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Optical and dielectric properties of borophosphates $A_{1-x}Eu_xBPO_5$ (A=Ca, Sr, Ba and Pb)

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Abstract

Europium alkaline earth borophosphates $A_{1-x}Eu_xBPO_5$ (A=Ca, Sr, Ba or Pb), were synthesized in two ways: solid state reaction or coprecipitation. The dielectric measurements were performed to resolve the ambiguity between different space groups. The optical properties of these compounds were investigated using the trivalent europium ion as the local structural probe. Under 465.8 nm excitation, intense red emission of the trivalent europium ion was observed. Several groups of bands were recorded corresponding to the $^5D_1 \rightarrow {}^7F_{0-3}$ and $^5D_0 \rightarrow {}^7F_{0-4}$ transitions. The emission from the two emitting levels was separated using different time delays after the laser pulse. Lifetime measurements of $^5D_0$ and $^5D_1$ levels were performed and differences in the kinetic process were discussed.

Keywords: Borophosphates; X-Ray diffraction; Optical properties; Luminescence; Dielectric response

1. Introduction

A great deal of effort has been devoted to investigate the spectroscopic properties of rare earth borogermanates with the stillwellite type structure. The interest in these compounds is their potential use as an effective self-frequency-doubling mini-laser. Verwey et al. have studied the luminescence processes in the crystalline and glass modifications of Eu^{3+} doped $REBGeO_5$ and $CaBPO_5$ [1]. Kaminskii et al. were the first to grow single crystals of trigonal $LaBGeO_5$ doped with Pr^{3+} and Nd^{3+} and use these materials as a new nonlinear crystal laser [2,3]. Antic-Fidancev et al. have shown the luminescence properties of the Eu^{3+} ion in the two $REBMO_5$ trigonal and monoclinic varieties (RE, rare earth; M=Ge, Si) [4,5].

On the other hand, these oxides exhibit interesting dielectric properties. It is well known that $REBGeO_5$ crystals with the stillwellite type structure have a ferroelectric phase transition [6,7].

The stillwellite structure offers the possibility of cationic substitution. For example, trivalent and tetravalent cations in borogermanates $REBGeO_5$ can be easily exchanged by divalent and pentavalent cations, respectively, to obtain borophosphates with the general formula $ABPO_5$ where A is alkaline earth ion or Pb. These borophosphates were first prepared in crystalline form by Bauer (A=alkaline earth) and by Tarte et al. (A=Pb), and shown to be isostructural with stillwellite [8–10]. The crystal structure of borophosphates has been resolved from powder data using the Rietveld method. The authors proposed two possible space groups ($P3_1$ or $P3_121$) [11].

This work deals with the spectroscopic investigation of Eu^{3+} used as a local structural probe in the $A_{1-x}Eu_xBPO_5$ (A=alkaline earth or Pb) compounds. Lifetime measurements of the emission from $^5D_0$ and $^5D_1$ levels are performed and differences in the kinetic process are discussed. The investigation of dielectric constant was carried out to confirm the correct space group, to assign the X-ray diffraction spectra and determine the crystallographic parameters.

2. Experimental details

Polycrystalline samples of $ABPO_5$:5% Eu_2O_3 were synthesized by a solid state reaction between high-purity ACO_3 (A=Ca, Sr and Ba), $Pb(NO_3)_2$, H_3BO_3,

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$(NH_4)_2HPO_4$, and Eu_2O_3. The stoichiometic mixtures were ground and progressively heated in a platinum crucible at 400°C for 12 h. The resulting compound was ground again and heated for a further 72 h at 900°C for A=Ca, 800°C for A=Sr, 1000°C for A=Ba and 680°C for $PbBPO_5$. An appropriate excess of H_3BO_3 was added to compensate the B_2O_3 loss. The $CaBPO_5$ compound doped with Eu^{3+} was also prepared by coprecipitation process: $CaCO_3$ and Eu_2O_3 were weighed and dissolved in a small amount of hot hydrochloric acid. H_3BO_3 and $(NH_4)_2HPO_4$ dissolved in distilled water were added to the solution. The precipitate obtained was dried and then fired for 1 h in air at 800°C.

The crystal structure was checked with X-ray powder diffraction using a Siemens D-5000 diffractometer and Cu Kα radiation.

The dielectric constant (ϵ) and dielectric loss (tgδ) measurements have been made using an HP 4284A LCR meter in the temperature interval 300–1000 K on powder pellets heated to 50 degrees below their melting points at different frequencies. Silver was used as the electrode on plane surfaces. These measurements confirm the space group selected to assign the X-ray diffraction lines of the compounds.

The luminescence spectra were recorded on powder samples of $A_{1-x}Eu_xBPO_5$ (5% Eu) with excitation coming from an OPO (optical parametric oscillator) pumped by the third harmonic of a Q-switched Nd:YAG laser, at several wavelengths corresponding to the $^7F_0 \rightarrow ^5D_J$ absorption transitions (at 580 nm for an excitation in the $^5D_0$ and at 525 nm for the $^5D_1$ levels). An intensified optical multichannel analyzer (OMA) was used for the detection of the luminescence. With this apparatus, it is also possible to record the emission at various times after the laser pulse and therefore to obtain the lifetime decay profiles.

3. Results and discussion

3.1. Dielectric properties and crystallographic background

In Fig. 1 we compare the behavior of the dielectric constant ϵ of borophosphates and $PrBGeO_5$ as a function of temperature at 10 kHz. The $PrBGeO_5$ curve shows a maximum at about 930 K corresponding to a ferroelectric transition as reported before [12]. For the group of borophosphates $ABPO_5$, this anomaly was not found. This result suggests a higher symmetry space group ($P3_121$) for our compounds. The trigonal cell parameters deduced from the X-ray diffraction patterns are given in Table 1. The crystal structure of borophosphates is closely related to the stillwellite structure. It contains BO_4 and PO_4 tetrahedra joined by a common vertix [13].

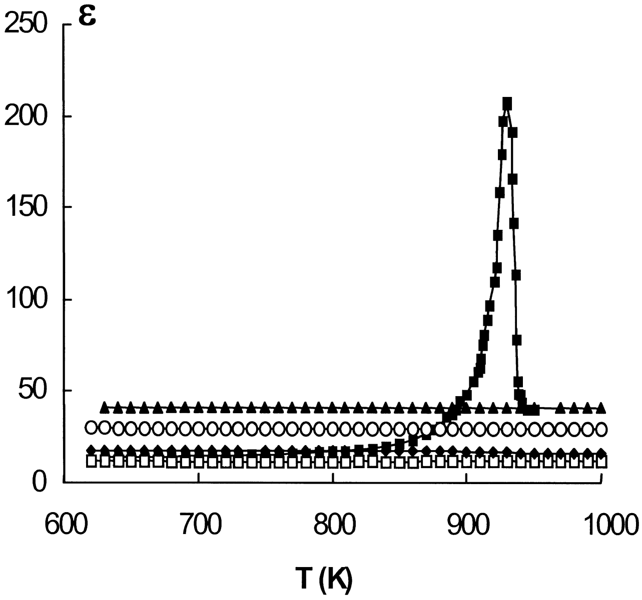

Fig. 1. Variation of the dielectric constant as a function of temperature at 10 kHz for ■, $PrBGeO_5$; □, $CaBPO_5$; ♦, $SrBPO_5$; ○, $BaBPO_5$ and ▲, $PbBPO_5$.

3.2. Luminescence properties

3.2.1. Luminescence spectra of the $Ca_{1-x}Eu_xBPO_5$ compounds

The $^5D_0 \rightarrow ^7F_0$ transition, forbidden by the J selection rules, is observed due to the mixing with the excited configuration with odd parity. The $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions, respectively magnetic and electric dipole transitions, are both allowed by the J selection rules [14]. They are clearly observed in the emission spectra. Fig. 2 compares the emission of two $Ca_{0.95}Eu_{0.05}BPO_5$ materials obtained by two different synthetic procedures, by solid state reaction or by coprecipitation. One can observe that the $^5D_0 \rightarrow ^7F_2 / ^5D_0 \rightarrow ^7F_1$ intensity ratio is very different for the two products. These ratios vary from 5 to 2 for the products obtained by solid state reaction and coprecipitation processes, respectively.

Non-centrosymmetric low symmetry sites lead to a predominance of electric dipole transitions, and a high $^5D_0 \rightarrow ^7F_2 / ^5D_0 \rightarrow ^7F_1$ intensity ratio. This is observed for the $Ca_{0.95}Eu_{0.05}BPO_5$ material obtained by the solid state reaction process. In addition, the intensity of the $^5D_0 \rightarrow ^7F_0$ forbidden transition is higher in this compound than in $Ca_{0.95}Eu_{0.05}BPO_5$ obtained by the coprecipitation process [15]. The emission spectra indicate therefore that the local symmetry around the Eu^{3+} ions is affected by the synthesis procedure; lower symmetry being obtained for the 'solid state' material.

The lifetime values of the $^5D_0$ level of the studied compounds are also in good agreement with this analysis.

Table 1
Trigonal unit cell parameters of borophosphates $A_{0.95}Eu_{0.05}BPO_5$

	$Ca_{0.95}Eu_{0.05}BPO_5$	$Sr_{0.95}Eu_{0.05}BPO_5$	$Ba_{0.95}Eu_{0.05}BPO_5$	$Pb_{0.95}Eu_{0.05}BPO_5$
a (Å)±0.01	6.69	6.86	7.11	6.91
c (Å)±0.01	6.62	6.83	6.99	6.87

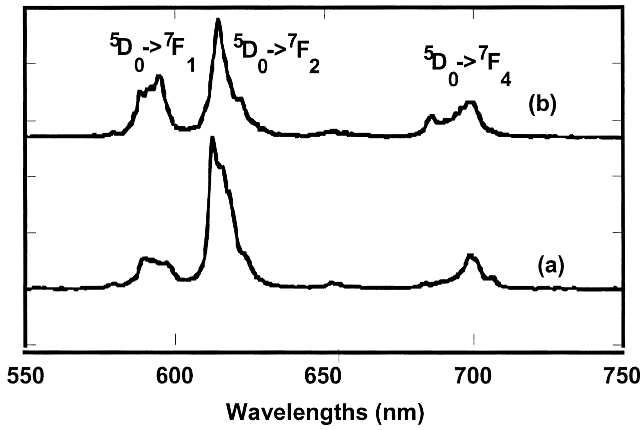

Fig. 2. Room temperature luminescence spectra for the $Ca_{0.95}Eu_{0.05}BPO_5$ material obtained by (a) the 'solid' process and (b) the 'liquid' procedure (465.8 nm excitation; pulse delay: 100 μs, pulse width: 1 μs).

Exponential behaviour is obtained for the two products (Fig. 3) with a lifetime of 1.6 ms for the $Ca_{0.95}Eu_{0.05}BPO_5$ material obtained by the 'solid state' process and a lifetime of 2 ms for the material obtained by the coprecipitation route. Indeed, this corroborates the lower symmetry (and lower lifetime value) obtained for the first process.

3.2.2. Evolution of the emission properties in $A_{1-x}Eu_xBPO_5$ (A=Ca, Sr, Ba and Pb)

Substitution of different divalent cations by Eu^{3+} is possible in these borophosphates. However, due to the different sizes of these cations, the homogeneity of the material will be quite different. Calcium is the most suitable as its ionic radius is closest to trivalent europium (1.12 and 1.066 Å, respectively) in eight coordination [16].

Figs. 4 and 5 show the decay profiles for two emitting levels of Eu^{3+}, $^5D_0$ and $^5D_1$ respectively.

Table 2 lists the ionic radii (CN=8) of A cations and the lifetime values obtained for the different Eu^{3+} doped materials.

As most of these decay profiles have a non-exponential behaviour, the mean lifetime values are expressed as:

$$\tau_{\text{mean}} = \frac{\int_0^{\theta} I(t)\,\mathrm{d}t}{I_0}$$

where θ is the time value when the luminescence intensity reaches background.

Only calcium ions which have a size not too different from that of Eu^{3+}, also have an exponential behavior for the decay profile. For the other divalent cations, the europium emission is a sum due to different surroundings.

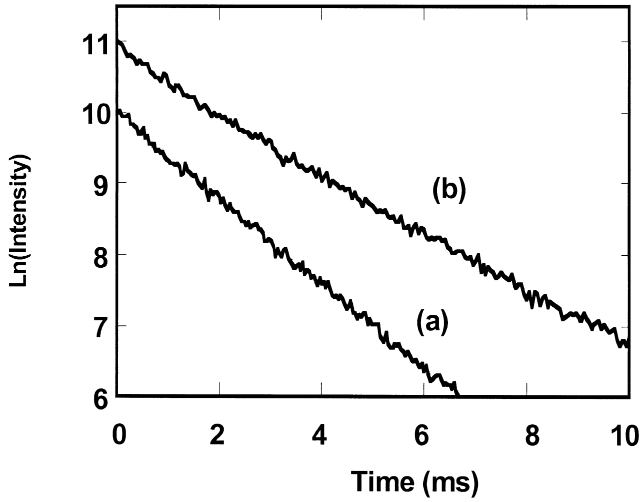

Fig. 3. $^5D_0$ emission decay profiles of (a) $Ca_{0.95}Eu_{0.05}BPO_5$ obtained by the 'solid state' process and (b) by the coprecipitation process.

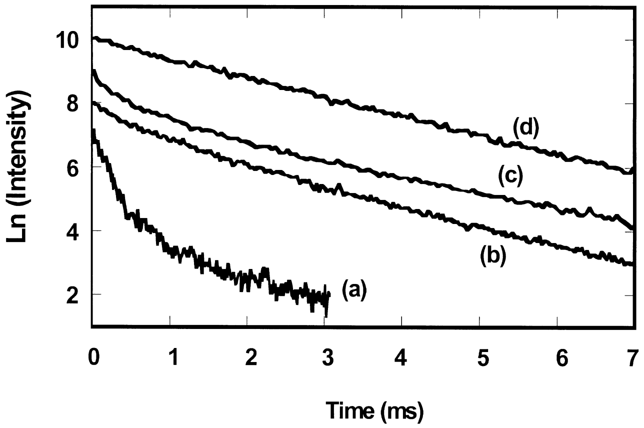

Fig. 4. Room temperature $^5D_0$ fluorescent decay profiles for different europium borophosphates (a) Pb; (b) Ba; (c) Sr and (d) Ca (excitation at 612 nm).

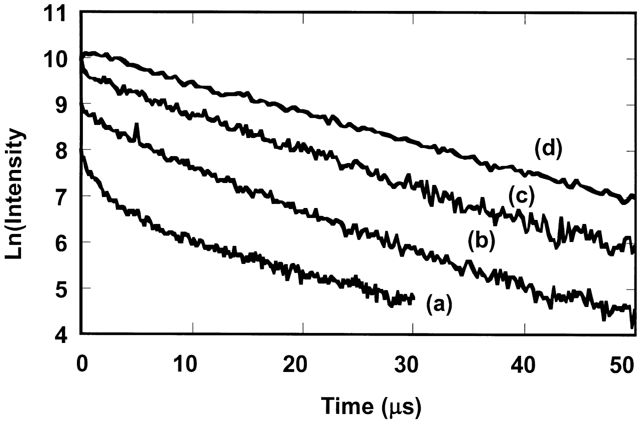

Fig. 5. Room temperature $^5D_1$ fluorescent decay profiles for different europium borophosphates (a) Pb; (b) Ba; (c) Sr and (d) Ca (excitation at 535 nm).

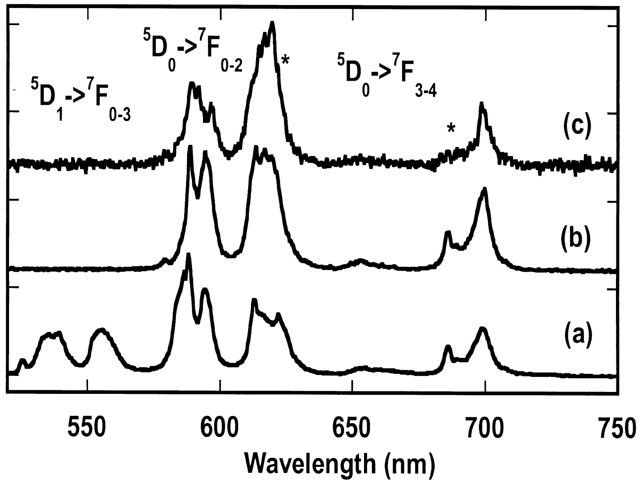

Fig. 6. Emission spectra for $Pb_{0.95}Eu_{0.05}BPO_5$ at different pulse delays: (a) 0 s; (b) 100 μs and (c) 2 ms.

As an example, the emission spectra of $Pb_{0.95}Eu_{0.05}BPO_5$ are reported in Fig. 6. These spectra were recorded using different time delays after the laser pulse in order to observe the kinetic variations. The $^5D_0$ emitting level presents very different kinetics, as observed for instance in the $^5D_0 \rightarrow {}^7F_4$ transition. Indeed, the emission band corresponding to the higher energy, around 680 nm, vanished for a 2-ms pulse delay. Moreover, the $^5D_0 \rightarrow {}^7F_2$/$^5D_0 \rightarrow {}^7F_1$ intensity ratio is quite different between (b) and (c) spectra.

This indicates that Eu^{3+} ions in $Pb_{0.95}Eu_{0.05}BPO_5$ are located in several surroundings, some (in aggregates for instance) presenting very short decay times. Further experiments at low temperature and several europium concentrations are required to confirm this.

4. Conclusion

The anomaly of dielectric properties in the interval 300–1000 K was not found for the synthesized compounds $ABPO_5$:Eu^{3+} (A = Ca, Sr, Ba and Pb), and a higher symmetry space group $P3_121$ is suggested. The emission spectra of trivalent europium ion in new rare earth-alkaline borophosphates, $A_{1-x}Eu_xBPO_5$ (A = Ca, Sr, Ba or Pb), were analyzed. The kinetic processes of $^5D_{0,1}$ levels in these materials were discussed. We demonstrate that the size of the A cation has a great influence on the homogeneity of the material. This preliminary study must be continued on samples doped with various europium concentrations.

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Table 2
Ionic radius of A cations and $^5D_0$ and $^5D_1$ mean lifetime values for different europium borophosphates

Material	Ionic radius of A^{2+} (Å)	Mean lifetime	
	(CN = 8) [16]	$^5D_0$ (ms)	$^5D_1$ (μs)
$Ca_{0.95}Eu_{0.05}BPO_5$ (solid)	1.12	1.60	17.5
$Ca_{0.95}Eu_{0.05}BPO_5$ (liquid)	1.12	2	8.2
$Sr_{0.95}Eu_{0.05}BPO_5$	1.26	0.76	4.4
$Ba_{0.95}Eu_{0.05}BPO_5$	1.42	0.96	7.5
$Pb_{0.95}Eu_{0.05}BPO_5$	1.29	0.25	8.4

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