size is believed to accounts for excellent high-drain properties, while minimizing the need for conductive additives. The narrow distribution facilitates the electrode manufacturing process and ensures a homogeneous current distribution within the battery.

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Synthesis of crystalline nanometric $LiFeMPO_4$

The invention relates to a crystalline nanometric $LiFe_{1-x}M_xPO_4$ (LFMP) powder with small particle size and narrow particle size distribution for use as positive electrode material in Li batteries. It also describes a preferred manufacturing method by precipitation at low temperature and atmospheric pressure of the crystalline nanometric powder.

Since the original work of Padhi et al. (JES, 144 (1997), 1188), phospho-olivines $LiMPO_4$ (with M = Fe, Ni, Co, Mn, ...) have appeared to be potential candidates to be used as cathode materials for Li batteries. Among all these isostructural compositions, $LiFePO_4$ was the most investigated and its commercialization is now a reality thanks to very high performances in term of reversible capacity, rate properties and cycle life (International Publication Number WO2004/001881 A2).

$LiCoPO_4$ (Amine et al., ESSL, 3, (2000), 178) and $LiMnPO_4$ (Okada et al., J. Power Sources, 97-98 (2001) 430), due to their higher redox potential values oft 4.8 V and 4.1 V *vs.* Li respect., are of particular interest because of the higher energy density they offer compared to $LiFePO_4$ (3.5V *vs.* Li, Chen et al., JES, 149 (2002) A1184).

However, it is now well known that these phospho-olivines materials suffer from poor electronic and ionic conductivity (Delacourt et al., JES, 152 (2005) A913) so that the need for optimising the microstructure of these compounds is essential. Striebel et al. (JES, 152, (2005), A664) insisted on the fact that, even if the matrix conductivity has been improved by conductive coating, the battery developer would welcome so-far inexistent compounds having a primary particle size in the 50 to100 nm range and, overall, attempts should be made to minimise the particle size distribution, in order to yield better power efficiency.

Most promising results on mixed metal phosphates such as $LiFe_{1-x}Mn_xPO_4$ materials were obtained on $C/LiFe_{0.4}Mn_{0.6}PO_4$ composites, in which C acts as a sintering inhibitor. This approach leads to mixed C/$LiFeMnPO_4$ composites with particles in the 100 to 200 nm range (Mi et al., Mater. Sci. Eng., 129 (2006) 8). Similar results were obtained by Lloris et al. (ESSL, 5 (2002) A234), on pure $LiCoPO_4$ with small particles in the 200 to 300nm range. No data were published on $LiFe_1$-xCo_xPO_4 materials so far.

In addition to the small particle size, emphasis must be put on narrowing the particle size distribution in order to ensure a homogeneous current distribution in the electrode and thus achieve better battery performances, in particular high power efficiency and long cycle life. The present invention therefore aims at providing a crystalline LFMP powder with small particle size and narrow particle size distribution.

To this end, a process is disclosed yielding metal phosphate powders offering essential improvements over the materials cited above.

The invented process for the synthesis of crystalline $LiFe_{1-x}M_xPO_4$ powder where M is one or both of Co and Mn, and $0<x<1$, preferably $0.4<x<0.95$, comprises the steps of:
- providing a water-based mixture having a pH between 6 and 10, containing a dipolar aprotic additive, and $Li^{(I)}$, $Fe^{(II)}$, $P^{(V)}$, and one or both of $Co^{(II)}$ and $Mn^{(II)}$ as precursor components;
- heating said water-based mixture to a temperature less than or equal to its boiling point at atmospheric pressure, thereby precipitating crystalline $LiFe_{1-x}M_xPO_4$ powder. The obtained powder can be subjected to a post-treatment by heating it in non-oxidising conditions.

A pH of between 6 and 8 is however preferred to avoid any precipitation of Li_3PO_4. The additive is preferably a dipolar aprotic compound without chelating or complexation propensity. The heating temperature of the water-based mixture of at least 60 °C is preferred.

The production of the crystalline $LiFe_{1-x}M_xPO_4$ powder or the thermal post-treatment can advantageously be performed in the presence of at least one further component, in particular a carbon containing or electron conducting substance, or the precursor of an electron conducting substance.

It is useful to introduce at least part of the $Li^{(I)}$ is as LiOH. Similarly, at least part of the $P^{(V)}$ can be introduced as H_3PO_4. The pH of the water-based mixture can be obtained by adjusting the ratio of LiOH to H_3PO_4.

It is advisable to use a water-based mixture with an atmospheric boiling point of between 100 and 150 °C, and preferably between 100 and 120 °C. Dimethylsulfoxide (DMSO) is preferably used as the dipolar aprotic additive. The water-based mixture advantageously contains between 5 and 50 %mol, and preferably between 10 and 30 %mol, of DMSO. A lower DMSO concentrations result in a coarser particle size distribution; higher concentrations limit the availability of water, forcing to increase the volume of the apparatus.

The step of post treatment of the $LiFe_{1-x}M_xPO_4$ is advantageously performed at a temperature of up to 675 °C, and preferably of at least 300 °C. The lower limit is chosen in order to enhance the crystallinity of the precipitated $LiFe_{1-x}M_xPO_4$; the upper limit is chosen so as to avoid the decomposition of the $LiFe_{1-x}M_xPO_4$ into manganese phosphides.

The electron conducting substance can be carbon, in particular conductive carbon or carbon fibres. Alternatively, a precursor of an electron conducting substance can be used, in particular a polymer or sugar-type macromolecule.

The invention also pertains to a crystalline $LiFe_{1-x}Mn_xPO_4$ powder with $0<x<1$, preferably $0.4<x<0.95$, for use as electrode material in a battery, having a particle size distribution with an average particle size d50 of less than 100 nm, and preferably of more than 30 nm. The maximum particle size is preferably less than or equal to 500 nm. The particle size distribution is preferably mono-modal and the ratio (d90 - d10) / d50 is advantageously less than 1.5, preferably less than 1.3.

Another embodiment of this invention concerns a composite powder containing the above-defined crystalline $LiMnPO_4$ powder, and up to 10 %wt of conductive additive. A further embodiment concerns the electrode mix that can be prepared using this composite powder. Conductive carbons, carbon fibres, amorphous carbons resulting from decomposition of organic carbon containing substances, electron conducting polymers, metallic powders, and metallic fibres are particularly well suited as conductive additives.

Another embodyment of this invention concerns the use of the composite powder for the manufacture of a lithium insertion-type electrode, by mixing said powder with a conductive carbon-bearing additive.

The invention also pertains to a crystalline $LiFe_{1-x}Co_xPO_4$ powder with $0<x<1$, preferably $0.4<x<0.95$, for use as electrode material in a battery, having a particle size distribution with an average particle size d50 of less than 300 nm, and preferably of more than 30 nm. The maximum particle size is preferably less than or equal to 900 nm. The particle size distribution is preferably mono-modal and the ratio (d90 - d10) / d50 is advantageously less than 1.5, preferably less than 1.1.

Another embodiment of this invention concerns a composite powder containing the above-defined crystalline $LiFe_{1-x}Co_xPO_4$ powder, and up to 10 %wt of conductive additive. A further embodiment concerns the electrode mix that can be prepared using this composite powder. Conductive carbons, carbon fibres, amorphous carbons resulting from decomposition of organic carbon containing substances, electron conducting polymers, metallic powders, and metallic fibres are particularly well suited as conductive additives.

Another embodyment of this invention concerns the use of the composite powder for the manufacture of a lithium insertion-type electrode, by mixing said powder with a conductive carbon-bearing additive.

Compared to prior art, this product lists all the advantages needed for being considered as potential cathode material in lithium battery:

- the direct precipitation of crystalline LFMP at low temperature prevents any grain growth linked to sintering processes. Nanometric particle sizes are obtained. This reduces kinetic limitations due to Li ions transport within the particle, thereby enhancing the fast charge/discharge behaviour of the batteries.
- the narrow particle size distribution ensures a homogeneous current distribution within the battery. This is especially important at high charge/discharge rates, where finer particles would get more depleted than coarser ones, a phenomenon leading to the eventual deterioration of the particles and to the fading of the battery capacity upon use. Furthermore, it facilitates manufacturing of the electrode.

The atmospheric boiling point of the water-based mixture is advisably between 100 and 150 °C, preferably between 100 and 120 °C. Use is made of a water-miscible additive as a co-solvent that will increase the precipitate nucleation kinetics thus reducing the size of the $LiMnPO_4$ nanometric particles. In addition to be miscible with water, useful co-solvents should be aprotic, i.e. show only a minor or complete absence of dissociation accompanied by release of hydrogen ions. Co-solvents showing complexation or chelating properties such as ethylene glycol do not appear suitable as they will reduce the kinetics of precipitation of $LiMnPO_4$ and thus lead to larger particle sizes. Suitable dipolar aprotic solvents are dioxane, tetrahydrofuran, N-(C_1-C_{18}-alkyl)pyrrolidone, ethylene glycol dimethyl ether, C_1-C_4-alkylesters of aliphatic C_1-C_6-carboxylic acids, C_1-C_6-dialkyl ethers, N,N-di-(C_1-C_4-alkyl)amides of aliphatic C_1-C_4-carboxylic acids, sulfolane, 1,3-di-(C_1-C_8-alkyl)-2-imidazolidinone, N-(C_1-C_8-alkyl)caprolactam, N,N,N', N'-tetra-(C_1-C_8-alkyl)urea, 1,3-di-(C_1- C_8-alkyl)-3,4,5,6-tetrahydro-2(1H)-pyrimidone, N,N,N',N'-tetra-(C_1-C_8-alkyl)sulfamide, 4-formylmorpholine, 1-formylpiperidine or 1-formylpyrrolidine, N-(C_1-C_{18}-alkyl)pyrrolidone, N-methylpyrrolidone (NMP), N-octylpyrrolidone, N-dodecylpyrrolidone, N,N-dimethylformamide, N,N-dimethylacetamide or hexamethylphosphoramide. Other alternatives such as tetraalkyl ureas are also possible. Mixtures of the abovementioned dipolar aprotic solvents may also be used. In a preferred embodiment, dimethylsulfoxide (DMSO) is used as solvent.

The Figures illustrating the invention are summarized as follows.

Fig. 1: XRD of the $LiFe_{0.5}Mn_{0.5}PO_4$ precipitate after 18 h reaction time.

Fig. 2: SEM picture of the $LiFe_{0.5}Mn_{0.5}PO_4$.

Fig.3: Volumetric particle size distribution and cumulative distribution (% *vs*. nm) of the $LiFe_{0.5}Mn_{0.5}PO_4$.

Fig. 4: XRD of the $LiFe_{0.5}Co_{0.5}PO_4$ precipitate after 18 h reaction time.

Fig. 5: SEM picture of the $LiFe_{0.5}Co_{0.5}PO_4$.

Fig. 6: Volumetric particle size distribution and cumulative distribution (% *vs*. nm) of the $LiFe_{0.5}Co_{0.5}PO_4$.

The invention is further illustrated in the following examples.

Example 1: Synthesis of $LiFe_{0.5}Mn_{0.5}PO_4$

In a first step, DMSO is added to an equimolar solution of 0.05 M $Mn^{(II)}$ in $MnNO_3.4H_2O$, 0.05 M $Fe^{(II)}$ in $FeSO_4.7H_2O$ and 0.1 M $P^{(V)}$ in H_3PO_4, dissolved in H_2O while stirring. The amount of DMSO is adjusted in order to reach a global composition of 50 %vol water and 50 %vol DMSO corresponding to respectively about 80 %mol and 20 %mol.

In a second step, an aqueous solution of 0.3 M $LiOH.H_2O$ is added to the solution at 25 °C; the pH hereby increases to a value between 6.5 and 7.5. The final Li:Fe:Mn:P ratio is close to 3:0.5:0.5:1.

In a third step, the temperature of the solution is increased up to the solvent boiling point, which is 108 to 110 °C. After 18 h, the obtained precipitate is filtered and washed thoroughly with water. The pure crystalline $LiFe_{0.5}Mn_{0.5}PO_4$ obtained is shown in Fig. 1.

The refined cell parameters are a = 10.390 Å, b = 6.043 Å; c = 4.721 Å, with a cell volume of 296.4 $Å^3$. This is in good agreement with Vegard's law specifying that, in case of solid solution, the cell volume of mixed product should be in-between that of end products (291 $Å^3$ for pure $LiFePO_4$, 302 $Å^3$ for pure $LiMnPO_4$).

The picture on Fig. 2 shows monodisperse small crystalline particles in the 50-100nm range. The volumetric particle size distribution of the product was measured using image analysis. As shown in Fig. 3, the d50 values is about 80 nm, while the relative span, defined as (d90 - d10) / d50, is about 1.2 (d10 = 45 nm, d90 = 145 nm).

Example 2: Synthesis of $LiFe_{0.5}Co_{0.5}PO_4$

In a first step, DMSO is added to an equimolar solution of 0.05 M $Mn^{(II)}$ in $MnSO_4.H_2O$, 0.05 M $Co^{(II)}$ in $CoNO_3.6H_2O$ and 0.1 M P(V) in H_3PO_4, dissolved in H_2O while stirring. The amount of DMSO is adjusted in order to reach a global composition of 50 %vol. water and 50 %vol. DMSO.

In a second step, an aqueous solution of 0.3 M $LiOH.H_2O$ is added to the solution at 25 °C; the pH hereby increases to a value between 6.5 and 7.5. The, the final Li:Fe:Co:P ratio is close to 3:0.5:0.5:1.

In a third step, the temperature of the solution is increased up to the solvent boiling point, which is 108 to 110°C. After 18 h, the obtained precipitate is filtered and washed thoroughly with water. The pure crystalline $LiFe_{0.5}Co_{0.5}PO_4$ obtained is shown in Fig. 4.

The refined cell parameters are a =10.292 Å, b = 5.947 Å; c = 4.712 Å with a cell volume of 288.4 $Å^3$. This is again in good agreement with Vegard's law specifying that, in case of solid solution, the cell volume of mixed product should be in-between that of end products (291 $Å^3$ for pure $LiFePO_4$, 284 $Å^3$ for pure $LiCoPO_4$).

The picture on Fig. 5 shows monodisperse small crystalline particles in the 200-300nm range. The volumetric particle size distribution of the product was measured by using image analysis. As shown in Fig. 6, the d50 values is about 275 nm, while the relative span, defined as (d90 - d10) / d50, is about 1.0 (d10 = 170 nm, d90 = 450 nm).

CLAIMS:

1. A process for preparing crystalline $LiFe_{1-x}M_xPO_4$ powder where M is one or both of Co and Mn, and $0<x<1$, comprising the steps of:

   a) providing a water-based mixture having a boiling point and a pH between 6 and 10, containing a dipolar aprotic additive, and Li(I), Fe(II) and P(V), Co(II) and Mn(II) as precursor components; and

   b) heating said water-based mixture to a temperature less than or equal to said boiling point at atmospheric pressure, thereby precipitating crystalline $LiFe_{1-x}M_xPO_4$ powder.

2. The process according to claim 1, followed by a step of post-treatment of the $LiFe_{1-x}M_xPO_4$ powder by heating said powder in non-oxidizing conditions.

3. The process of claim 1 or 2, wherein the production of the crystalline $LiFe_{1-x}M_xPO_4$ powder or the post treatment by heating in non oxidising atmosphere takes place in the presence of at least one further component selected from the group consisting of a carbon containing substance, an electron conducting substance and a precursor of an electron conducting substance.

4. The process of claim 1, wherein at least part of the Li(I) is introduced as LiOH.

5. The process of claim 1, wherein at least part of the P(V) is introduced as H_3PO_4.

6. The process of claim 4 or 5, wherein the pH of the water-based mixture is obtained by adjusting the ratio of LiOH to H_3PO_4.

7. The process of any one of claims 1 to 6, wherein the atmospheric boiling point of the water-based mixture is between 100 and 150°C.

8. The process of claim 7, wherein the atmospheric boiling point of the water-based mixture is between 100 and 120°C.

9. The process of any one of claims 1 to 8, wherein the aprotic dipolar additive contained in the water-based mixture is dimethylsulfoxide.

10. The process of any one of claims 2 to 9, wherein the step of post treatment of the $LiFe_{1-x}M_xPO_4$ is performed at a temperature of up to 675°C.

11. The process of claim 10, wherein the temperature is in the range of 300 to 675°C.

12. The process of any one of claims 3 to 11 wherein the electron conducting substance is carbon.

13. The process of claim 12 wherein the carbon is conductive carbon or carbon fibres.

14. The process of any one of claims 3 to 11, wherein the precursor of an electron conducting substance is a carbon conducting substance.

15. The process of claim 14 wherein the carbon conducting substance is a polymer or sugar-type macromolecule.

16. A crystalline $LiFe_{1-x}M_xPO_4$ powder with $0 < x < 1$, for use as electrode material in a battery, having a particle size distribution with an average particle size d50 of less than 100 nm.

17. The crystalline powder of claim 16 wherein the average particle size d50 is in the range of 30 nm to 100 nm.

18. The $LiFe_{1-x}M_xPO_4$ powder of claim 16 or 17, wherein the maximum particle size is less than or equal to 500 nm.

19. The $LiFe_{1-x}M_xPO_4$ powder of claim 16, 17 or 18, characterised in that the particle size distribution is mono-modal and in that the ratio (d90 - d10)/d50 is less than 1.5.

20. The $LiFe_{1-x}M_xPO_4$ powder of claim 19 wherein the ratio (d90 - d10)/d50 is less than 1.3.

21. A composite powder containing the $LiFe_{1-x}M_xPO_4$ powder of any one of claims 16 to 20 and up to 10 wt% of a conductive additive.

22. An electrode mix containing the composite powder of claim 21.

23. Use of the composite powder of claim 21 and a conductive carbon-bearing additive to manufacture a lithium insertion-type electrode.

24. A crystalline $LiFe_{1-x}M_xPO_4$ powder with $0 < x < 1$, for use as electrode material in a battery, wherein the powder has a particle size distribution with an average particle size d50 of less than 300 nm.

25. The crystalline $LiFe_{1-x}M_xPO_4$ powder of claim 24 wherein the powder has a particle size distribution with an average particle size d50 in the range of 30 nm to 300 nm.

26. The $LiFe_{1-x}M_xPO_4$ powder of claim 24 or 25, wherein the maximum particle size is less than or equal to 900 nm.

27. The $LiFe_{1-x}M_xPO_4$ powder of claim 24, 25 or 26, wherein the particle size distribution of the powder is mono-modal and the ratio (d90 - d10)/d50 of the powder is less than 1.5.

28. The $LiFe_{1-x}M_xPO_4$ powder of claim 27, wherein the ratio (d90 - d10)/d50 of the powder is less than 1.1.

29. A composite powder containing the $LiFe_{1-x}M_xPO_4$ powder of any one of claims 24 to 28, and up to 10 wt% of a conductive additive.

30. An electrode mix containing the composite powder of claim 29.

31. Use of the composite powder of claim 29 and a conductive carbon-bearing additive to manufacture a lithium insertion-type electrode.

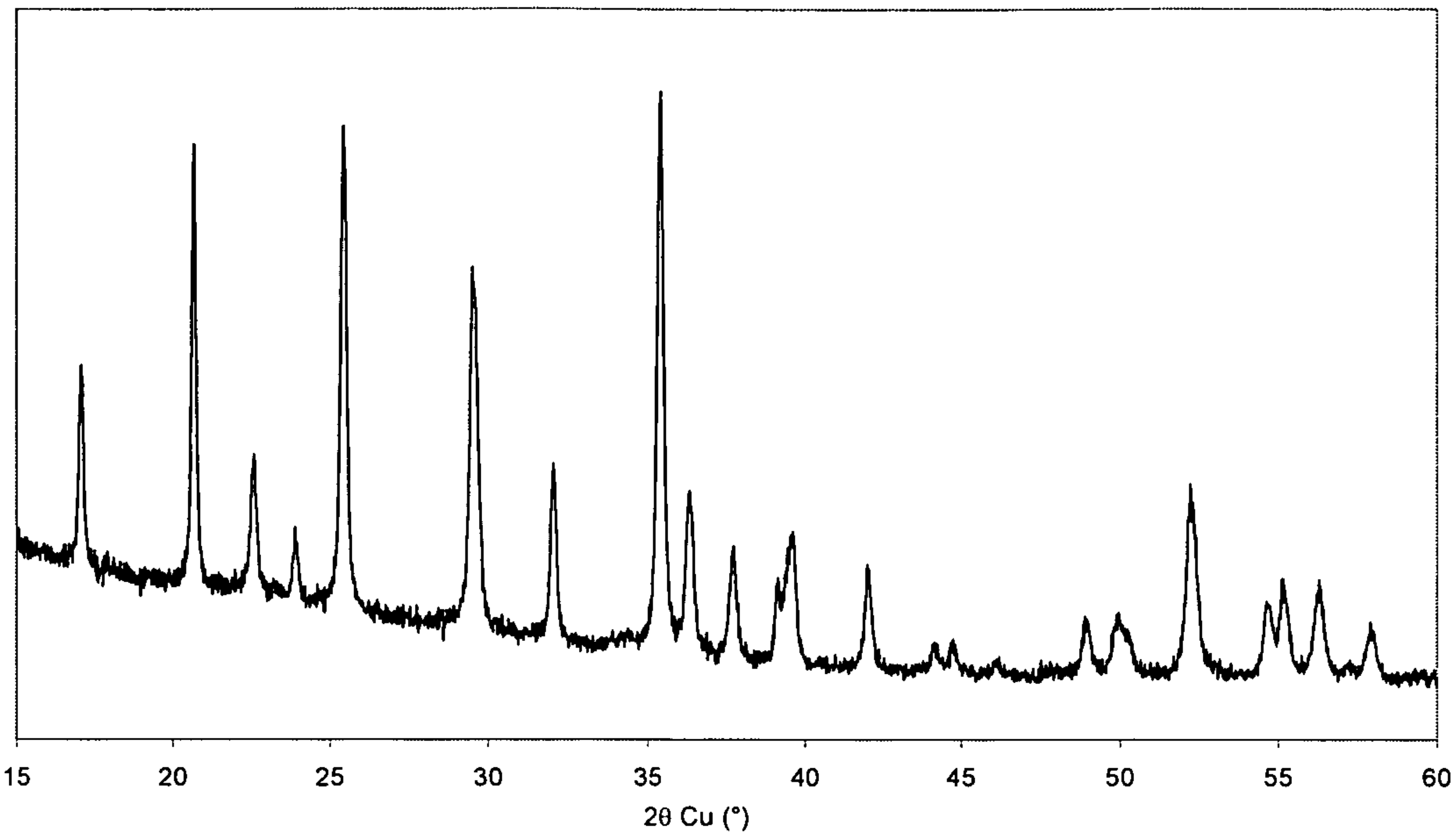

Fig. 1

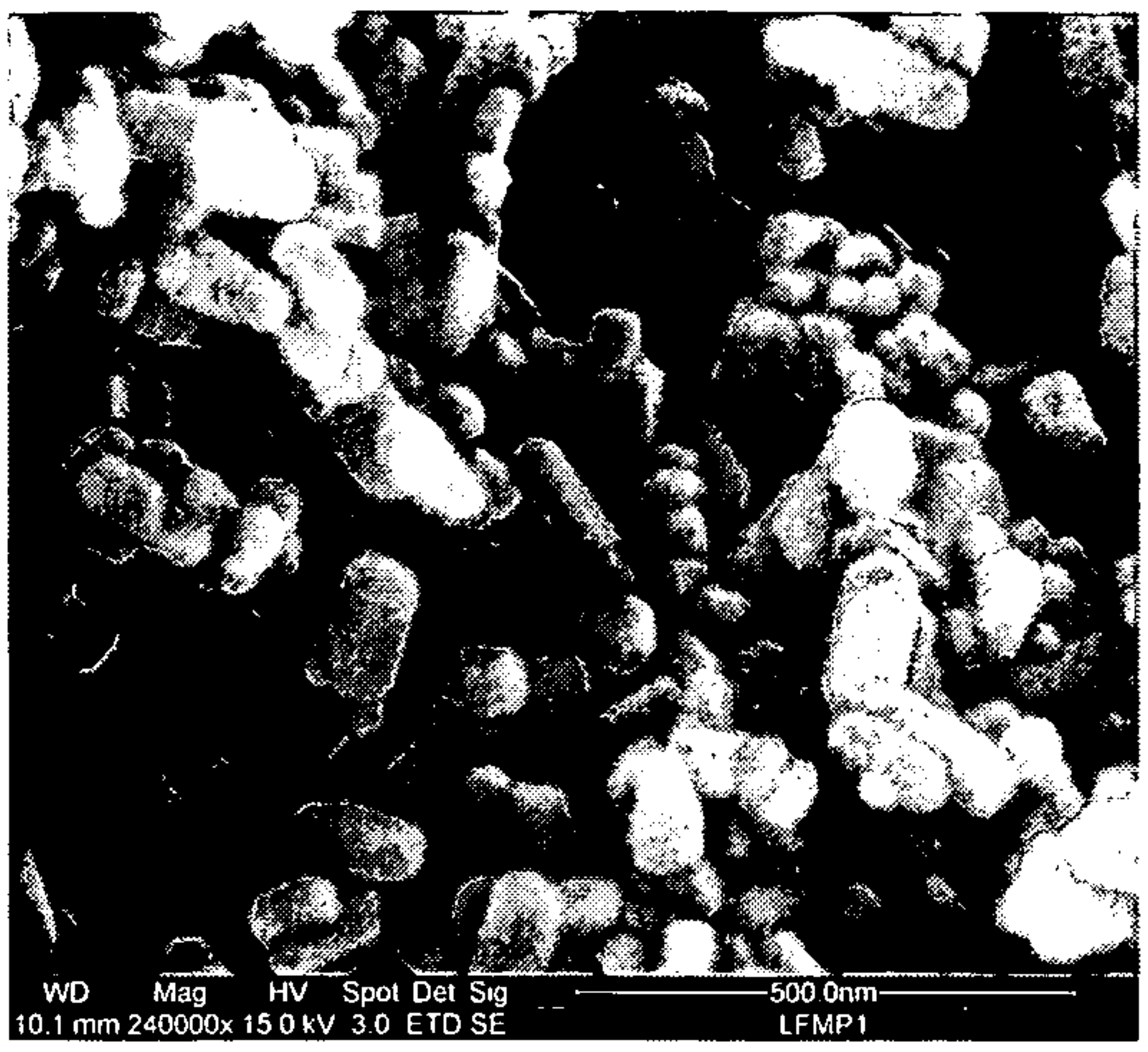
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Fig. 2

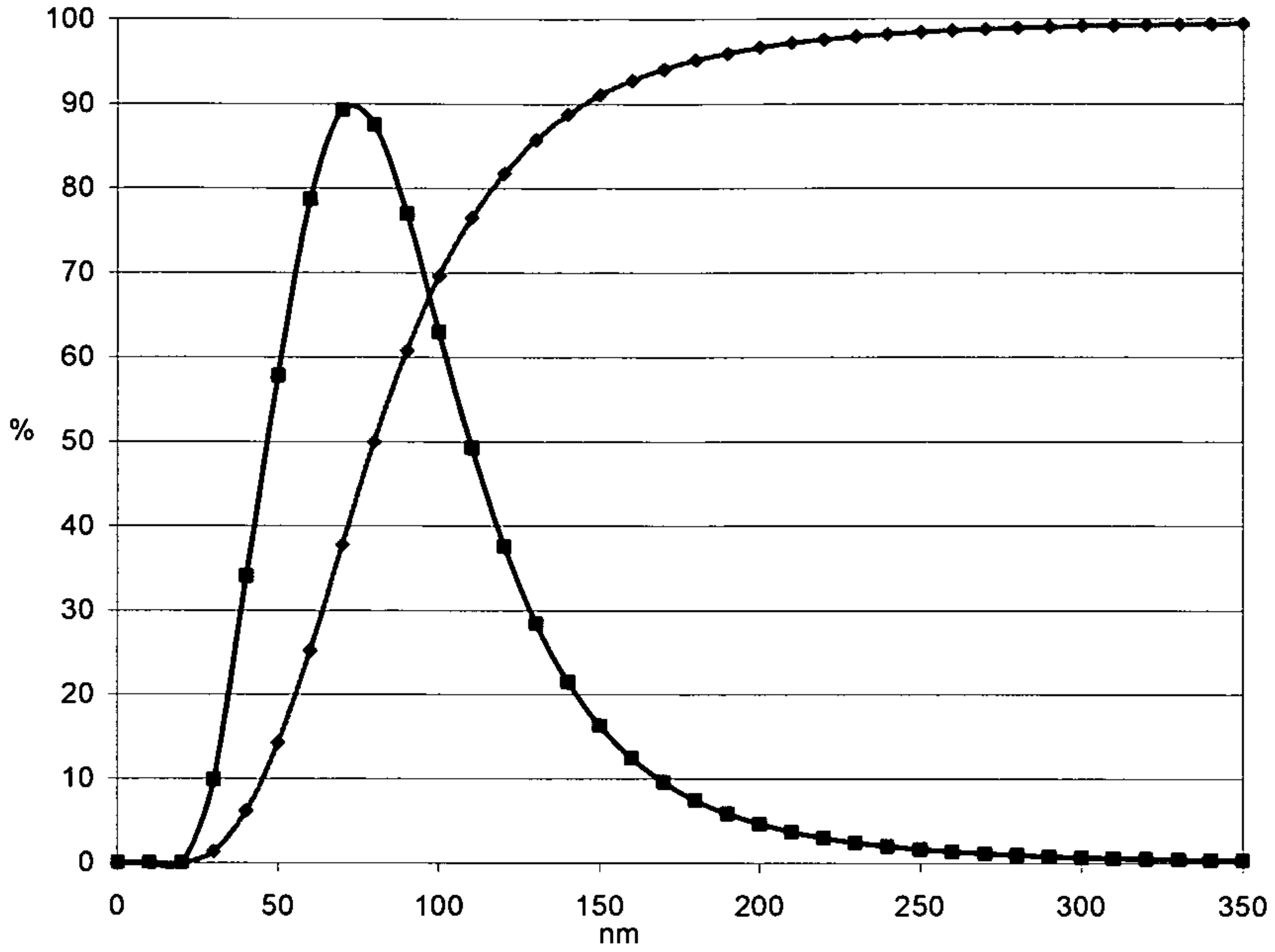


Fig. 3

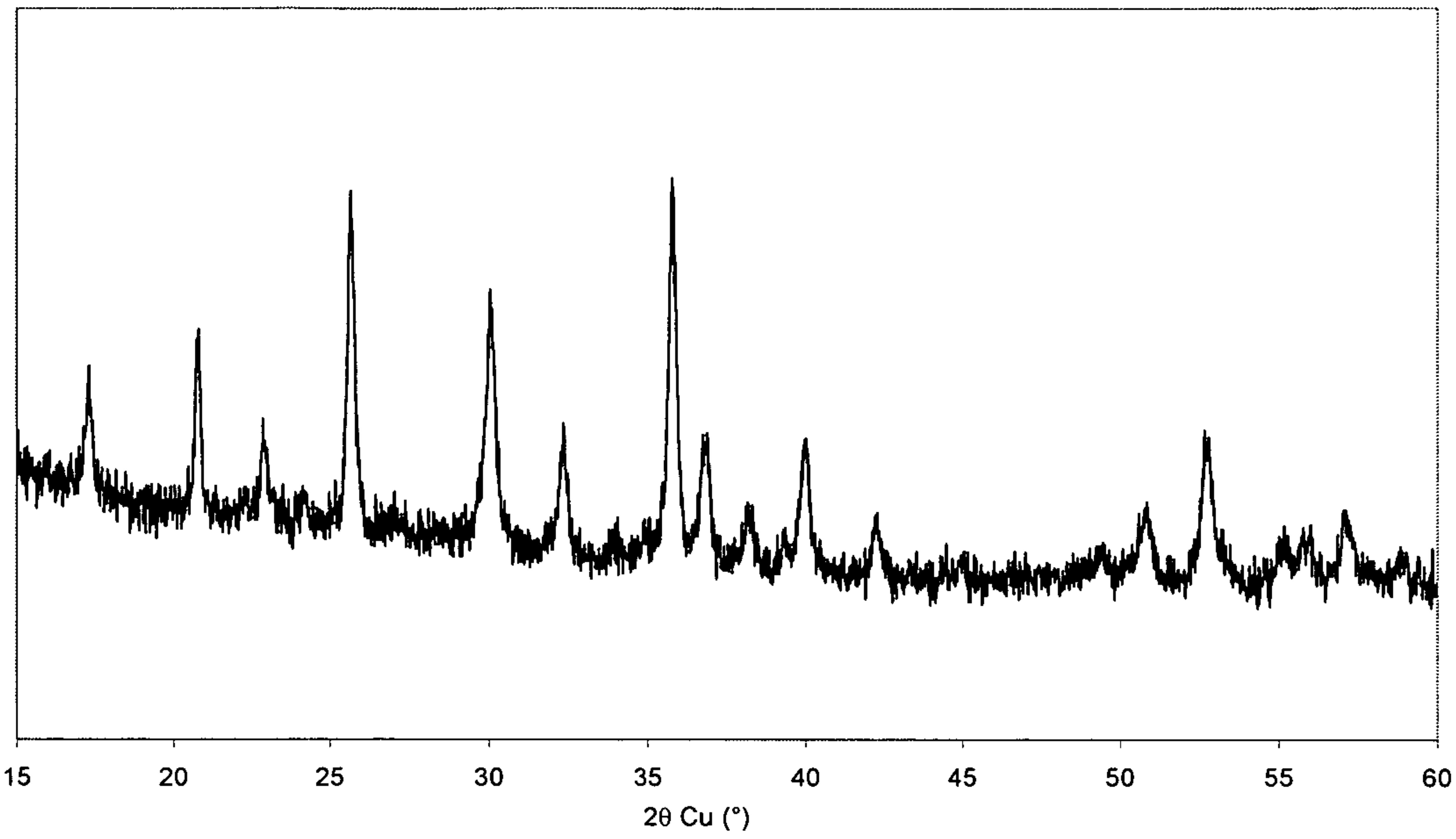


Fig. 4

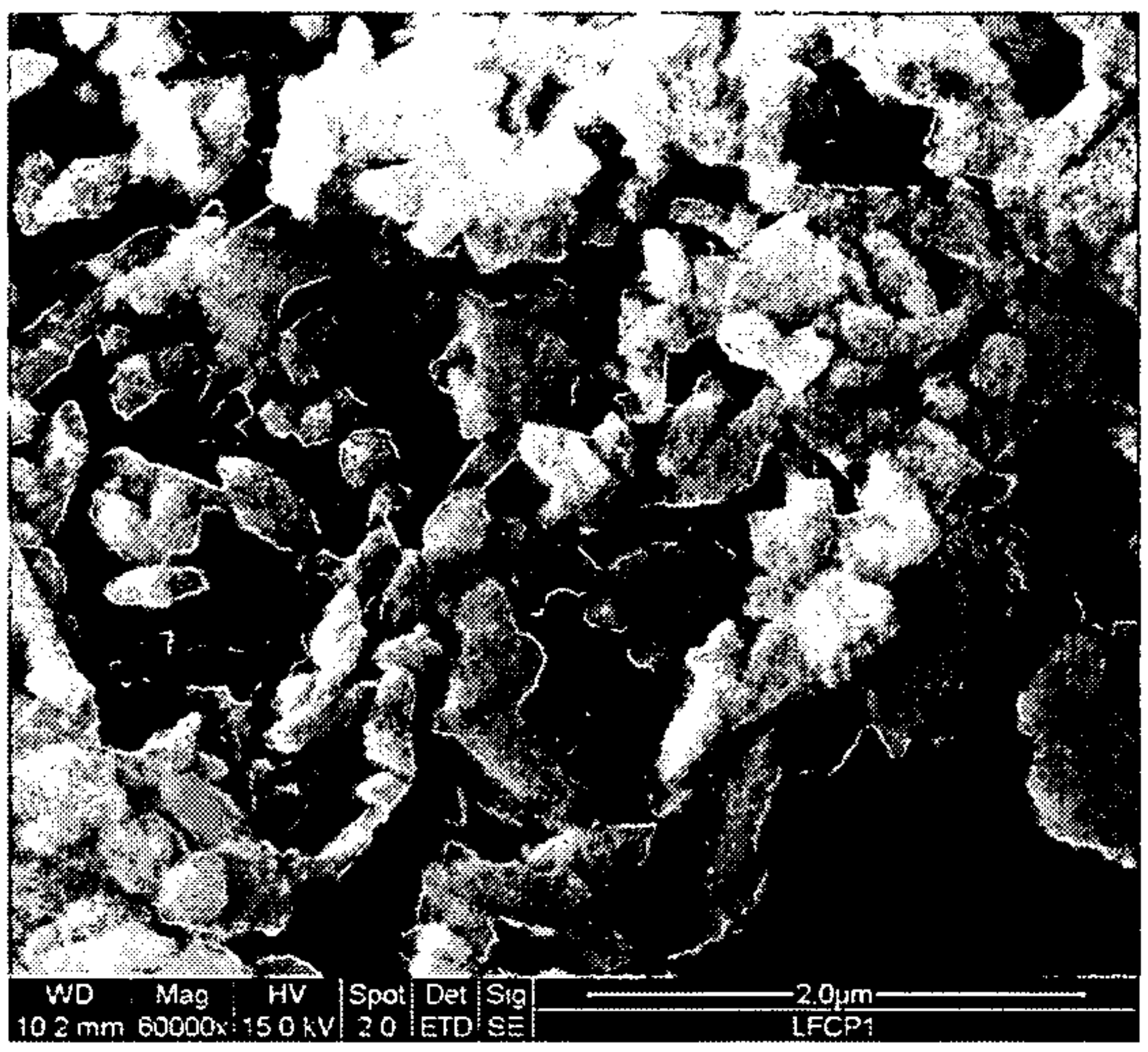
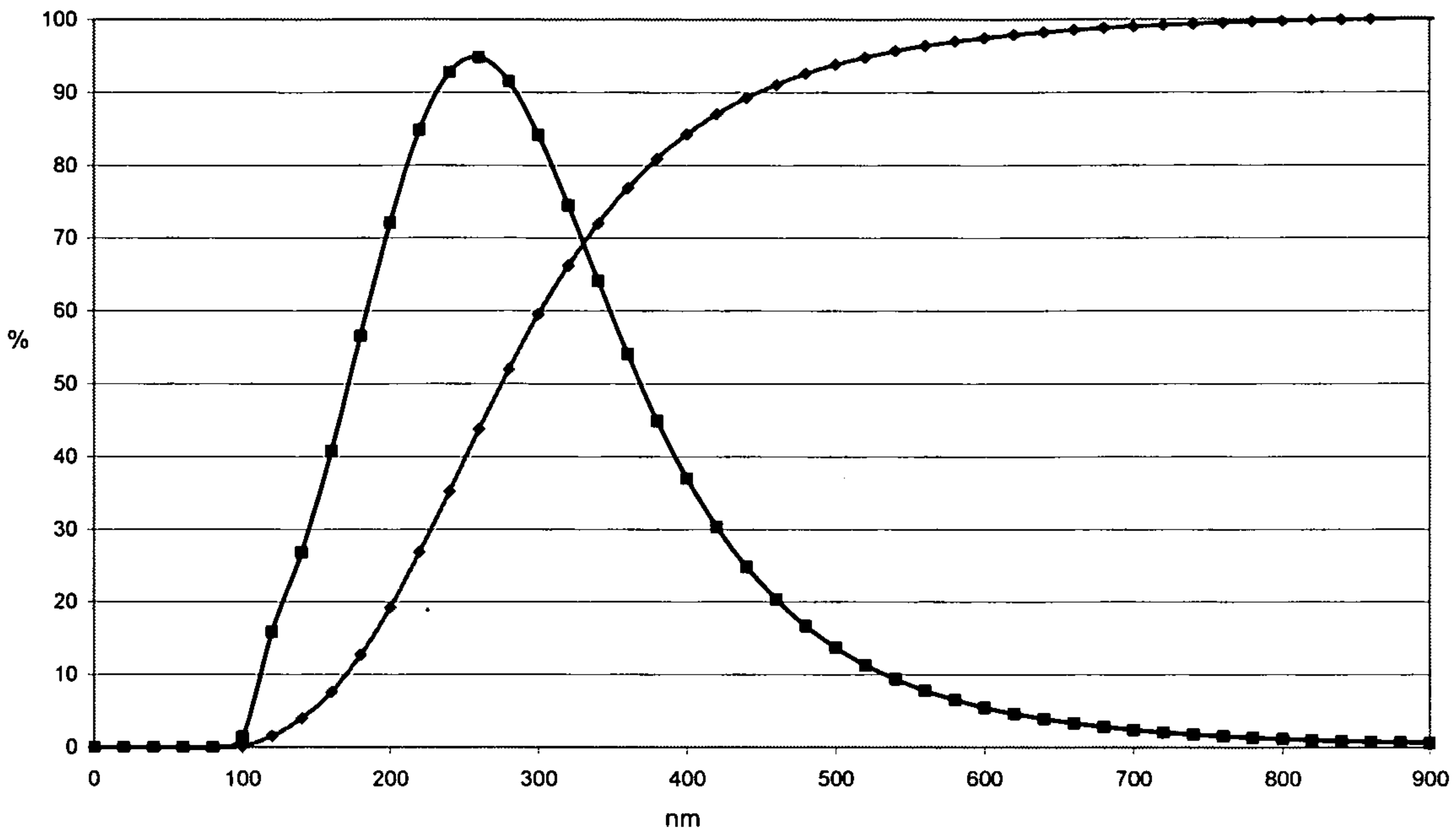


Fig. 5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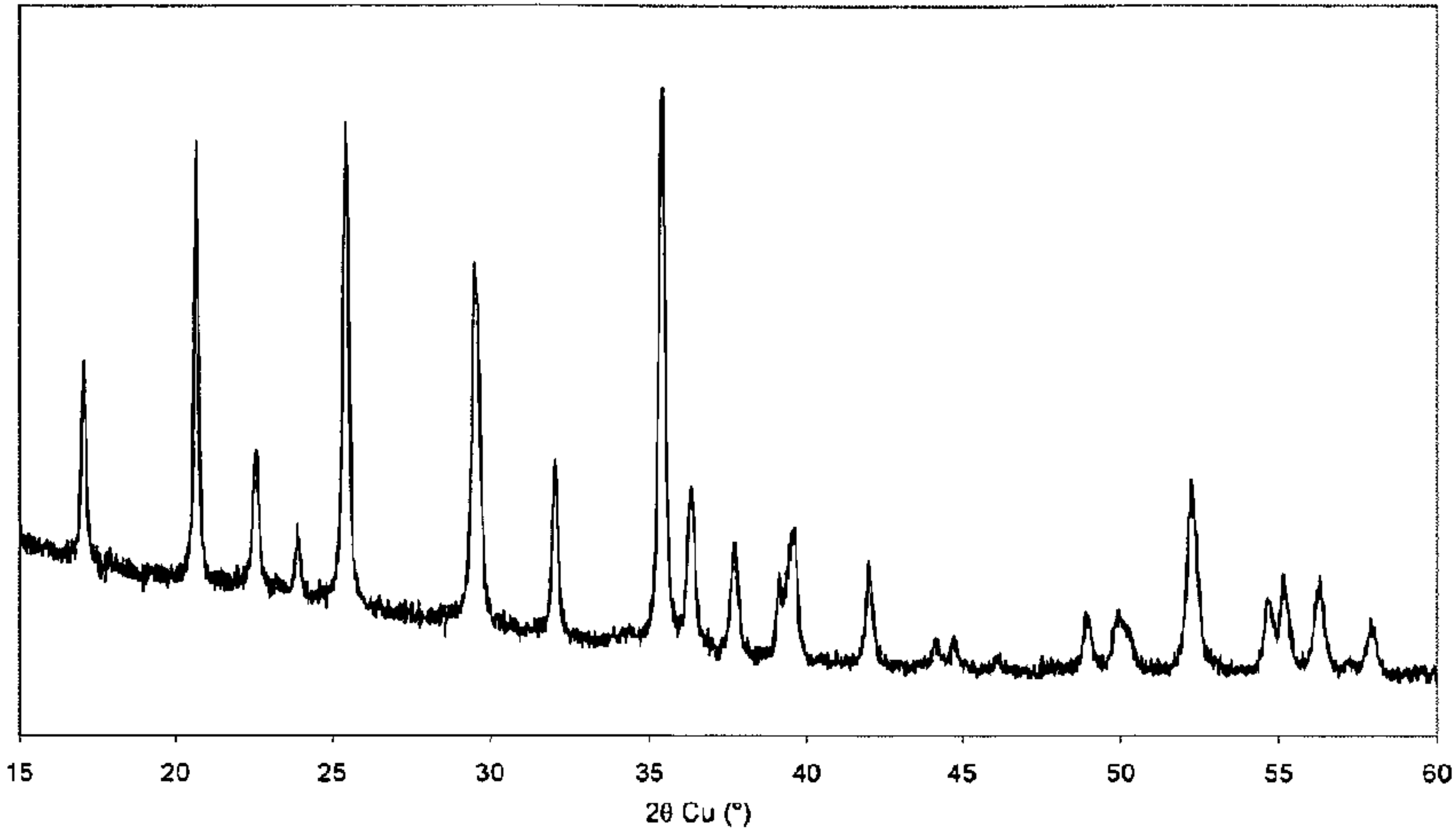
700
800
900
nm

Fig. 6


15
20
25
30
35
40
45
50
55
60
2θ Cu (°)