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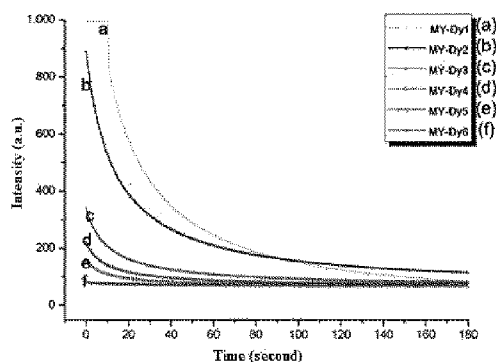
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(54) Title: LONG LASTING BLUISH-GREEN EMITTING PHOSPHORESCENT PIGMENTS IN THE STRONTIUM ALUMINATE (Sr₄Al₁₄O₂₅) SYSTEM

[Fig. 4]



(57) Abstract: Long lasting bluish-green emitting phosphorescent pigments in the strontium aluminate (Sr₄Al₁₄O₂₅) system. This invention is about pigments with phosphorescence property, having long lasting luminescence of bluish-green colour in the dark and wide usage areas requesting optimum specifications in the product obtained.

Description

Title of Invention: Long lasting bluish-green emitting phosphorescent pigments in the strontium aluminate ($\text{Sr}_4\text{Al}_{14}\text{O}_{25}$) system

[0001] This invention is about pigments with phosphorescence specification, having long term luminescence of bluish-green color in the dark and wide usage areas requiring optimum specifications in the product obtained.

The Known Related Technical Condition

[0002] Phosphorescence (or luminescence) is an event that diffusion of insulator at room temperature even after exciting (generally UV ray) is suspended. This is a process occurring during trapping or detrapping in specific defected regions of the charge carriers (e^- or gaps) formed with this detained light exciting. Phosphorescence event besides luminescence center requires the presence of discrete layers in forbidden bandgap related with chemical and physical defects (contributions and gaps) in the main lattice. Some electrons and gaps occur with excitation under UV emission are entrapped at these kind of layers. According to these defects and dimensional split between luminescence centers or more precisely direct re-combination has low possibility in the lack of orbital overlaps. As a result, the trapped charge carriers stay at metastable state unless there is not enough energy to trigger of reunification.

[0003] Phosphorescent pigments that absorb a certain wavelength of light diffuse to surrounding when the light source is removed.

[0004] In recent years the strontium aluminate hosts such as $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$ and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ had been studied intentionally as their advantages of high quantum efficiency, long lasting phosphorescence and stability.

[0005] SrAl_2O_4 , $\text{SrAl}_{12}\text{O}_{19}$, $\text{Sr}_2\text{Al}_6\text{O}_{11}$ and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phases in the $\text{SrO}-\text{Al}_2\text{O}_3$ system are well known 4 main crystals. The green emission from SrAl_2O_4 crystal phase obtained by recrystallizing of utilizing melting property of B_2O_3 is known as long-afterglow phosphor that Eu^{2+} and Dy^{3+} ions are used as co-dopants. The phosphorescence characteristic of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ system is explained as a mechanism which occurs with thermal emissions of charge carriers and trapments at room temperature where Dy^{3+} ion is worked as trapment center and Eu^{2+} ion is emission center. It is also observed that B_2O_3 improved the long lasting luminescence of phosphorous system. B_2O_3 is used as high temperature melter in reducing medium to quicken the growth of particles of strontium aluminate. This had increased the penetration of trapment centers in ceramics. Improvement of brightness and long term luminescence is provided by doping the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ lattice with univalent ions such as K^+ and Na^+ or bivalent ions like Mg^{2+}

and Zn^{2+} . This kind of balancing decreases charge defects by taking place of trivalent rare earth ions in alkali earth ion areas inside aluminate. In the studies performed by Han et al. the optimum concentrations were set as 2, 4, 6 mole % of Eu^{2+} , Dy^{3+} and B_2O_3 respectively for optimum phosphorescent properties in SrAl_2O_4 . Apart from this 4 moles % Mg^{2+} ion doping had provided the improvement in the luminescence. The improvement of photoluminescence and long lasting luminescence properties with doping B_2O_3 had been based to liquid phase sintering at 1350 °C. The presence of charge stabilizer Mg^{2+} is for the decrease of the defects of interstitial oxygen which lead to the reduction in phosphorescence.

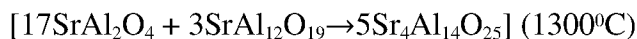
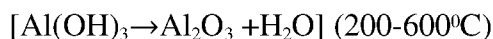
[0006] During the development process of phosphorescence, the researchers emphasise on the effects of various additions, molar rates of components and preparation methods on SrAl_2O_4 and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phosphors doped with Eu^{2+} and Dy^{3+} . It was discovered that shape and size of phosphors particles affect the specifications of phosphorescence in these researches. New properties as emission intensity turning to blue when particle size reached to nano level had been discovered. It is expected that the light absorbtion is to be better and to generate a high density compact as a result of its orientations when the phosphorous particles are in proper form and plate-like structure. This situation provides obtaining higher luminescence intensity. Particle size and shape of phosphor powders can be depended on the type of the crystal, particle size of starting materials and preparation process.

[0007] Long lasting luminescence specification of small particle sized phosphors can be explained with passing of excited Eu^{2+} to 4f-5d and consisting of so many holes near the valance gap. Some of these independed holes left on valency band thermally, immigrate towards the valence band and got trapped by Dy^{3+} –borate complex. When excitation source is removed, the trapped holes are released thermally towards valence band, they immigrate towards Eu^{2+} and as a result re-unification which provides long lasting luminescence occurs (Figure 1). It is understood that the long lasting luminescence depends on the number of hole which is held. The number of them is depending on the concentration of Dy-borate complexes and deepness of trapments. As long as the particle size decreases the color transforms to blue with deepness of trapments and this provides increase in the luminescence permanence.

[0008] Wang et. al prepared $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$, Dy^{3+} phosphors by using solid-state reaction method and studied on the chemical reaction process.

[0009] It is clear that; $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ synthesis consists of a complex reaction process. Until they go into a reaction, they perform dehydration [$\text{Al}(\text{OH})_3$] at 1000 °C with the decomposition process (SrCO_3) and followed by solid-state reaction without weight loss at higher temperatures. The final product $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ is obtained after SrAl_2O_4 and $\text{SrAl}_{12}\text{O}_{19}$ intermediate phases occur. Chemical reactions of synthesizing process are as

mentioned below:



- [0010] $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ system phosphors activated by bivalent europium shows emission (~500 nm) in the bluish-green area of spectrum. These phosphors present long lasting, permanent phosphorescence specifications when Dy^{3+} doping is used and they become attractive because of their desired specifications. Up to now, orthorhombic structure of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$, Dy^{3+} has been prepared with single crystal, polycrystalline or as thin film, solid-state reaction, sol-gel method, chemical sediment methods, combustion reaction and microwave methods and photoluminescence specifications are examined in details.
- [0011] The orthorhombic $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase consists of 3 dimensional network sharing from corners of AlO_6^- octahedra and AlO_4^- tetrahedra planes which form channels of a- and c- where Sr^{2+} ions are placed. These channels have very large radius.
- [0012] The chemical reductive atmospheres as H_2 and CO are required to obtain Eu^{2+} ion when Eu_2O_3 used as europium source.
- [0013] $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ is crystallized in Pmma space group in the orthorhombic system and consist of alternative planes which include tetrahedral AlO_4^- and octahedral AlO_6^- anions. The octahedral and tetrahedral platforms connect with the additional AlO_4^- tetrahedra and surrounded by three dimensional network structure.
- [0014] Reduction process of Eu^{3+} to Eu^{2+} for $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$ system which is prepared in air atmosphere can be explained with charge balancing model as: Eu^{3+} ions which doped to $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ structure are replaced with Sr^{2+} ions. To provide charge balance, it can be as replacing three Sr^{2+} with two Eu^{2+} . As a result, a hole defect V''_{Sr} together with two negative charges with two positive Eu_{Sr} defect can form both two Eu^{3+} ions to replace in the structure of the compound. Afterwards, while V''_{Sr} is acting as a donor of electrons, two Eu_{Sr} defect acts as electron acceptor. Accordingly, negative charges in V''_{Sr} hole defect with heat exciting move to Eu^{3+} area and reduce Eu^{3+} to Eu^{2+} . As reduced Eu^{2+} ions placed in the holes of three dimensional network structure, they are protected from oxygen effects under normal atmosphere conditions. Therefore, $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ compound can stabilize bivalent europium ions.
- [0015] The $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}$, Dy^{3+} system, after excitation, spreads visible light in two different wavelength (400 and 486 nm). The presence of this two different diffusion peaks are different characteristic comparing to aluminate phosphors with long lasting luminescence. The other aluminates have only one diffusion wavelength according to

the literature. For example, 520 nm for $\text{SrO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Eu}^{2+}, \text{Dy}^{3+}$, 500 nm for $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Eu}^{2+}, \text{Dy}^{3+}$ and 440 nm for $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Eu}^{2+}, \text{Nd}^{3+}$. This two diffusion peaks originate in the nature of luminescence of Eu^{2+} in the $4\text{SrO} \cdot 7\text{Al}_2\text{O}_3$ ceramic matrix.

Technical Problems And Solutions

- [0016] Until a few years ago, the only practically known phosphorescence compound was copper and cobalt-doped zinc sulfate ($\text{ZnS} \cdot \text{Cu}^+, \text{Co}^{2+}$). Phosphorescence applications remained limited due to the large number of defects. There are two undesired properties in the $\text{ZnS} \cdot \text{Cu}^+, \text{Co}^{2+}$ material; short decay time (nearly 1 hour) and sensitivity to humidity. These two properties have brought limitation seriously. But, this material is still used in watches and wall clocks to show the time in the dark. Tens of years ago, radioactive materials such as promethium, meitnerium and tritium were attached to the main lattice which consists of ZnS to eliminate the loss of luminescence intensity in a short time. On those days, Swiss producers managed to isolate microtubes consisting of a very little amount of gas tritium in glass. Inner wall of microtube was coated with ZnS which diffuses green light, doped and undoped. The tritium amount used was as little as it can be neglected and radioactive beta particles were not able to go out from the glass they locked in.

Explanation Of Images

- [0017] The figures to support description of phosphorescent pigments having bluish-green emission are given below:

In the bluish-green phosphorescent pigment recipe, if Dy_2O_3 content is in the 0.01-0.3 molar ranges, it affects the spectrophotometer results examined. When Dy_2O_3 content changed while Al/Sr molar ratio was 3.5 and Eu/Dy equal to 4; 6 different recipes were prepared (MY-Dy1, MY-Dy2, MY-Dy3, MY-Dy4, MY-Dy5 and MY-Dy6):

XRD graphs are presented in Figure 2.

Spectroscopic emission graphs (excitation wavelength ~240 nm) of each recipe are given in Figure 3.

The afterglow (decay) curves of phosphor powders are shown in Figure 4.

Sample Recipes

- [0018] The bluish-green phosphorescent pigment recipe in the $\text{Sr}_4\text{Al}_{14}\text{O}_{25} \cdot \text{Eu}, \text{Dy}, \text{Nd}$ system was studied by preparing 6 different Dy_2O_3 molar rates.

[0019]

[Table 1]

	SrCO_3 (gr)	H_3AlO_3 (gr)	Dy_2O_3 (gr)	Eu_2O_3 (gr)	Nd_2O_3 (gr)	H_3BO_3 (gr)
Recipe 1 0.01 mole Dy_2O_3	3.25	6	0.02	0.08	0.0037	0.64
Recipe 2 0.02 mole Dy_2O_3	3.20	5.88	0.04	0.078	0.0035	0.6
Recipe 3 0.04 mole Dy_2O_3	3.15	5.8	0.08	0.075	0.0032	0.0032
Recipe 4 0.08 mole Dy_2O_3	3.10	5.73	0.16	0.073	0.0030	0.55
Recipe 50.1 mole Dy_2O_3	3.05	5.69	0.2	0.072	0.0026	0.52
Recipe 60.3 mole Dy_2O_3	3	5.62	0.6	0.07	0.0022	0.50

[0020] When XRD graphs belong to the powders prepared by adding Dy_2O_3 to the system were presented in Figure 2. The phases of system were $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ and SrAl_4O_7 until Eu/Dy mole rate was the recipe. While Eu/Dy mole rate was higher than the recipe, $\text{Dy}_3\text{Al}_2(\text{AlO}_4)_3$ phase occurred as a result of the reaction between Dy_2O_3 and Al_2O_3 .

[0021] When spectroscopic measurement results shown in Figure 3 are examined, it could be seen that the change in Dy_2O_3 amount doesn't affect the emission wavelength of phosphorescent pigments excessively and the prepared pigments have emission wavelength of 483-494 nm ranges (blue-region). Dy^{3+} has a very important role in creating holes and phosphorescence mechanism occurring by thermal emission in the long-afterglow phosphor systems. This trapping-emission process provides a long lasting luminescence property. Lin et. al indicated that there would be enough amounts of traps in the main matrix together with Dy^{3+} being doped to structure but, if doped amount was too much, there would be concentration quenching and luminescence effect may be decreased.

[0022] It can be clearly seen that the luminescence intensities and decay times of MY-Dy1 and MY-Dy2 coded compositions were higher in the decay curves seen in Figure 5.

[0023] The particle sizes were determined as $\sim 10 \mu\text{m}$ according to the scanning electron microscope (SEM) results of phosphorescent pigments, grain sizes of which were examined after sintering and dry grinding. SEM results corresponded with particle-size analysis ones.

Explanation Of The Invention

[0024] Earth alkali aluminate systems activated with rare earth elements are long-lasting phosphorescent pigment systems. The most important property of these systems are strong light absorbtion, storage and emission ability thanks to their structure and then, long-afterglow property with high brightness, eventually. According to the light source (generally room light), they show emission for more than 12 hours after light source is removed. Their brightness and decay times are ten times more than that of well known zinc sulphate phosphors. Earth alkali aluminate systems do not show any harmful effects to the health not containing radioactive contribution. Apart from this, they are stable and resistant to atmospheric effects unlike zinc sulphate system. Light absorbtion and emission go on continuously.

[0025] In this invention, the bluish-green colour emitting phosphorescent pigments of strontium aluminates being most common and accomplished in the earth alkali aluminate systems were developed under the light of previous studies reported in the literature.

[0026] When we characterize the aluminate phosphors $[(\text{M}_4\text{Al}_{14}\text{O}_{25} : \text{R}(\text{x}, \text{y}, \text{z}, \text{t}, \text{k}, \text{l}, \text{m}, \text{r}, \text{a}, \text{b}, \text{c}, \text{d}))]$ which have long lasting luminescence in bluish-green colour in the dark.

[0027] M:Strontium (Sr) element

R:Europium (Eu) as emission center, one or more from Dysprosium (Dy), Yttrium (Y) or Neodymium (Nd) Yttrium (Y), Praseodymium (Pr), Ytterbium (Yb), Erbium (Er), Gadolinium (Gd), Cerium (Ce), Samarium (Sm), Hafmium (Hf), Thulium (Tm) occur as co-dopant in the structure.

[0028] 1. In the phosphorescent pigments having long lasting bluish-green emission mentioned in the claim 1 the molar ranges of rare earth elements; $\text{Eu}_x, \text{Dy}_y, \text{Nd}_z, \text{Yt}, \text{Pr}_k, \text{Yb}_l, \text{Er}_m, \text{Gd}_r, \text{Ce}_a, \text{Sm}_b, \text{Hf}_c, \text{Tm}_d$ which can be added to $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$, the main phase are as follows:

[0029] [Table 2]

$\text{Sr}_4\text{Al}_{14}\text{O}_{25} : \text{Eu}_x, \text{Dy}_y, \text{Nd}_z, \text{Y}_t, \text{Pr}_k, \text{Yb}_l, \text{Er}_m, \text{Gd}_r, \text{Ce}_a, \text{Sm}_b, \text{Ho}_c, \text{Tm}_d, \text{B}_e$	$0.0001 \leq x, y, z, t, k, l, m, r, a, b, c, d \leq 0.1$
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[0030] 2. The phosphorescent pigments with long lasting bluish-green emission mentioned

in the claim 1-2 have been characterized by synthesizing via solid-state reaction method under reductive nitrogen (N_2) – hydrogen (H_2) gas atmosphere.

[0031] 3. Claim 3 indicates the synthesizing method and its specification consists of the relevant steps as follows:

- Mentioned gas atmosphere is nitrogen (N_2) – hydrogen (H_2) mixture. 90-98.5 % N_2 and 1.5-10 H_2 % is used.
- Appropriate raw materials are chosen for solid-state reaction method of the phosphorescence pigment (in oxide, carbonate, hydroxide etc. forms). The determined raw materials are selected with the proper purities (>99.5 %).
- To get long-afterglow phosphorescent pigment by the synthesizing method mentioned wet milling is applied for appropriate time by planetary mill (30 minutes – 6 hours).
- In the wet milling process mentioned the proper wet medium (ethanol, propanol-2 pure water, etc.), appropriate milling and mixing media, aluminum and zirconium oxide balls in the diameter of 1mm-, and their jars are provided.
- A) In the synthesizing method mentioned to get long-afterglow phosphorescent pigment a proper gas flow rate (0.1-0.50 lt/min) is set in the sintering furnace.
- B) In the synthesizing method mentioned to obtain $Sr_4Al_{14}O_{25}$ phase a proper sintering temperature (1250-1600 °C) and time (30 minutes-6 hours) are set in the furnace.
- In the synthesizing method mentioned the wet-milled and then dried batch is loaded in proper crucibles. The conditions indicated in A and B are followed:
- In the synthesizing method mentioned to get long-afterglow phosphorescent pigment dry milling to the bulk phosphor is performed under proper conditions for certain time to obtain particle sizes previously determined depending on the application field of the pigment.

Implementation Of The Invention To Industry

[0032] Phosphorescent pigments are used in coating of products surfaces and can also be mixed with plastic, elastic, polyvinyl chloride (PVC), other synthetic resins and glass.

[0033] They find themselves a wide usage area in traffic safety signs, traffic control gloves, reflection plates of vehicles, reflection flags, highway signs, tyres, shoes, trench coats, telephone keypad overlays, watches, stair edges, emergency exit signs, the surface of the fire extinguisher cylinder, toys, writing tools. Apart from these, ceramic glazes doped with phosphorescence pigment have potential usage in apartments, especially in the well as skirting (ceramic production used in area where the wall and ground intersect). It can be a practical solution in the case of sudden electric cut, afterwards in emergency when the phosphorescent signs are placed beside stairs. Ceramic and glass product with phosphorescence pigment can be used as decor. As a border, glow stone,

overlays in kitchen, bathroom or pool, ceramics with phosphorescent pigments containing glazes also provide visual richness which could be of ceramic artists interest.

Claims

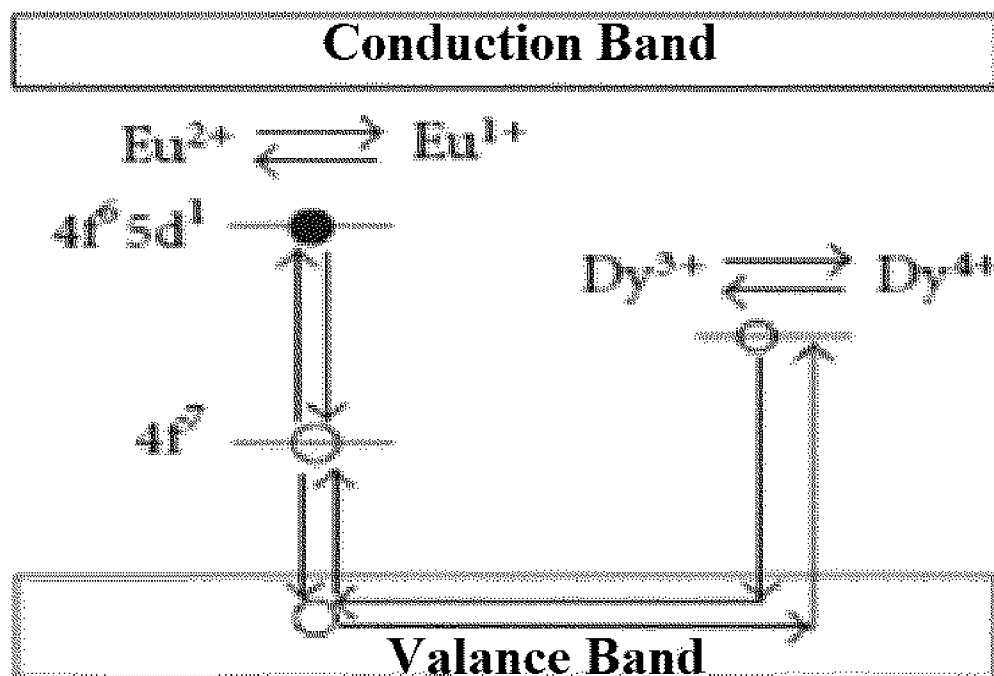
- [Claim 1] When we characterize the long lasting bluish-green colour emitting phosphorescent pigments $M_4Al_{14}O_{25}$: R(x, y, z, t, k, l, m, r, a, b, c, d is valid:
M:Strontium (Sr) element
R:Europium (Eu) as emission center, one or more from Dysprosium (Dy), Yttrium (Y) or Neodymium (Nd) Yttrium (Y), Praseodymium (Pr), Ytterbium (Yb), Erbium (Er), Gadolinium (Gd), Cerium (Ce), Samarium (Sm), Hafmium (Hf), Thulium (Tm) occur as co-dopant in the structure.
- [Claim 2] In the phosphorescent pigments having long lasting bluish-green emission mentioned in the claim 1, the molar ranges of rare earth elements; $Eu_x, Dy_y, Nd_z, Yt, Pr_k, Yb_l, Er_m, Gd_r, Ce_a, Sm_b, Hf_c, Tm_d$ which can be added to $Sr_4Al_{14}O_{25}$, the main phase, are as follows:
Refence ---Table 2.
- [Claim 3] The phosphorescent pigments with long lasting bluish-green emission mentioned in the claim 1-2 have been characterized by synthesizing via solid-state reaction method under reductive nitrogen (N_2) – hydrogen (H_2) gas atmosphere.
- [Claim 4] Claim 3 indicates the synthesizing method and its specifications consist of the relevant steps as follows:
- Mentioned gas atmosphere is nitrogen (N_2) – hydrogen (H_2) mixture. 90-98.5 % N_2 and 1.5-10 H_2 % is used.
- Appropriate raw materials are chosen for solid-state reaction method of the phosphorescence pigment (in oxide, carbonate, hydroxide etc. forms). The determined raw materials are selected with the proper purities (>99.5 %).
- To get long-afterglow phosphorescent pigment by the synthesizing method mentioned wet milling is applied for appropriate time by planetary mill (30 minutes – 6 hours).
- In the wet milling process mentioned, the proper wet medium (ethanol, propanol-2 pure water, etc.), appropriate milling and mixing media, aluminum and zirconium oxide balls in the diameter of 1mm-, and their jars are provided.
C) In the synthesizing method mentioned to get long-afterglow phosphorescent pigment a proper gas flow rate (0.1-0.50 lt/min) is set in the sintering furnace.

D) In the synthesizing method mentioned to obtain $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase a proper sintering temperature (1250-1600 °C) and time (30 minutes-6 hours) are set in the furnace.

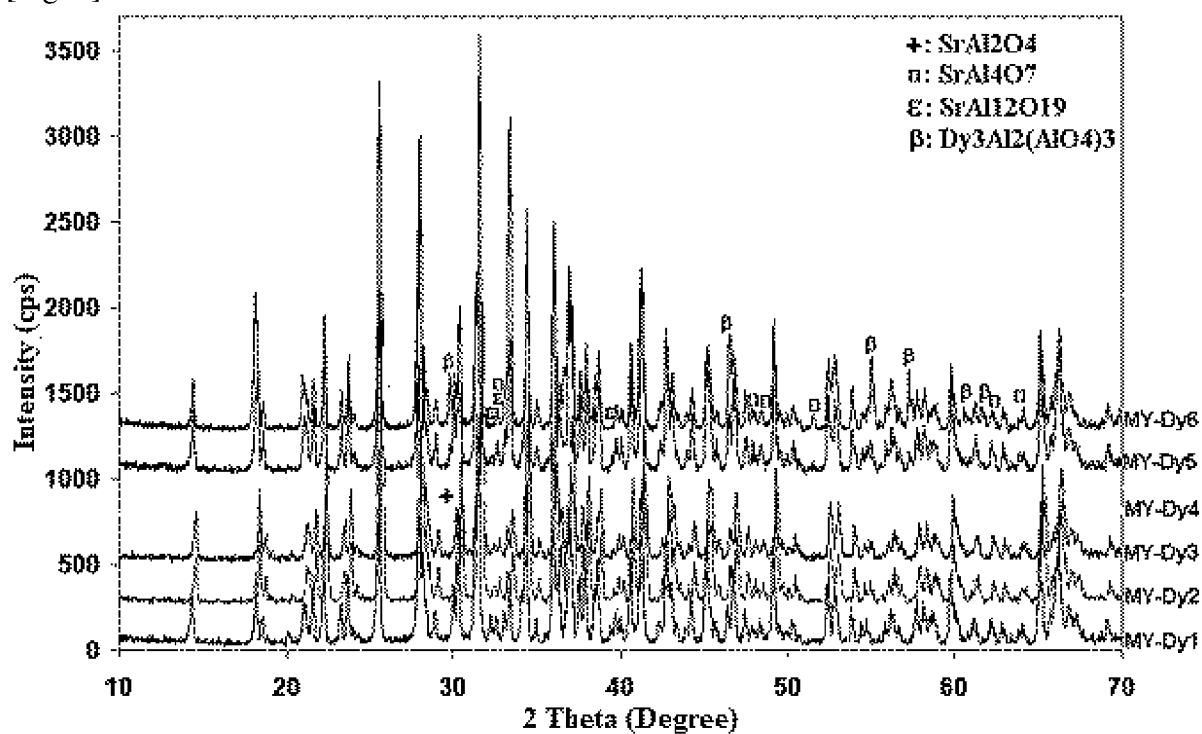
- In the synthesizing method mentioned the wet-milled and then dried batch is loaded into proper crucibles. The conditions indicated in A and B are followed:

- In the synthesizing method mentioned to get long-afterglow phosphorescent pigment dry milling to the bulk phosphor is performed under proper conditions for certain time to obtain particle sizes previously determined depending on the application field of the pigment.

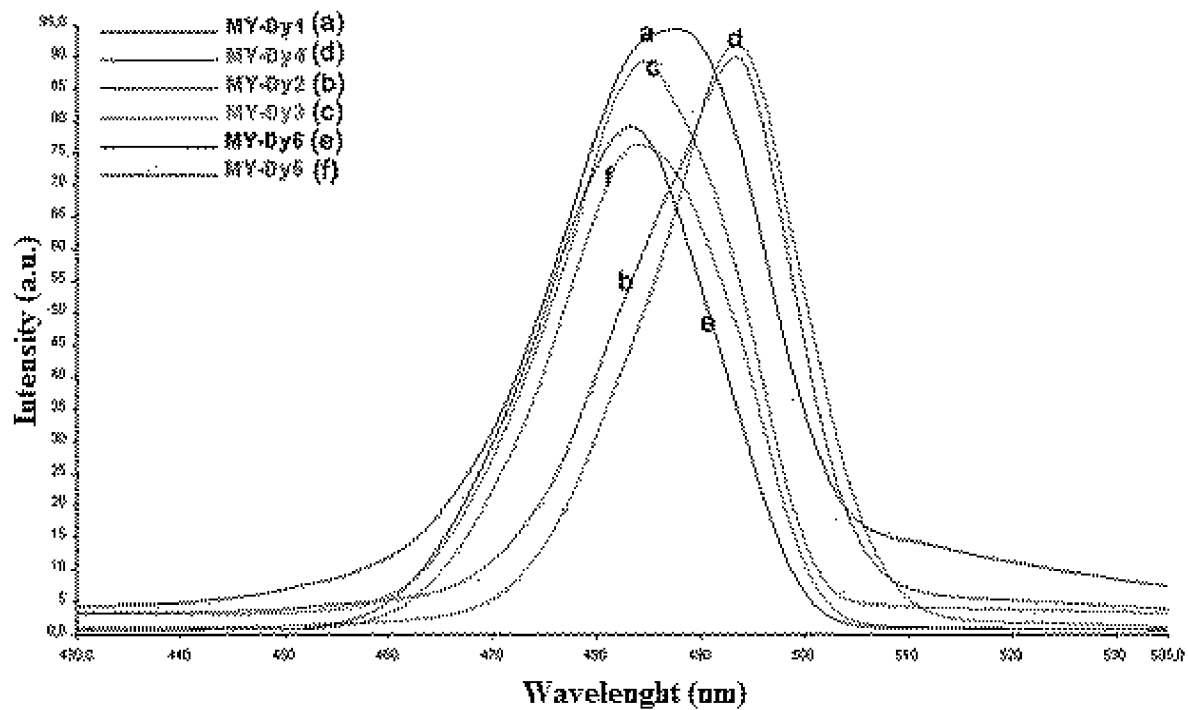
[Fig. 1]



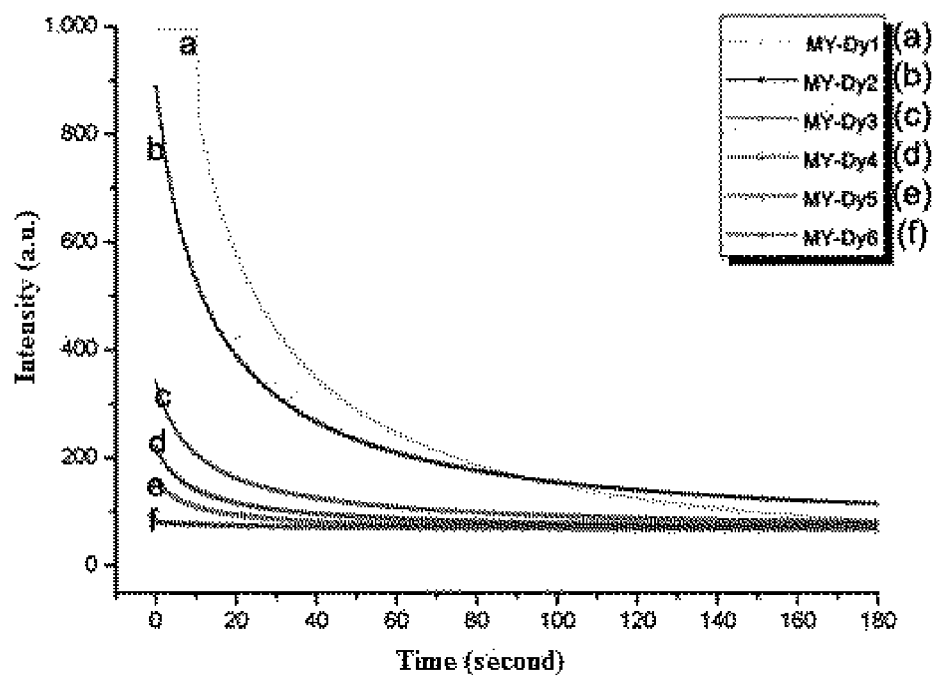
[Fig. 2]



[Fig. 3]



[Fig. 4]



INTERNATIONAL SEARCH REPORT

International application No

PCT/TR2015/050004

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09K11/77

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	LIN YUANHUA ET AL: "Anomalous luminescence in Sr4Al14O25:Eu, Dy phosphors", APPLIED PHYSICS LETTERS, AMERICAN INSTITUTE OF PHYSICS, 2 HUNTINGTON QUADRANGLE, MELVILLE, NY 11747, vol. 81, no. 6, 5 August 2002 (2002-08-05), pages 996-998, XP012033209, ISSN: 0003-6951, DOI: 10.1063/1.1490631 page 996; figure 3	1-4
X	EP 2 626 401 A1 (ROLEX SA [CH]) 14 August 2013 (2013-08-14) paragraph [0071]; example 1; table 1a ----- -/--	1-4



Further documents are listed in the continuation of Box C.



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INTERNATIONAL SEARCH REPORT

International application No

PCT/TR2015/050004

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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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