

# Synthesis and characterization of $\text{Eu}^{3+}$ activated hexagonal $\text{ABaGd}(\text{PO}_4)_2$ ( $\text{A}^+ = \text{Li}, \text{Na}, \text{or K}$ ) phosphates

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**Abstract.**  $\text{BaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  and  $\text{ABaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  (where  $\text{A}^+ = \text{Li}, \text{Na}$  or  $\text{K}$ ) double phosphates were synthesized by solid state diffusion method. These powders were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. XRD results showed many distinct lines in the XRD spectra. SEM measurement showed grains of different sizes in double phosphates. The  $\text{Eu}^{3+}$ -ion emission lines for  ${}^5D_0 \rightarrow {}^7F_j$  ( $j = 1, 2, 3,$  and  $4$ ) transitions showed a splitting into 3, 2, 1, and 2 components, respectively. Strength of these lines was enhanced by the addition of alkali ion to  $\text{BaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  double phosphate. However, as the alkali ion varied from  $\text{Li}^+$  to  $\text{K}^+$ , the intensity of  ${}^5D_0 \rightarrow {}^7F_2$  line (617 nm) in the red region increased at the cost of  ${}^5D_0 \rightarrow {}^7F_1$  line (599 nm) in the orange region. Suitable explanation has been proposed for this phenomena.

**Keywords.** Double phosphate; solid state diffusion; XRD; SEM; photoluminescence.

## 1. Introduction

Research on the luminescence properties of europium ions (divalent and trivalent) has been an important topic. This study has resulted in a variety of applications. The  $\text{Eu}^{3+}$ -doped materials have been used in lamp phosphor as a red luminescent material, laser materials, and X-ray storage phosphors. The well-known phosphors such as  $\text{Gd}_2\text{O}_3 : \text{Eu}^{3+}$ ,  $\text{La}_2\text{O}_3 : \text{Eu}^{3+}$ , and  $\text{Y}_2\text{O}_3 : \text{Eu}^{3+}$  (Ropp 1965),  $\text{YVO}_4 : \text{Eu}^{3+}$ , and  $\text{YPO}_4 : \text{Eu}^{3+}$  (Bril and Wanmaker 1964; Burrus and Paulusz 1968),  $\text{CaWO}_4 : \text{Bi}^{3+}, \text{Eu}^{3+}$  (Pode and Dhoble 1997), show intense luminescence of  $\text{Eu}^{3+}$  ion. The  $\text{Eu}^{2+}$ -doped materials are useful in fluorescent lamps and as X-ray storage phosphor (Blasse and Grabmaier 1994). A number of efficient  $\text{Eu}^{2+}$  phosphors have been reported (Jenkins and McKeag 1950; Jaffe and Banks 1955; Papilla and O'Reilly 1968; Wanmaker and ter Vrugt 1968; Gomes de Mesquita and Bril 1969; Wachtel 1969; Peters and Baglio 1970; Stevels 1978; Kobayashi *et al* 1980; Smets and Verlijndonk 1986; Smets *et al* 1989; Meijerink and Blasse 1990; Systma and Blasse 1991; Smets 1991). In recent years, considerable interest has been directed towards the discovery and characterization of economical and efficient  $\text{Eu}^{3+}$ -doped luminescent materials. The double phosphates with general formula  $\text{ABR}(\text{PO}_4)_2$  (where  $\text{A} = \text{alkali}$ ,  $\text{B} = \text{alkaline earth}$ , and  $\text{R} = \text{rare earth}$ ) have been studied extensively, as a host material (Et-Tabirou and Daoudi 1980; Bouchu *et al*

1981; Parent *et al* 1981, 1982, 1984; Arhus *et al* 1991). Recently, luminescence of  $\text{Ln}^{3+}$  ( $\text{Ln} = \text{Eu}$  and  $\text{Dy}$ ) in gadolinium-based double phosphates has been investigated (Shaolong Tie *et al* 1995). The present work is an attempt to investigate photoluminescence in  $\text{ABaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  (where  $\text{A}^+ = \text{Li}, \text{Na}$ , and  $\text{K}$ ) double phosphate, synthesized by solid state diffusion process. The XRD and SEM techniques are used for their characterization. As the alkali ion varies from  $\text{Li}^+$  to  $\text{K}^+$  ions, the intensity of  ${}^5D_0 \rightarrow {}^7F_2$  line (617 nm) in the red region increases at the cost of  ${}^5D_0 \rightarrow {}^7F_1$  line (599 nm) in the orange region.

## 2. Experimental

Double phosphates  $\text{ABaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  (where  $\text{A}^+ = \text{Li}, \text{Na}$ , and  $\text{K}$ ) were prepared by solid state diffusion method. GR grade powders of  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{A}_2\text{CO}_3$  ( $\text{A} = \text{alkali}$ ),  $\text{BaCO}_3$ ,  $\text{Gd}_2\text{O}_3$ , and  $\text{Eu}_2\text{O}_3$  (both 99.9% pure, obtained from Indian Rare Earths Ltd.) were mixed thoroughly together stoichiometrically with  $\text{NH}_4\text{Cl}$  flux (10 mol% of  $\text{Gd}_2\text{O}_3$ ) for 1 h. Mixed powders were transferred to porcelain crucibles and heated at  $300^\circ\text{C}$ ,  $880^\circ\text{C}$  and  $1020^\circ\text{C}$  for 6 h. The  $\text{NH}_4\text{Cl}$  flux was added with two interposed grindings to reduce annealing time and to obtain a single phase (Shaolong *et al* 1995).

\*The formation of the material was checked by X-ray diffraction measurement (XRD). The surface morphology was investigated using scanning electron microscopy (SEM) analysis. The excitation and emission spectra were measured on a Jobin Yvon Spectrofluorometer.

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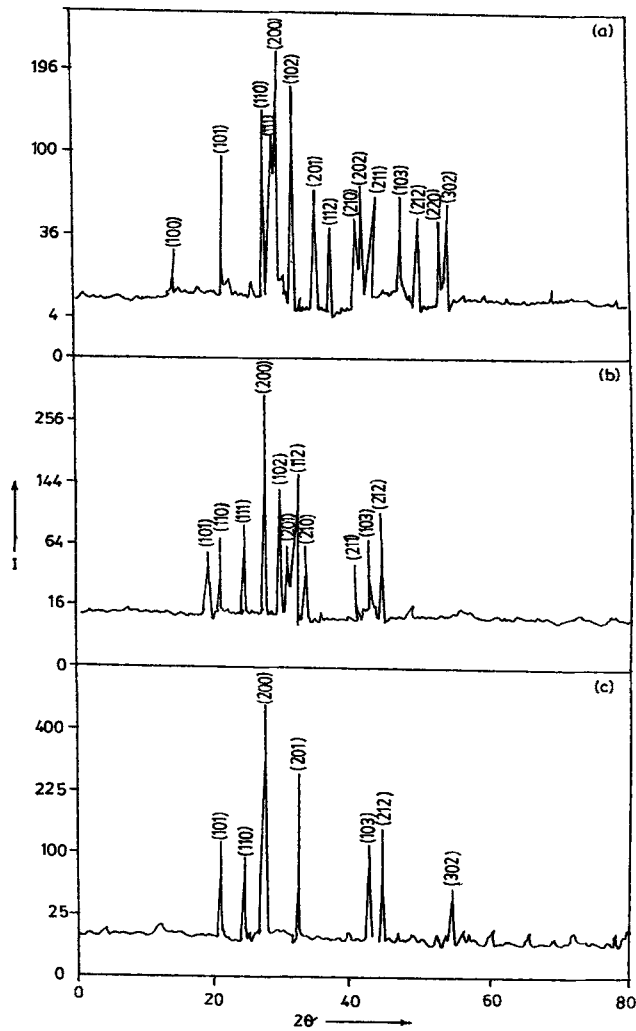


Figure 1. X-ray powder diffraction patterns of: (a)  $\text{LiBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$ , (b)  $\text{NaBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$ , and (c)  $\text{KBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$ .

### 3. Results and discussion

The XRD patterns were recorded using a Philips PW 1710 X-ray diffractometer.  $\text{CuK}_\alpha$  wavelength ( $1.54056 \text{ \AA}$ ) was used in the experiment. Figures 1a, b and c show the X-ray diffraction patterns of  $\text{LiBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$ ,  $\text{NaBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  and  $\text{KBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  double phosphates, respectively. Many well resolved lines were obtained in XRD pattern of all the powders. The presence of large distinct lines confirmed the crystalline behaviour and formation of double phosphates. Earlier, XRD patterns of  $\text{KCaDy}(\text{PO}_4)_2$ ,  $\text{KCaHo}(\text{PO}_4)_2$  (Et-Tabirou and Daoudi 1980), and  $\text{KCaGd}(\text{PO}_4)_2$  (Keller *et al* 1985),  $\text{KCaY}(\text{PO}_4)_2$  (Shaolong *et al* 1995) were reported. Results in double phosphates prepared by us are nearly similar to those of  $\text{KCaGd}(\text{PO}_4)_2$  (JCPDS File No. 34-125) except for the different intensities of some reflection planes. Table 1 gives the information about the XRD data of double phosphates.

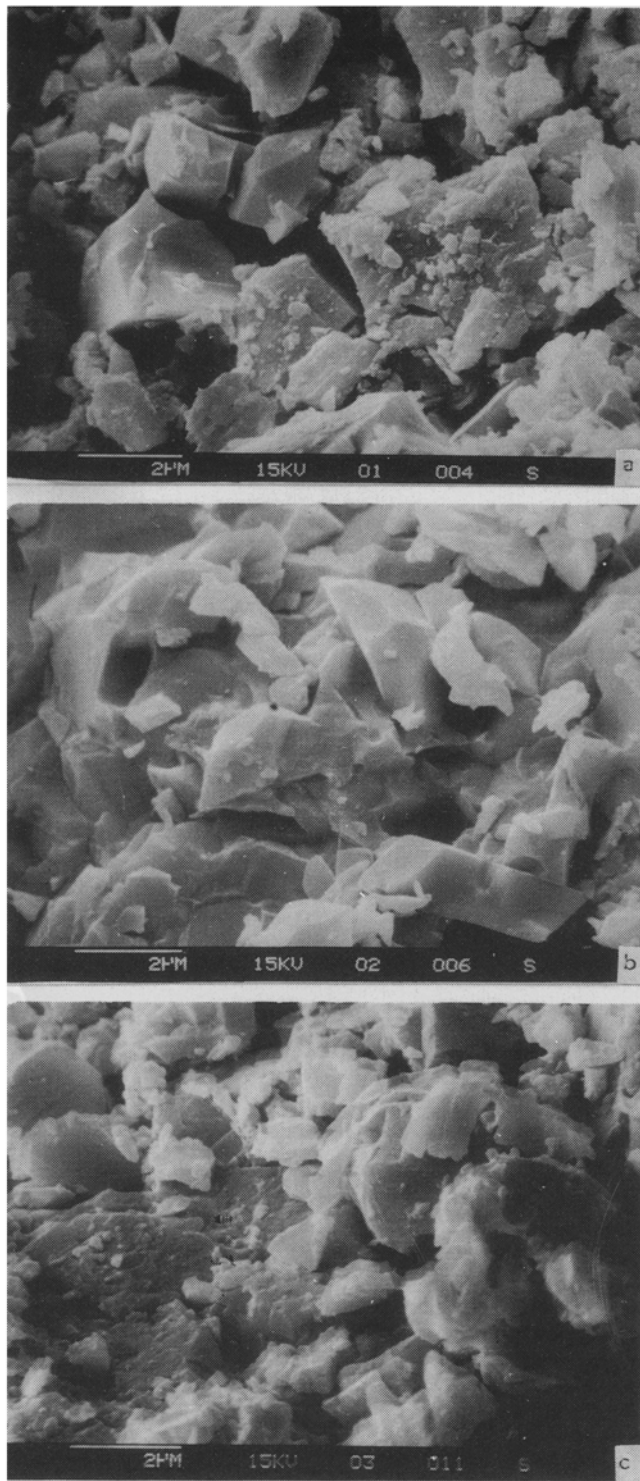
Particle size of phosphor material plays an important role in deciding the luminescence quality of the material. Uniform particle size distribution and fine particles are some of the requirements of good luminescent materials. Figures 2a, b, and c show the SEM microphotographs of  $\text{ABaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  ( $A^+ = \text{Li, Na, and K}$ ) double phosphates. Similar surface morphology was observed in all the powders, except that some change in particle sizes was observed as the alkali ion was varied from  $\text{Li}^+$  to  $\text{K}^+$ . Average particle sizes were 2.3, 2.1, and  $1.97 \mu\text{m}$ , respectively.

The excitation spectrum of  $\text{KBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  monitored at 617 nm is shown in figure 3a. A broad band was observed from 240 to 270 nm; small peaks were observed at 372 and 390 nm; and a prominent line was observed at 399 nm. The broad band was perhaps due

Table 1. The XRD data of  $\text{ABaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  phosphates ( $A^+ = \text{Li, Na and K}$ ).

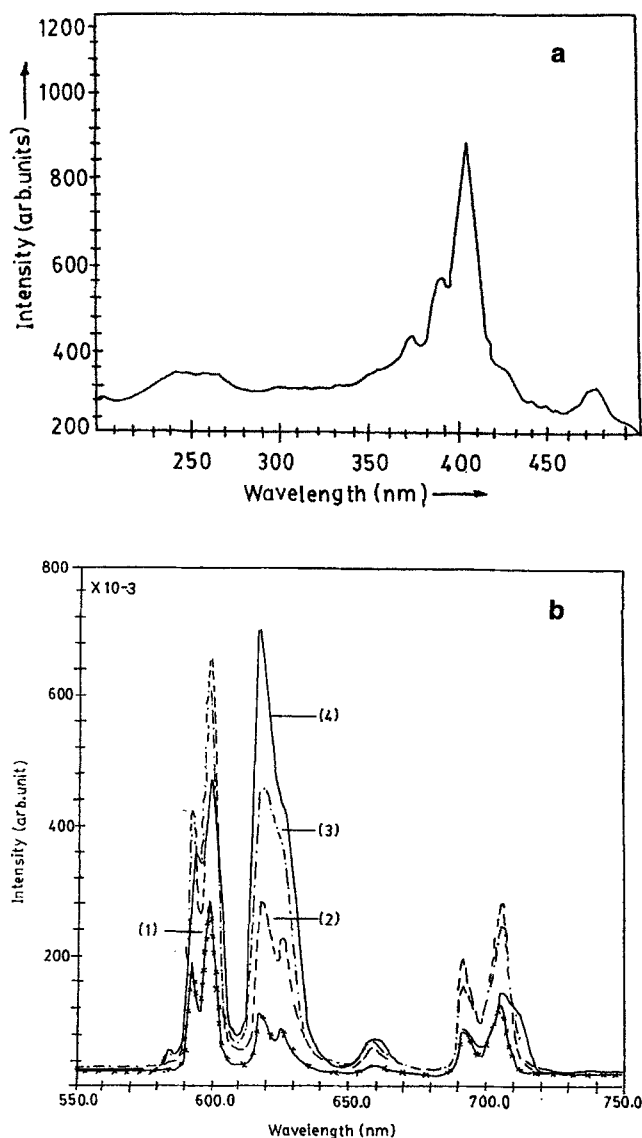
$\text{LiBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$		$\text{NaBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$		$\text{KBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$	
d-value ( $\text{\AA}$ )	Relative intensity (%)	d-value ( $\text{\AA}$ )	Relative intensity (%)	d-value ( $\text{\AA}$ )	Relative intensity (%)
6.1079	12.6	4.6488	17.8	4.2268	20.4
4.1033	46.4	4.2579	19.3	3.6628	18.5
3.2350	75.6	3.6874	22.8	3.2770	100.0
3.0635	60.1	3.2960	100.0	2.7709	48.6
3.0330	100	3.0284	39.4	2.1170	21.6
2.8112	92.9	2.8974	14.7	2.0323	31.0
2.5602	31.1	2.7865	50.6	1.6826	9.2
2.3954	18.3	2.6825	16.0		
2.1941	19.5	2.2210	11.5		
2.1453	20.2	2.1286	18.8		
2.1097	25.7	2.0454	26.7		
1.9223	26.5				
1.8374	26.5				
1.7328	21.5				
1.7030	26.5				

to presence of  $\text{Gd}^{3+}$ , whereas the prominent line at 399 nm was perhaps due to the transition from  ${}^7F_0 \rightarrow {}^5L_6$  (Shaolong Tie *et al* 1995). The excitation curves for other powders were similar and hence are not reported here.



**Figure 2.** SEM microphotographs ( $\times 10,000$ ) of: (a)  $\text{LiBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}^{3+}$ , (b)  $\text{NaBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}^{3+}$ , and (c)  $\text{KBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}^{3+}$ .

The  $\text{GdPO}_4 : \text{Eu}^{3+}$  (5 mol%) powder was synthesized by solid state diffusion method, and photoluminescence spectrum was recorded. No emission line in the red region was observed in this powder, in contrast to a very strong emission line due to  $\text{Eu}^{3+}$  in  $\text{YPO}_4 : \text{Eu}^{3+}$  reported earlier by Brill and Wanmaker (1964). On the other hand, the emission spectra of  $\text{BaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}^{3+}$  and  $\text{ABaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}^{3+}$  (where  $\text{A}^+ = \text{Li}, \text{Na}$  and  $\text{K}$ ) showed three lines at 585, 593, and 599 nm due to  ${}^5D_0 \rightarrow {}^7F_1$  transition, and two lines at 617 and 626 nm due to  ${}^5D_0 \rightarrow {}^7F_2$  transition (figure 3b). Besides these lines, two emission lines at higher wavelength side due to  ${}^5D_0 \rightarrow {}^7F_3$  and  ${}^5D_0 \rightarrow {}^7F_4$  transitions were also observed, respectively. These results are consistent with the earlier



**Figure 3.** (a) Photoluminescence excitation spectrum of  $\text{KBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}^{3+}$ , monitored at 617 nm. (b) Photoluminescence emission spectra of double phosphates, excited at 399 nm: (1)  $\text{BaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}^{3+}$ ; (2)  $\text{LiBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}^{3+}$ , (3)  $\text{NaBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}^{3+}$ , and (4)  $\text{KBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}^{3+}$ .

reported results, except for the non-appearance of line for  ${}^5D_0 \rightarrow {}^7F_0$  transition in the emission spectrum, as had been reported by Shaolong Tie *et al* (1995). For the  $D_2$  site symmetry of the  $\text{Eu}^{3+}$  ions in a hexagonal phosphate, three lines for each transitions,  ${}^5D_0 \rightarrow {}^7F_1$  and  ${}^5D_0 \rightarrow {}^7F_2$ , and absence of emission line for  ${}^5D_0 \rightarrow {}^7F_0$  transition are to be expected, as reported earlier by Zhang (1983). Earlier, splitting of various emission lines were observed in  $\text{Eu}^{3+}$ -doped  $\text{MgSiO}_3$  gel, which were attributed to the lowering of local site symmetry of  $\text{Eu}^{3+}$  ions (Fan *et al* 1996). In  $\text{BaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  and  $\text{ABaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  double phosphates, the point symmetry of  $\text{Eu}^{3+}$  lowers from  $D_2$  to  $C_2$  due to the addition of  $\text{Ba}^{2+}$  (unmatched ionic radii between  $\text{Ba}^{2+}$  (0.13 nm) and  $\text{Gd}^{3+}$  (0.111 nm)) and by an unequal distribution of  $\text{A}^+$  alkali ions into neighbouring channels along the  $c$ -axis, and the splitting of emission lines occurs owing to this lowering of local site symmetry of the  $\text{Eu}^{3+}$  ion from  $D_2$  (four-symmetry elements) to  $C_2$  symmetry (two-symmetry elements). In 1978, Imbush had discussed the crystal field splitting of  ${}^7F_j$  levels of  $\text{Eu}^{3+}$

ion. Our results are consistent with the reported results. The splitting was prominent in  $\text{BaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  and  $\text{LiBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  powders for all the emission lines, and in the other two samples,  $\text{NaBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  and  $\text{KBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$ , well-resolved lines for  ${}^5D_0 \rightarrow {}^7F_1$  transition, and no appreciable splitting for  ${}^5D_0 \rightarrow {}^7F_2$  transition emission line were observed. Table 2 shows the emission intensities of various lines.

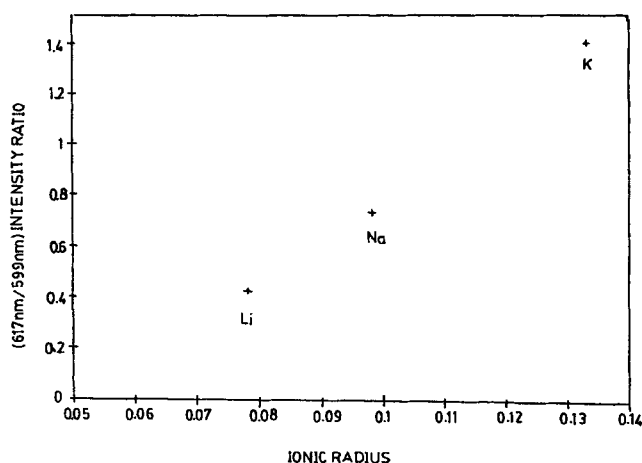
Moreover, the above-given results show that the 593 and 599 nm (orange region) emission lines ( ${}^5D_0 \rightarrow {}^7F_1$  transition) were intense compared to the emission lines at 617 and 626 nm ( ${}^5D_0 \rightarrow {}^7F_2$  transition) in the red region in  $\text{BaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$ . With the addition of  $\text{Li}^+$  to  $\text{BaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$ , intensities of all the emission lines enhanced at least by two folds. As the alkali ion was varied from  $\text{Li}^+$  to  $\text{K}^+$ , the red emission lines became stronger and stronger at the cost of the orange lines. In  $\text{KBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  powder, the 617 nm line (intensity 0.7 arb. unit) was 1.4 times intense than 599 nm line (0.48 arb. unit). Figure 4 shows the variation of (617 nm/599 nm) intensity ratio with the ionic radius of alkali ion. The intensity ratio enhanced linearly with the ionic radius and was found to be maximum for  $\text{K}^+$  ion. An explanation of these results is given below.

The splitting and the strength of emission lines are dependent on the symmetry of the crystal field, and are also related to the surroundings of the impurity  $\text{Eu}^{3+}$  ion in the crystal lattice. The  $\text{ABR}(\text{PO}_4)_2$  double phosphate has a hexagonal structure like  $\text{LnPO}_4$  (Vlasse *et al* 1982). Figure 5 gives the projection of the structure on the (001) plane. There are  $\text{Gd}-\text{PO}_4-\text{Gd}$  chains leaving large open tunnels running along the hexagonal axis. The  $\text{A}^+$  alkali ion (Li, Na or K) occupies the positions in these tunnels as the charge compensator, and lowers the point symmetry of the  $\text{Eu}^{3+}$  ions which are at the  $\text{Ba}^{2+}$  or  $\text{Gd}^{3+}$  sites (Vlasse

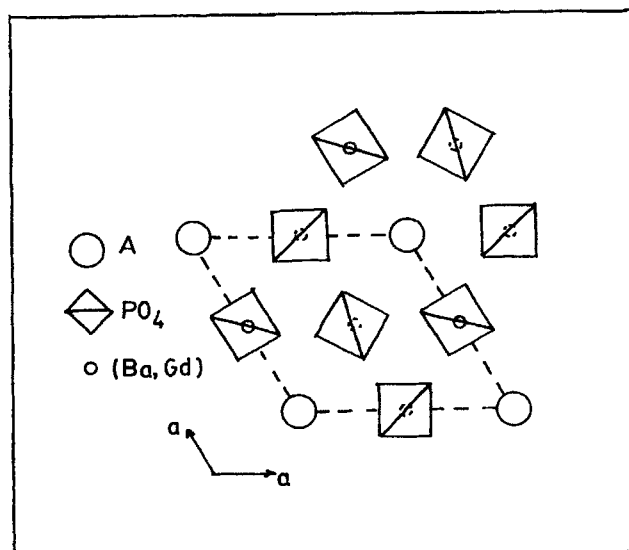
**Table 2.** Emission lines of  $\text{Eu}^{3+}$  ion in  $\text{ABaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  double phosphates, excited at 399 nm at 300 K.

Sample	Emission intensity (arb. units)			
	${}^5D_0 \rightarrow {}^7F_1$ transition		${}^5D_0 \rightarrow {}^7F_2$ transition	
	593 nm	599 nm	617 nm	626 nm
$\text{BaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$	0.19	0.3	0.12	0.1
$\text{LiBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$	0.43	0.66	0.29	0.23
$\text{NaBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$	0.41	0.62	0.46	sh
$\text{KBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$	0.36	0.48	0.70	sh

sh: shoulder



**Figure 4.** (617 nm/599 nm) intensity ratio as a function of ionic radius of alkali ions.



**Figure 5.** Projection of the  $\text{ABaGd}(\text{PO}_4)_2$  structure of double phosphate on the (001) plane.

*et al* 1982). The distortion in the symmetry gets enhanced as the ionic radius of alkali ions is varied from  $\text{Li}^+$  (0.078 nm) to  $\text{K}^+$  (0.113 nm). In  $\text{ABaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  (where  $\text{A}^+ = \text{Li}, \text{Na}, \text{and K}$ ), emission lines for magnetic ( $^5D_0 \rightarrow ^7F_1$ ) and forced electric dipole transitions ( $^5D_0 \rightarrow ^7F_2$ ) were observed as suggested by Oomen and van Dongen (1989). In  $\text{BaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  and  $\text{ABaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  (where  $\text{A}^+ = \text{Li}$  and  $\text{Na}$ ), the emission for  $^5D_0 \rightarrow ^7F_1$  transition is much more intense than  $^5D_0 \rightarrow ^7F_2$  transition. The strength of emission for the  $^5D_0 \rightarrow ^7F_1$  transition is higher for  $\text{Li}^+$  (0.078 nm ionic radius) than  $\text{Na}^+$  (0.098 nm). This shows that most of the  $\text{Eu}^{3+}$  ions are situated at the symmetry sites in these powders, and therefore the  $D_2$  symmetry component of  $\text{Eu}^{3+}$  ions is higher than the  $C_2$  symmetry. In contrast, in  $\text{KBaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$ , the forced electric dipole transition due to  $^5D_0 \rightarrow ^7F_2$  is intense than the magnetic dipole transition,  $^5D_0 \rightarrow ^7F_1$ , and the relative concentration of  $C_2$  symmetry sites of  $\text{Eu}^{3+}$  ions is higher, which may be surrounded by same environment in this powder. This therefore results in enhancing the emission strength of 617 and 626 nm lines.

#### 4. Conclusions

(I) The XRD patterns of all double phosphates showed sharp lines, which indicate the formation of crystalline powder.

(II) The SEM results showed uniform surface morphology in all the powders, except some morphology changes were observed as the alkali ion was varied from  $\text{Li}^+$  to  $\text{K}^+$ .

(III) The emission lines for  $^5D_0 \rightarrow ^7F_j$  ( $j = 1, 2, 3, \text{and } 4$ ) transitions (both magnetic as well as forced electric dipole) were observed in europium-doped double phosphates. All emission showed splitting because of the lowering of the local symmetry from  $D_2$  to  $C_2$  of  $\text{Eu}^{3+}$  ions.

(IV) The strength of emission lines  $^5D_0 \rightarrow ^7F_2$  transition (red region) enhanced as the alkali ion was varied from  $\text{Li}^+$  to  $\text{K}^+$  at the cost of  $^5D_0 \rightarrow ^7F_1$  emission lines (orange region) in  $\text{ABaGd}_{0.5}(\text{PO}_4)_2 : \text{Eu}_{0.5}^{3+}$  phosphates.

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