Environmentally Benign Rare Earth Pigments: Effect of Calcium Dopant and Tuning of Bandgaps for Different Color Hues

Divya V (✉️ divyavchem@gmail.com)
Sree Narayana College Kollam  https://orcid.org/0000-0002-6065-3658

Divya Jayan
Sree Narayana College Kollam

Research Article

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Abstract

Environmentally benign rare earth pigments having the general formula \( \text{Ca}_{0.1} \text{Ln}_{0.9} \text{PO}_4 \) (\( \text{Ln} = \text{Y}, \text{Pr}, \) mixed rare earth oxides, \( \text{RE} \) and \( \text{Di} \)) have been prepared by a traditional solid state route. The samples were characterized by X-ray diffraction, UV–vis Spectroscopy, scanning electron microscope (SEM), particle size distribution, color coordinates determination, acid/alkali test, thermo gravimetric (TG) analysis and CIE–1976 \( L^*a^*b^* \) color scales. Among the various lanthanide ions and calcium ion as dopant, the pigment composition shows various hues ranges from green to yellow. The coloring mechanism is based on the tuning of band gap by the dopant like calcium in various rare earth host lattice. The designed pigments consist of non–toxic elements and were further found to possess high thermal and chemical stability. The pigments were also found to be appropriate candidates for the coloration of polymer substrates. Thus, the present environmental friendly pigment powders may find potential alternative to the classical toxic inorganic pigments for various applications.

Introduction

Lanthanide ions have attracted tremendous attention due to their unique optical properties and specific functions which make them useful in a wide range of industrial applications that includes tunable lasers, amplifiers for optical communications, organic light–emitting diodes and inorganic pigments [1–4]. There is a strong inducement to develop new colored inorganic materials to substitute the current industrial pigments that are based on toxic metals hazardous to health and the environment [6–9]. Recently, the industrial utilization of lanthanides has a swift in growing because of their known low toxicity and economic availability. Hence in the contemporary, a large number of rare earth based pigments have been proposed as alternatives to traditional toxic inorganic pigments [10–14]. Especially, Rare earth phosphate is a well known material that exists in nature as a main component of monazite minerals which is abundant on the beach sands of Kerala and they are prominent for their high stability heat and UV rays[1, 10].

Monazites (orthophosphate of \( \text{LnPO}_4 \)) has currently generating intense scientific interest because of their potential to store high-level nuclear waste, high resistance to self irradiation and its low solubility [15]. Mechanism of the color appearance using band calculations and on possible applications of rare earth phosphate powders as pigments in plastics and paints have not been explored much [16]. However, the properties of the Ca-doped rare earth phosphate implies that this material has a potential to be applied as a satisfactory pigment for coating or coloring except for glaze which may cause a side reaction at high temperatures, especially taking into consideration the economics and ecologies[17]. The possibility of \( \text{Ca}^{2+} \) incorporation in \( \text{CePO}_4 \) with monazite structure-type has been established[17].

In the present investigation, a series of new rare earth pigments have been synthesized and their properties are investigated. The pigments in this study are nontoxic, safe and inert, not to give ant side effects to the human body because metal phosphate is the main component of tooth and bone. In this
work, a series of coloured pigments of formula \( \text{Ca}_{0.1} \text{Ln}_{0.9} \text{PO}_4 \) (\( \text{Ln} = \text{Y}, \text{Pr}, \text{mixed rare earth oxides, RE} \) and Di) were synthesized and applied to plastic material like PMMA.

**Experimental**

**Materials**

The materials used for the preparation of nontoxic inorganic pigments are \( \text{Ln}_2\text{O}_3 \) (\( \text{Ln} = \text{Y}, \text{Pr}, \text{RE}, \text{Di}, \) (Fig1)) (Indian rare earth limited), \( \text{CaCO}_3 \) (Merck limited), \( (\text{NH}_4)_2\text{H}_2\text{PO}_4 \) (Merck limited), acetone (S D Fines chemicals) as solvent. [Di -Didymium, RE -Mixed rare earth].

**Apparatus used**

The apparatus used for these experiments are Agate mortar, Electronic Balance, Microwave oven and High temperature electronic furnace, Magnetic stirrer.

**Characterization Techniques**

The crystalline nature and phase purity of the synthesized samples were characterized by powder X-ray diffraction using the conventional powder techniques in a diffractometer (Bruker D 8 Advance) with Ni-filtered Cu K\( \alpha \) (\( \lambda = 0.154060 \) nm) radiation. Data were collected by step scanning over a 2\( \theta \) range from 10\( ^\circ \) to 70\( ^\circ \) with a step size of 0.08\( ^\circ \) and 5s counting time at each step. The morphology of the synthesized samples was recorded on a scanning electron microscope (SEM) JEOL JSM–5600 model, with an acceleration voltage of 15 kV.

The particle size distribution of the typical pigment sample was investigated in water medium with calgon as the dispersing agent using the Laser Scattering Particle Size Distribution Analyzer (CILAS 930 Liquid). The samples were ultrasonically homogenized for 180 s during measurement and the signal was evaluated on the basis of Fraunhofer bending.

The diffuse reflectance of the powdered pigment samples were measured (380–780 nm) with a UV–vis Spectrometer (Perkin elner lamda) using barium sulfate as a reference. The measurement conditions were as follows: an illuminant D\(_{65}\), 10\( ^\circ \) complementary observer and measuring geometry d/8\( ^\circ \). The band gap values were calculated from the corresponding absorbance spectra by straight forward extrapolation method [18] using the formula \( E(\text{eV}) = 1236/l \) (where \( l \) represents the wavelength in nm).

The color coordinates were determined by coupling an analytical software (UVPC Color Analysis Personal Spectroscopy Software V3, Shimadzu) to the UV–2450 spectrophotometer. The CIE 1976 \( L^*a^*b^* \) colorimetric method was used, as recommended by the Commission Internationale de l’Eclairage (CIE). In this method, \( L^* \) is the lightness axis [black (0) to white (100)], \( a^* \) is the green (–ve) to red (+ve), and \( b^* \) is the blue (–ve) to yellow (+ve) axis. The parameter \( C^* \) (chroma) represents saturation of the color and \( \theta \) represents the hue angle. The chroma is defined as \( C^* = \sqrt{(a^*)^2 + (b^*)^2} \). The hue angle, \( \theta \) is
expressed in degrees and ranges from 0° to 360° and is calculated using the formula

$$h^o = \tan^{-1}\left(\frac{b^*}{a^*}\right)$$ [19-21]

For each colorimetric parameter of a sample, measurements were made in triplicate and an average value was chosen as the result. Typically, for a given sample, the standard deviation of the measured CIE–$L^*a^*b^*$ values is less than 0.10, and the relative standard deviation is not higher than 1%, indicating that the measurement error can be ignored.

**Synthesis**

Powder samples of the system, Ca$_{0.1}$ Ln$_{0.9}$ PO$_4$ ( Ln = Y, Pr, RE, Di ) were synthesized by a solid state reaction, using precursor Ln$_2$O$_3$ ( Ln= Y, Pr, RE, Di ), CaCO$_3$ and (NH$_4$)$_2$H$_2$PO$_4$ (Fig.2). Stoichiometric proportions of the precursors were transferred into an agate mortar and homogenized by wet milling in acetone media. Residual acetone was removed by evaporation using an oven and repeated this three times. The resultant powder was calcinated in a crucible in high temperature electric furnace at 1000 °C for 4h followed by auto–cooling in the furnace. The heating of the furnace was programmed to increase the temperature at 5°C/min. The pigment compositions thus obtained were ground in an agate mortar in order to refine and homogenize the particle size. The obtained pigment powder samples are sieved through a three micro meter sieve to get the fine particle.

**Thermal stability of the pigments**

The thermal stability (TG analysis) of the typical synthesized pigments, namely Ca$_{0.1}$ Y$_{0.9}$ PO$_4$ and Ca$_{0.1}$ Pr$_{0.9}$ PO$_4$ were examined in the temperature range of 30–1000 °C. Thermo gravimetric (TG) analysis was performed in a Pyris Diamond TG Perkin Elmer. The pigments placed in a platinum crucible and heated at the temperature ranging from 50°C to 1000°C with a heating rate of 20°C/min in nitrogen atmosphere.

**Chemical stability of the pigments**

Chemical resistance of the pigment samples Ca$_{0.1}$ Y$_{0.9}$ PO$_4$ and Ca$_{0.1}$ Pr$_{0.9}$ PO$_4$ were assessed using 10% HCl/H$_2$SO$_4$/NaOH. A known weight (0.1g) of the pigment was taken in beaker containing acid/alkali, soaked for 30 min with constant stirring using a magnetic stirrer. It was then filtered, washed with water, dried and weighed.

**Applications in coloring of plastics**

Coloration of plastics Poly (methyl methacrylate) (PMMA; S.D. Fine chemicals, India) was utilized as a binder phase for fabricating the pigmented compact. The typical pigment samples, Ca$_{0.1}$ Y$_{0.9}$ PO$_4$ and Ca$_{0.1}$ Pr$_{0.9}$ PO$_4$ was ultrasonicated in an alcohol/water (1:4) mixture for 10 min to ensure the complete dispersion of the pigment particles. A viscous solution consists of PMMA (90 wt %) was made using a conventional electrical coil heater. The pigment dispersion was slowly added while stirring and converted
into a thick paste. The paste after 2 h of curing, compressed uniaxially into a form of cylindrical discs using a hydraulic press at a pressure of 25 MPa. Both sides of the pigmented polymer were lapped using a fine grade emery sheet for obtaining a polished surface. The intensity of the color of plastics will depend on the concentration of the pigment.

The coloring performance of the typically synthesized pigments Ca$_{0.1}$Y$_{0.9}$PO$_4$ and Ca$_{0.1}$Pr$_{0.9}$PO$_4$ were tested for its coloring application in a substrate material like PMMA Poly(methyl methacrylate). Typically, 10 wt. % pigment sample was dispersed in PMMA with constant stirring using a magnetic stirrer and compressed to a cylindrical disc.

Results And Discussion

Powder X–ray diffraction analysis.

XRD patterns of Ca$_{0.1}$Pr$_{0.9}$PO$_4$

The phase formation and phase purity of the pigment Ca$_{0.1}$Pr$_{0.9}$PO$_4$ were characterized and shown in Fig 3. PrPO$_4$ crystallizes in monazite structure, in which the praseodymium ion is nine-coordinated by oxygen atoms with a distorted monocapped square antiprism geometry and phosphorus is four-coordinated by oxygen [22] Isolated irregular PO$_4$ tetrahedra are linked by PrO$_9$ polyhedra to form a network structure. It is possible to substitute praseodymium in PrPO$_4$ by calcium to form a solid solution, as the ionic radii are similar. The powder XRD patterns show a monoclinic monazite structure and we have not observed any weak reflections due to $\alpha$-Ca$_2$P$_2$O$_7$ for any of the compositions, contrary to earlier observations [23]. It is probably difficult to detect $\alpha$-Ca$_2$P$_2$O$_7$ reflections by X-ray diffraction as the phase is monoclinic and contains ions of low atomic number. All the peaks are indexed on the basis of monoclinic unit cell with space group $P21/n$.

(b) XRD patterns of Ca$_{0.1}$Y$_{0.9}$PO$_4$

The phase formation and phase purity of the pigment Ca$_{0.1}$Y$_{0.9}$PO$_4$ were checked by powder X-ray diffraction. XRD pattern of calcium doped YPO$_4$ is shown in Fig. 4. The diffraction peak of calcium doped YPO$_4$ match well with the tetragonal phase of YPO$_4$. The quantity of dopant ion into YPO$_4$ structure slightly modifies the crystalline structure.

(c) XRD patterns of Ca$_{0.1}$RE$_{0.9}$PO$_4$

The phase formation and phase purity of the pigment Ca$_{0.1}$RE$_{0.9}$PO$_4$ were characterized by powder X-ray diffraction. XRD pattern of calcium doped rare earth phosphate is shown in Fig.5. As the rare earth comprises the major elements like Ce, La, Nd, Pr and Sm, XRD pattern of Ca$_{0.1}$RE$_{0.9}$PO$_4$ is obtained with the presence of many phases like monazite monoclinic, hexagonal structures. But the major contributed structure may be monazite monoclinic due to the presence of 47.5% CePO$_4$. 
(d) XRD patterns of Ca_{0.1}Di_{0.9}PO_4

The XRD pattern of Ca_{0.1}Di_{0.9}PO_4 is shown in fig.6. These are also the same case as that of Ca_{0.1}Di_{0.9}PO_4. But here the major contributed structure may be monazite monoclinic due to the presence of 45% LaPO_4.

Optical properties: Diffuse reflectance and chromatic properties

(a) Ca doped PrPO_4 or Ca_{0.1}Pr_{0.9}PO_4

The effect of alkaline-earth metal ion Ca^{2+} doping on the optical properties of the pigments Ca_{0.1}Pr_{0.9}PO_4 was analyzed from the diffuse reflectance spectra (DRS) and the results are shown in Fig 20. It is well known that Pr^{3+} has several metastable multiplets such as ^3P_{0,1,2}, ^1D_2, and ^1G_4 [24]. In the present study, we observe several bands in the visible region and these could be assigned to the electronic transitions between 4f^2 \rightarrow 4f^1 5d^1 states. There are bands around 445, 471, 485, 591 and 602 nm, which can be assigned based on the energy levels ^3H_4 \rightarrow ^3P_2, ^3H_4 \rightarrow ^3P_1, ^3H_4 \rightarrow ^3P_0, ^3H_4 \rightarrow ^3D_2 (upper) and ^3H_4 \rightarrow ^3D_2 (lower), respectively [25]. The pigment exhibits a green color, since red is complementary color to green. Photograph of synthesized pigment of Ca doped Pr_{0.9}PO_4 or Ca_{0.1}Pr_{0.9}PO_4 is shown in the below figure 7.

Ca doped YPO_4 or Ca_{0.1}Y_{0.9}PO_4

The diffuse reflectance spectra (DRS) of Ca-doped YPO_4 is also shown in Fig. 7. A strong absorption noted below 465 nm in the UV–vis reflectance spectrum. This absorption in the blue region is responsible for the yellow color of Ca_{0.1}Y_{0.9}PO_4, since blue is a complimentary color to yellow. The band gap of the pigment Ca_{0.1}Y_{0.9}PO_4 is found to be 1.78 eV, which has been calculated by a straight forward extrapolation method from the corresponding absorption spectrum [26]. Picture of prepared pigment Ca doped Pr_{0.9}PO_4 or Ca_{0.1}Pr_{0.9}PO_4 is shown in the below figure 23.

(c) Ca doped REPO_4 or Ca_{0.1}RE_{0.9}PO_4 (RE=Rare earth oxide)

The effect of alkaline-earth metal ion Ca^{2+} doping on the optical properties of the pigments Ca_{0.1}RE_{0.9}PO_4 was analyzed from the diffuse reflectance spectra (DRS) and the results are shown in Fig 7. A strong absorption in the red region can be noted from the absorption spectrum of the pigment Ca_{0.1}RE_{0.9}PO_4. Thus, the pigment exhibits dark green color, since red is complementary color to green. The band gap of the pigment Ca_{0.1}Y_{0.9}PO_4 is found to be 2.26eV, which has been calculated by a straight forward extrapolation method from the corresponding absorption spectrum [26].

(d) Ca doped DiPO_4 or Ca_{0.1}Di_{0.9}PO_4 (Di = Didymium)
The diffuse reflectance spectra (DRS) of Ca-doped DiPO\textsubscript{4} compositions and that of parent DiPO\textsubscript{4} are shown in Fig. 7. A weak absorption in the blue region and a strong absorption in the red region can be noted from the absorption spectrum of the pigment Ca\textsubscript{0.1} Di\textsubscript{0.9} PO\textsubscript{4}. Thus, the pigment exhibits yellowish green color, since red is complementary color to green and blue is complementary color to yellow.

**Color Coordinate Values**

The chromatic properties of the synthesized Ca\textsubscript{0.1} Ln\textsubscript{0.9} PO\textsubscript{4} (Ln = Y, Pr, RE, Di) powder pigments can be assessed from their CIE 1976 color coordinate values depicted in Table 3. The $L^*$, $a^*$ and $b^*$ parameters were computed from DRS for the parent and the Ca-doped composition Ca\textsubscript{0.1} Pr\textsubscript{0.9} PO\textsubscript{4} and the results show that the brightness as well as green and yellow components are much better as compared to chromium oxide [27] and the values are presented in Table 1. The color coordinates of the typical Ca\textsuperscript{2+} doped pigment, Ca\textsubscript{0.1} Y\textsubscript{0.9} PO\textsubscript{4} ($L^* = 86.7$, $a^* = -9.2$, $b^* = 54.7$), especially yellow hue was found to be higher than that of the commercially available pigment ($L^* = 87.5$, $a^* = -26.2$, $b^* = 34.6$) Zircon Yellow [24].

Table 1. The color coordinates (±0.1) of the Ca\textsubscript{0.1} Ln\textsubscript{0.9} PO\textsubscript{4} (Ln = Y, Pr, RE, Di) pigments and band gap values.

| Pigment composition | Color coordinates | Band gap (eV) |
|---------------------|-------------------|--------------|
|                     | $L^*$  | $a^*$  | $b^*$  | $C^*$  | $h^\circ$ |           |
| Ca\textsubscript{0.1} Y\textsubscript{0.9} PO\textsubscript{4} | 86.7  | -9.2   | 54.7   | 55.5   | 80.5     | 1.78      |
| Ca\textsubscript{0.1} Pr\textsubscript{0.9} PO\textsubscript{4} | 87.5  | -26.2  | 34.6   | 45.6   | 118.4    | 2.43      |
| Ca\textsubscript{0.1} RE\textsubscript{0.9} PO\textsubscript{4} | 67.2  | -22.3  | 13.8   | 39.6   | 98.2     | 2.26      |
| Ca\textsubscript{0.1} Di\textsubscript{0.9} PO\textsubscript{4} | 87.0  | -10.9  | 52.0   | 53.1   | 78.2     | 2.38      |
| Cr\textsubscript{2}O\textsubscript{3} [27] | 53.58 | -16.21 | 14.48  |        |          |           |
| Zircon Yellow [24]   | 89.93 | -3.49  | 43.34  |        |          |           |

**Particle size and morphological analysis**

Color depends on several material properties of a pigment, among which particle size of the pigment is of prime importance. Decrease in particle size of the pigment increases the surface area which further contributes to high surface coverage, higher number of reflectance points and hence more scattering. The particle size distribution of the typical pigments Ca\textsubscript{0.1} Y\textsubscript{0.9} PO\textsubscript{4} and Ca\textsubscript{0.1} Pr\textsubscript{0.9} PO\textsubscript{4}, were investigated in water with calgon as the dispersing agent. The results reveal a distribution with 90% of the particles with size smaller than 7.54 µm, 50% smaller than 2.59 µm and 10% smaller than 0.36 µm. The mean particle diameter of the pigment sample was found to be 5.65 µm. The average particle size of the pigments as
observed from the SEM images shown in Fig. 9. is approximately 10 μm, which matches well with the results obtained from particle size analysis.

**Thermal stability of the pigments.**

The thermal stability (TG analysis) of the typical synthesized pigments, namely Ca_{0.1}Y_{0.9}PO_4 and Ca_{0.1}Pr_{0.9}PO_4 were examined in the temperature range of 30–1000 °C and the results are depicted in Fig. 10. The thermo gravimetric analysis results clearly indicate that there is negligible weight loss and phase transition of the pigments up to 1000 °C.

**Chemical stability of the pigments**

To facilitate the use of these colorants in various applications, it is necessary to establish its chemical and thermal stability. Chemical resistance of the pigment samples Ca_{0.1}Y_{0.9}PO_4 and Ca_{0.1}Pr_{0.9}PO_4 were assessed using 10% HCl/H_2SO_4/NaOH. A known weight (0.1g) of the pigment was taken in beaker containing acid/alkali, soaked for 30 min with constant stirring using a magnetic stirrer. It was then filtered, washed with water, dried and weighed. Negligible weight loss was noted in all the cases. The color coordinates of the ensuing powders were then measured and the results are given in Table 2 and 3. The total color difference (Δ) is negligible indicating an imperceptible color change to the human eye.

**Table 2.** The color coordinates (±0.1) of the Ca_{0.1}Y_{0.9}PO_4 powder pigments after chemical resistance test.

| 10% Acid/Alkali | Color coordinates | a  |
|-----------------|-------------------|----|
|                 | L*    | a*      | b* |
| HCl             | 87.1  | -8.6    | 55 | 0.78 |
| H_2SO_4        | 87.0  | -8.5    | 55.3 | 0.97 |
| NaOH            | 87.6  | -9.4    | 54.9 | 0.94 |

\[ a = \sqrt{\left( DL^* \right)^2 + \left( Da^* \right)^2 + \left( Db^* \right)^2} \]

**Table 3.** The color coordinates (±0.1) of the Ca_{0.1}Pr_{0.9}PO_4 powder pigments after chemical resistance test.

| 10% Acid/Alkali | Color coordinates | a  |
|-----------------|-------------------|----|
|                 | L*    | a*      | b* |
| HCl             | 87.7  | -26.5   | 55.5 | 0.62 |
| H_2SO_4        | 88.3  | -26.4   | 55.4 | 0.91 |
| NaOH            | 87.6  | -26.5   | 55.2 | 0.87 |
\[ a = [(DLx)^2 + (Da)^2 + (Db)^2]^{\frac{1}{2}} \]

Applications of inorganic rare earth pigments: Coloring of plastics

The coloring performance of the typically synthesized pigments (a) Ca\textsubscript{0.1} Y\textsubscript{0.9} PO\textsubscript{4} and (b) Ca\textsubscript{0.1} Pr\textsubscript{0.9} PO\textsubscript{4} was tested for its coloring application in a substrate material like PMMA Poly(methyl methacrylate). Typically, 10 wt. % pigment sample was dispersed in PMMA and compressed to a cylindrical disc (Fig. 11).

Conclusions

We have synthesized four different nontoxic inorganic pigment samples Ca\textsubscript{0.1} Pr\textsubscript{0.9} PO\textsubscript{4} (green), Ca\textsubscript{0.1} Y\textsubscript{0.9} PO\textsubscript{4} (yellow), Ca\textsubscript{0.1} RE\textsubscript{0.9} PO\textsubscript{4} (dark green), Ca\textsubscript{0.1} Di\textsubscript{0.9} PO\textsubscript{4} (yellowish green) by simple calcination route in air atmosphere. The samples were characterized by X–ray diffraction diffraction, UV–vis Spectroscopy, scanning electron microscope (SEM), particle size distribution, color coordinates determination, acid/alkali test, thermo gravimetric (TG) analysis etc.

The crystalline nature and phase purity of the synthesized pigments were studied from powder X–ray diffraction pattern. The effects of alkaline earth metals like calcium ion doping on color of LnPO\textsubscript{4} or Ca\textsubscript{0.1} Ln\textsubscript{0.9} PO\textsubscript{4} (Ln = Pr, Y, RE, Di) based pigments were analyzed by the diffuse reflectance spectra and they shows colors of green, yellow, dark green and yellowish green respectively. The synthesized Ca\textsubscript{0.1} Pr\textsubscript{0.9} PO\textsubscript{4} and Ca\textsubscript{0.1} Y\textsubscript{0.9} PO\textsubscript{4} are found to be superior than the commercially available zircon yellow and Cr\textsubscript{2}O\textsubscript{3}.The present investigations establish that various color hues can be achieved by the incorporation of suitable chromophore metal ions like calcium in various rare earth host lattice by tuning of the band gaps. The particle size of the pigments as observed from the SEM images is approximately 10 \mu m, which matches well with the results obtained from particle size analysis. The newly developed pigment powders are found to be thermally and chemically stable and also do not contain toxic metals. The current results clearly demonstrate the potential of the designed yellow pigments for the coloration of substrate materials like plastics (PMMA). Thus, the present pigment powders may find potential alternative to the classical toxic inorganic pigments for various applications.

Declarations

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Conflicts of Interest

The authors declare no conflicts of interest.

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Figures

| Composition of didymium oxide(D_{2}O_{3}) | Composition of Rare earth oxide(RE_{2}O_{3}) |
|------------------------------------------|------------------------------------------|
| La - 45% | Ce - 47.5% |
| Pr - 10% | La - 22% |
| Nd - 34.6% | Pr - 6.4% |
| Sm - 4.8% | Nd - 18.1% |
| Gd - 2.3% | Sm - 3.2% |
| Ce - <0.1% | Gd - 1% |
| Tb - <0.1% | Tb - <0.1% |
| Eu - <0.1% | Eu - <0.1% |

Figure 1

Composition of mixed rare earth oxides
Figure 2

Schematic representation of the synthesis of pigments.

Figure 3

XRD patterns of Ca0.1 Pr0.9 PO4
Figure 4

XRD patterns of Ca0.1 Y0.9 PO4

Figure 5

XRD patterns of Ca0.1 RE0.9 PO4
Figure 6

XRD patterns of Ca0.1 Di0.9 PO4

Figure 7

Reflectance spectra of synthesized pigments
Figure 8

Photograph of synthesized pigments (a) Ca0.1 Pr0.9 PO4 (b) Ca0.1 Y0.9 PO4 (c) Ca0.1 RE0.9 PO4 (d) Ca0.1 Di0.9 PO4

Figure 9

SEM micrographs of a) Ca0.1 Pr0.9 PO4 and b) Ca0.1 Di0.9 PO4

Figure 10

The TG graph of (a) Ca0.1 Y0.9 PO4 and (b) Ca0.1 Pr0.9 PO4.
Figure 11

Photograph of (a) Ca0.1 Pr0.9 PO4(10%) + PMMA b) (a) Ca0.1 Y0.9 PO4(10%) + PMMA.