

## Environmentally benign novel green pigments: $\text{Pr}_{1-x}\text{Ca}_x\text{PO}_4$ ( $x = 0-0.4$ )

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**Abstract.** Rare earth based materials have recently attracted considerable attention as potential eco-friendly colourants for low temperature as well as high temperature applications. In the present study, we have synthesized a series of Ca-doped  $\text{PrPO}_4$  compounds with the general formula,  $\text{Pr}_{1-x}\text{Ca}_x\text{PO}_4$  ( $x = 0-0.4$  in steps of 0.1) and characterized the compounds by powder X-ray diffraction. All the compositions show a monoclinic monazite structure. The optical properties of the brilliantly coloured pigments [ $L$  (brightness),  $a^*$  (+ red – green),  $b^*$  (+ yellow – blue)] have been examined. These materials can find application as potential green colourants.

**Keywords.** Green pigment; monazite; diffuse reflectance spectroscopy;  $\text{PrPO}_4$ .

### 1. Introduction

Inorganic pigments have long been used for colouring glasses, glazes and ceramics; however, most of the inorganic pigments that are used for various applications contain transition metal/heavy metal ions such as Cd, Cr and Pb, which are environmentally hazardous. Rare earth based materials offer a vast opportunity for development of environmentally secure alternatives for many of the eco-constraint colourants (Olazcuaga *et al* 1987; Jansen and Letschert 2000; Diot *et al* 2001; Gauthier *et al* 2003). The possibility of  $\text{Ca}^{2+}$  incorporation in  $\text{CePO}_4$  with monazite structure-type has been established (Pepin *et al* 1981). The  $\text{CePO}_4$  monoclinic phase formation was observed for all compositions with weak reflections due to  $\mathbf{a}\text{-Ca}_2\text{P}_2\text{O}_7$  for compositions  $x \geq 0.2$  and none of the compositions exhibited green colour. Recently, a new inorganic pigment based on rare earth phosphate ( $\text{Ca-CePO}_4$ ) has been reported (Imanaka *et al* 2003). The origin of the colour has been attributed to the substitution of the trivalent cerium ions by divalent calcium ions creating oxide ion vacancy in the  $\text{CePO}_4$  lattice and this defect formation is responsible for change in band gap. With this in view, in the present study, we have synthesized Ca doped  $\text{PrPO}_4$  compositions and evaluated the same as pigments. These compounds exhibit various hues by varying the Ca content in the  $\text{PrPO}_4$  lattice.

### 2. Experimental

#### 2.1 Materials synthesis

The compounds were synthesized by a solution route: stoichiometric quantities of  $\text{Pr}_6\text{O}_{11}$  (Indian rare earth, 99.9%) and  $\text{CaCO}_3$  (Alfa aesar, 99.9%) were dissolved in dil.  $\text{HNO}_3$  to get the corresponding metal nitrates. To this nitrate mixture  $\text{NH}_4\text{H}_2\text{PO}_4$  (Merck 99.9%) solution was added dropwise with constant stirring. The precipitate formed was evaporated to dryness and then calcined at  $600^\circ\text{C}$  for 12 h to remove ammonia, nitrogen oxides and residual water. The obtained product was ground and heated at  $900^\circ\text{C}$  for 24 h and  $1100^\circ\text{C}$  for 24 h.

#### 2.2 Characterization

The phase formation and phase purity of the compounds were checked by powder X-ray diffraction (Rich Seifert P3000) with  $\text{Cu-K}_{\alpha 1}$  radiation at room temperature. A Jasco spectrophotometer (model V-560) equipped with 150 mm integrating sphere was used to record the UV-Vis diffuse reflectance spectra of the powder samples; the absorbance vs wavelength measurements were made in the 200–800 nm range (from 6.18–1.54 eV) and  $\text{BaSO}_4$  was used as reference for 100% reflectance.

### 3. Results and discussion

#### 3.1 Phase formation

$\text{PrPO}_4$  crystallizes in monazite structure, in which the praseodymium ion is nine-coordinated by oxygen atoms

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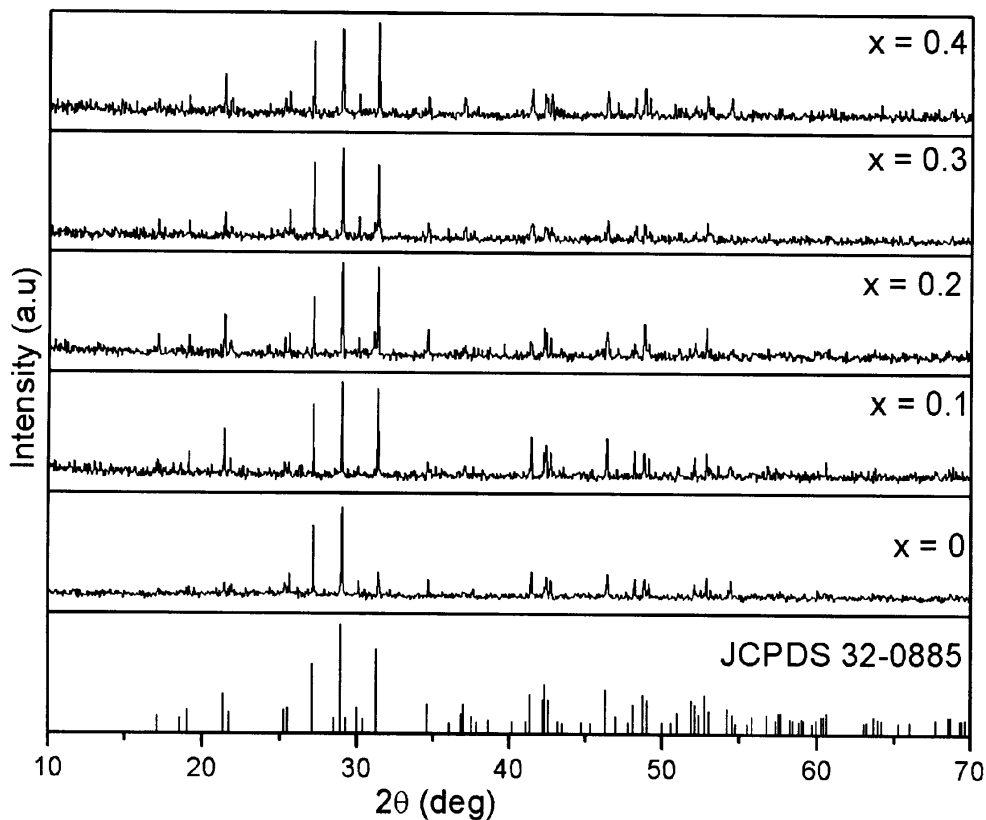


Figure 1. Powder XRD patterns of  $\text{Pr}_{1-x}\text{Ca}_x\text{PO}_4$  ( $x = 0-0.4$ ).

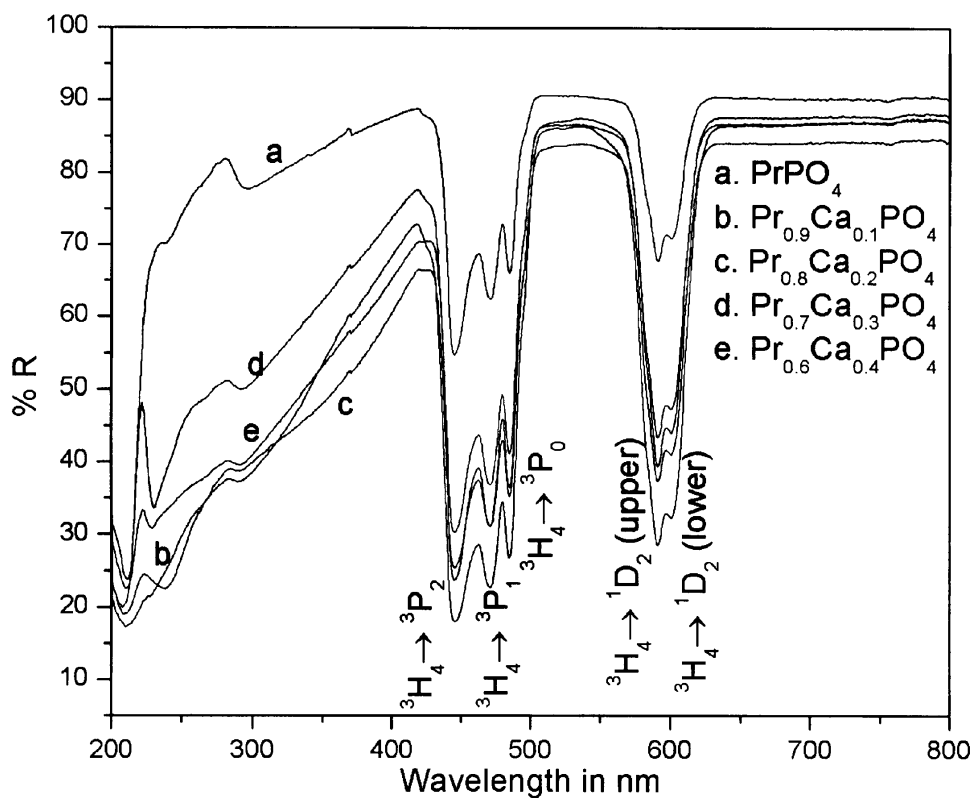


Figure 2. Diffuse reflectance spectra of  $\text{PrPO}_4$  and Ca-doped  $\text{PrPO}_4$  compositions.

**Table 1.**  $L$  (brightness),  $a^*$  (+ red – green),  $b^*$  (+ yellow – blue) parameters for Ca doped  $PrPO_4$  and  $PrPO_4$ .

| Sample                 | $L^*$ | $a^*$   | $b^*$ |
|------------------------|-------|---------|-------|
| $PrPO_4$               | 94.05 | – 8.67  | 11.61 |
| $Pr_{0.9}Ca_{0.1}PO_4$ | 87.28 | – 26.13 | 34.01 |
| $Pr_{0.8}Ca_{0.2}PO_4$ | 87.97 | – 20.93 | 28.25 |
| $Pr_{0.7}Ca_{0.3}PO_4$ | 89.95 | – 18.96 | 25.69 |
| $Pr_{0.6}Ca_{0.4}PO_4$ | 89.42 | – 20.12 | 27.76 |
| $Cr_2O_3$              | 53.98 | – 16.21 | 14.48 |
| $Ce_{0.6}Ca_{0.4}PO_4$ | 74.07 | – 9.20  | 16.09 |

with a distorted monocapped square antiprism geometry and phosphorus is four-coordinated by oxygen (Mullica *et al* 1985). 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 (figure 1) patterns show a monoclinic monazite structure and we have not observed any weak reflections due to  $a-Ca_2P_2O_7$  for any of the compositions, contrary to earlier observations (Pepin *et al* 1981). It is probably difficult to detect  $a-Ca_2P_2O_7$  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  $P2_1/n$  (No. 14).

### 3.2 Diffuse reflectance measurements

**3.2a Ca doped  $PrPO_4$ :** The diffuse reflectance spectra (DRS) of Ca-doped  $PrPO_4$  compositions and that of parent  $PrPO_4$  are shown in figure 2. It is well known that  $Pr^{3+}$  has several metastable multiplets such as  $^3P_{0,1,2}$ ,  $^1D_2$ , and  $^1G_4$  (Kao and Chen 2000). 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.

The transitions are well known in most of the  $Pr^{3+}$  activated phosphors (Ibragimov *et al* 1992; Kao and Chen 2001). The  $L^*$ ,  $a^*$  and  $b^*$  parameters were computed from DRS for the parent and the Ca-doped compositions and the results show that the brightness as well as green and yellow components are much better as compared to Ca-doped  $CePO_4$  and chromium oxide and the values are presented in table 1.

## 4. Conclusions

We have synthesized a series of Ca-doped praseodymium phosphate using solution route. We measured the  $L^*$ ,  $a^*$ , and  $b^*$  for all the compositions. We find that Ca-doped  $PrPO_4$  has excellent brightness as well as green and yellow components. These compounds may be useful as pigments for colouring paints, plastics and high temperature ceramic applications, replacing contemporary toxic metal containing pigments like chromium oxide pigment.

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## References

- Diot N, Larcher O, Marchand R, Kempft J Y and Macaudière P 2001 *J. Alloys Compd.* **323–324** 45
- Gauthier G, Jobic S, Evain M, Koo H-J, Whangbo M-H, Fouassier C and Brec R 2003 *Chem. Mater.* **15** 828
- Ibragimov I R, Faxlizhanov I I, Falin M L and Ulanov V A 1992 *Sov. Phys. Solid State* **34** 1745
- Imanaka N, Masui T and Itaya M 2003 *Chem. Letts* **32** 400
- Jansen M and Letschert H P 2000 *Nature* **404** 980
- Kao F and Chen T 2000 *J. Solid State Chem.* **155** 441
- Kao F and Chen T 2001 *J. Solid State Chem.* **156** 84
- Mullica D F, Grossie D A and Boatner A 1985 *J. Solid State Chem.* **58** 71
- Olazcuaga R, Polles G L, Kira A E, Flem G L and Maestro P 1987 *J. Solid State Chem.* **71** 570
- Pepin J G, Vance E R and McCarthy G J 1981 *Mater. Res. Bull.* **16** 627