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Eu^{2+} luminescence in *stillwellite*-type $SrBPO_5$ – a new potential X-ray storage phosphor

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Abstract

Eu^{2+}-doped $SrBPO_5$ with stillwellite structure has been identified as a new luminescent system which shows intense photostimulated luminescence for UV and X-ray radiations. Various spectral features observed for the new system are very much similar to $BaFBr:Eu^{2+}$, the extensively applied phosphor system in digital radiography. Apart from its potential for application, the unusually low wavelength Eu^{2+} emission observed has been explained by the absence of preferred orientation of d-orbital of Eu^{2+} as dictated by crystal chemistry of the system. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the field of medical diagnosis, digital radiography employing phosphor imaging-plates (IP) had replaced conventional photographic film-based radiography methods owing to several advantages [1]. The present day phosphor imaging plates use Eu^{2+}-activated barium fluoro-halide-based storage phosphors. Although the application of this phosphor system in imaging plates (IP) is a great success this system has several shortcomings too, for e.g., plate like morphological feature resulting in light piping [2] and the hygroscopic nature limiting the stability [3] etc. However, the problem due to plate-like morphology could be overcome by the ingenious spray-drying technique [4,5].

Still we thought, it would be more advantageous to have phosphor material(s) prepared by conventional methods that can address these issues straight away. Accordingly we could identify a Eu^{2+}-doped $SrBPO_5$ system that can be grouped under mineral *stillwellite* structure showing promising features for application as X-ray storage phosphor. Another interesting feature of this new luminescent system is the Eu^{2+} emission in short wavelengths (∼ 390 nm). This can be explained by the absence of preferred orientation of d-orbital [6] determined by the crystal chemistry of the system. Although there is a preliminary report on Eu^{2+} luminescence in this system, there is not much information concerning the crystal structure of the

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system [7]. Motivated by this, we have attempted in this investigation to have some insights on the possible correlation between the luminescent properties and crystal chemistry of the system. Furthermore, we have also given a special emphasis in evaluating the prospects of this system for storage phosphor application.

2. Experimental

Both Eu^{2+} doped ($x = 0.01$–5 mol%) and undoped ($x = 0$) strontium boro phosphate ($Sr_{1-x}Eu_xBPO_5$) samples were prepared by conventional solid state reaction method in a muffle furnace under mild reducing atmosphere with a heating schedule at 600°C for 2 h and at 800°C for 2 h. The starting materials used viz., $SrCO_3$, H_3BO_3, $(NH_4)_2HPO_4$ (all analyzed reagents) and $EuCl_3.6H_2O$ (99.9% purity) were taken in stoichiometric proportions and after homogenization the resulting mixture was transferred into an alumina crucible covered with lid for carrying out the solid state reaction. The white product thus obtained was checked for phase purity using a JEOL X-ray diffractometer (XRD) employing Cu K_α radiation. The sample(s) was found to be phase singular and the diffraction lines observed were consistent with the space group symmetry $P3_1$. The other experimental procedure pertaining to photoluminescence (PL), photo-stimulated luminescence (PSL) and X-band electron paramagnetic resonance (EPR) were the same as described earlier [8].

3. Results and discussion

3.1. Stillwellites-crystal chemistry

In general *stillwellites* are rare-earth(s) borosilicates built up of $(BO_4)^{3-}$ and $(SiO_4)^{4-}$ tetrahedra described by a generic formula $CeBO(SiO_4)$ [9]. The main constituents of *stillwellite* are $(SiO_4)^{4-}$ tetrahedra set on edges in the form of vertical column(s) parallel to *c*-axis. Each $(BO_4)^{3-}$ tetrahedron is connected by its free vertices with two $(SiO_4)^{4-}$ tetrahedra and has two common edges with Ce^{3+} (or lanthanide) polyhedra of adjacent columns. The arrangement of borate tetrahedra is in a fashion similar to helical chains so that the anionic network surrounding the lanthanide polyhedra form tortuous vertical channels (Fig. 1a). The Ce^{3+}/lanthanide ion is in a large 9-coordinated site with oxygens (Fig. 1b) and the large Ce-oxygen distance points to an ionic bonding between the cation and oxygen in the system. $SrBPO_5$ or $SrBO(PO_4)$ [expressed as SBP for reasons of brevity] the material of the present investigation can be grouped under mineral *stillwellite* adopting trigonal system with hexagonal setting and with the space group symmetry corresponding to $P3_121$ [10]. Although in the $SrBO(PO_4)$ system adopting $CeBO(PO_4)$ *stillwellite* structure, the charge neutrality is conserved on valence considerations, there seems to be some incommensurability

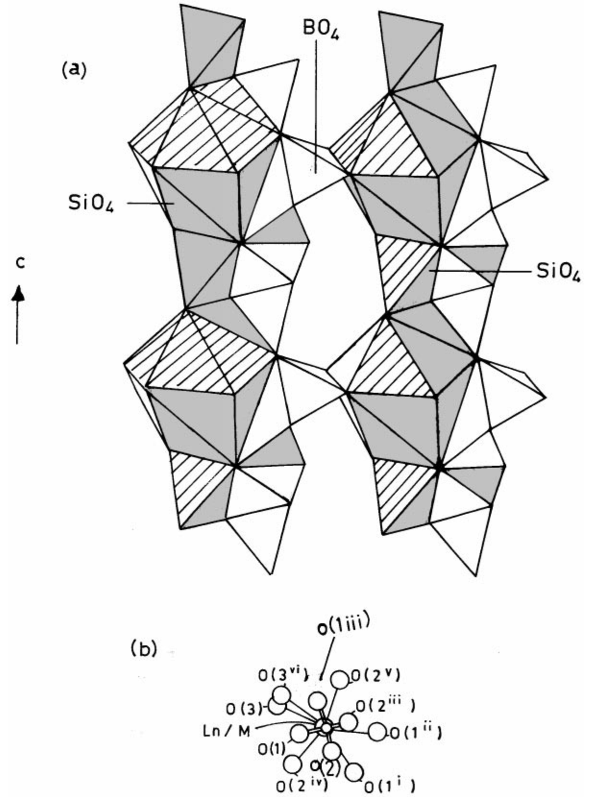

Fig. 1. (a) Crystal structure of *stillwellite* system. (b) Illustration of Sr^{2+}/Eu^{2+} site symmetry corresponding to Ln^{3+} site in the *stillwellite* structure.

in the arrangement of anionic network. This is because Sr^{2+} is too small in terms of charge-to-size ratio to fit into a nine-coordinated polyhedron of the Stillwellite structure. On the other hand an eight-coordinated Sr^{2+} site results in a more stable configuration [11]. Further the difference in the Madelung constants between Sr^{2+} (with $4p^6$ electron configuration) and Ce^{3+} (with $4f^1$ electron configuration) of the *stillwellite* structure will enforce some readjustment in the bond length of the anionic network as can be visualized through bond strength considerations [12]. This can lead to some kind of oxygen defects inline with similar reports in the other *stillwellite* structures [13]. In our opinion this may be the origin of defect centers that can be related to oxygen vacancies yielding intense photostimulated luminescence. It is important to note that the defect chemistry of the system can very much influence the PSL of the system. Hence in order to have some insight on the possible defect centers (having paramagnetic moment) we recorded the EPR spectra of $SrBPO_5$ samples having various levels of Eu^{2+} doping (including the undoped sample) as given in Fig. 2. From the figure it follows that in the case of the undoped sample there is no characteristic signal (dashed curve) while the Eu^{2+}-doped sample(s) yields two sets of signals. In the powder samples owing to the strong anisotropic nature of the fine structure (*fs*) transition(s) other than the central *fs* transition, it is possible to observe only the central fine-structure ($+1/2 \rightarrow -1/2$) transition. For this reason the information that can be deduced from a powder spectrum is considerably reduced. On inspection of Fig. 2 corresponding to the Eu^{2+}-doped sample(s), the first kind of signal with a characteristic $6 + 6 = 12$ fold

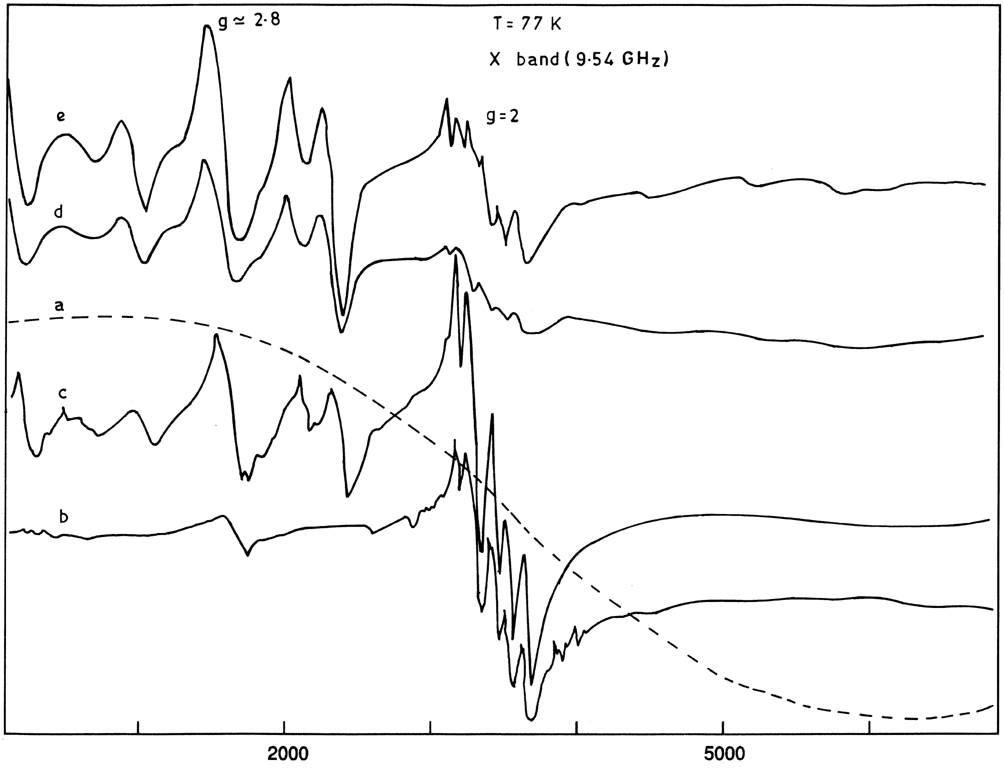

Fig. 2. X-band EPR spectra (at $T = 77$ K) of SBP : Eu^{2+} samples under various levels of Eu^{2+} doping; (a) UP0-no Eu^{2+}; (b) UP1-Eu^{2+} (0.01%); (c) UP2-Eu^{2+} (0.1%); (d) UP3-Eu^{2+} (1%) and (e) UP4-Eu^{2+} (5%).

structure having a g-value around 2 is observed. This is consistent with the hyperfine structure due to the two isotopes of europium viz., Eu^{151} and Eu^{153} (each with a nuclear spin $I = \frac{5}{2}$) in the central fine-structure ($+1/2 \rightarrow -1/2$) transition (as expected for an S impurity). This clearly fixes the origin of this signal to Eu^{2+} center(s). Further this signal goes down in intensity with Eu^{2+} concentration in favor of the second type of signals at higher g-values (with central component having maximum intensity at $g \sim 2.8$ and other components with decreasing intensity on either side). Hence it seems possible that this second kind of signal originates from altogether a different center. Further it is necessary to mention that the higher splitting values ($\sim$ 1000 G) observed confirms that this cannot be assigned to any *hfs* or *super hfs* signatures of a simple Eu^{2+} center. Also the higher g-values observed implies that this cannot be assigned to an electron center (hence a simple impurity center). Hence it is possible that this could be from a different kind of Eu^{2+}-defect center complex acquiring prominence at higher levels of Eu^{2+} doping. Furthermore this points to the possibility of multiple sites for Eu^{2+} having different configurations. More detailed studies are necessary to confirm this hypothesis which will be a part of out objectives in the future.

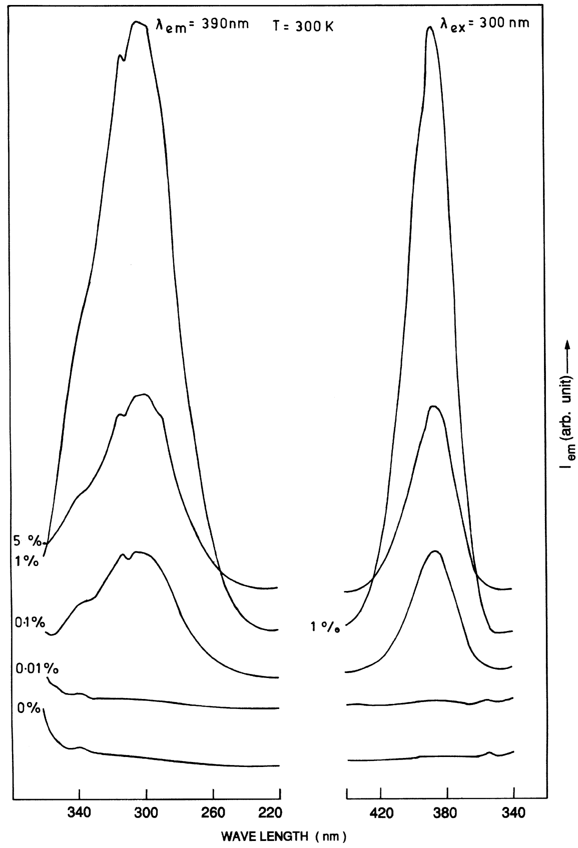

Fig. 3. Photoluminescence (emission and excitation) spectra of Eu^{2+} in SBP under various levels of Eu^{2+} doping at $T = 300$ K.

3.2. Photoluminescence of Eu^{2+} in $SrBPO_5$

Fig. 3 depicts the photoluminescence emission and excitation spectra of Eu^{2+} in $SrBPO_5$. From the figure it follows that under UV excitation ($\sim$ 310 nm excitation) sample containing no Eu^{2+}, does not show any characteristic signal while for samples with Eu^{2+} in $SrBPO_5$ yields intense photoluminescence (PL) in the violet region with maximum around 390 nm. This unambiguously fixes the origin of this emission to Eu^{2+}. The narrow band PL can be assigned to an allowed $4f^65d \rightarrow {}^8S_{7/2}$ electric dipole transition of Eu^{2+} experiencing high crystal field due to the phosphate network of the host matrix. The optimum Eu^{2+} concentration for both PL and PSL is found to be about 1 mol% and the critical distance of energy transfer between Eu^{2+} ions by spectral overlap method [14] is found to be 24 Å. The relative luminescence yield for Eu^{2+} emission with respect to strontium chloroapatite : Eu^{2+} (SCAP : Eu^{2+}), the well-known blue lamp phosphor is found to be about 55%. On lowering the temperature of the sample down to 12 K we observed a fine structure superimposed on the narrow band (Fig. 4). In the fine structure, the presence of a weak zero-phonon line (marked 0–0) can be observed. This points to a strong ion–lattice coupling strength prevailing for the Eu^{2+} center in this matrix which can be expressed as Huang–Rhys factor ($\boldsymbol{S}$). This value can be estimated with the knowledge of relative intensity of the zero-phonon line with respect to the total emission band given by $I_{0-0}/I\text{tot} = \exp(-\boldsymbol{S})$ [15,16].

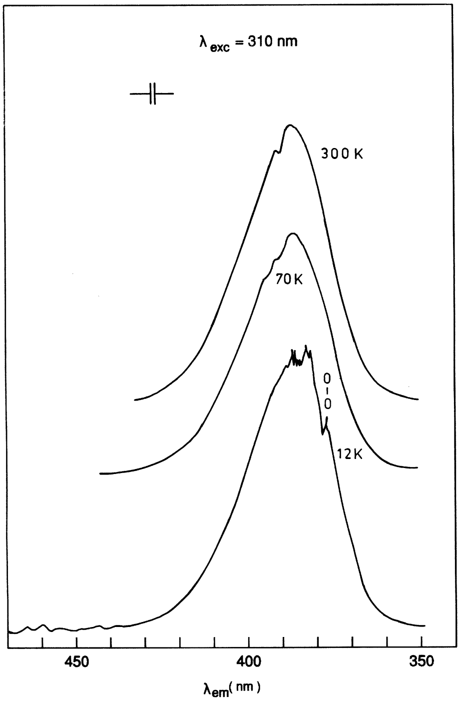

Fig. 4. Photoluminescence emission spectra of Eu^{2+} (1%) doped SBP at various temperatures. 0-0 denotes zero-phonon line.

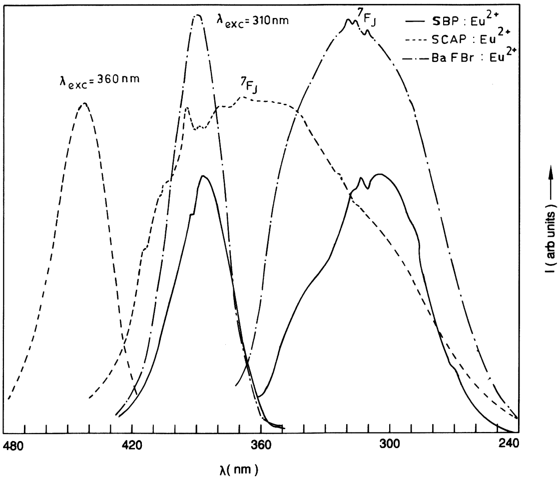

Fig. 5. Photoluminescence emission and excitation spectra of Eu^{2+} (1%) doped SBP (solid), SCAP (dashed) and BaFBr (dot–dashed) samples at $T = 300$ K.

The relative intensity of the zero-phonon line is found to be 0.01 which corresponds to an ***S*** value of 4.5. Further, from Fig. 5 it follows that the Stoke's shift for Eu^{2+} emission in this system is found to be $2900\,cm^{-1}$ as compared to $2700\,cm^{-1}$ in SCAP : Eu^{2+} while in BaFBr : Eu^{2+}, the Stoke's shift is considerably higher and is about $5400\,cm^{-1}$. From the crystallographic information documented in the literature, we have Eu^{2+} in SBP and SCAP under nearly similar conditions in that the crystal structure as known from the space group symmetries are akin viz., P_{31} and P_{63}, respectively [10,17] and hence the compatible lowest probable point group symmetry at the cationic site(s) is expected to be C_3. Further in both the cases of SCAP and SBP we have the phosphate network surrounding Eu^{2+} sites. So it is natural to expect a comparable splitting pattern in the excitation spectra (something like $A \rightarrow 3A + E$ for the lowest ^8H state of the $4f^65d$ level) in both the cases. Further to be more exact, in the SBP system we have the cationic site (Sr^{2+}/Eu^{2+}) in an irregular nine-coordinated polyhedron leaving no symmetry elements, i.e., C_1 symmetry which should only further split the degenerate Stark level *E* resulting in a more complicated spectrum in the latter. Surprisingly, we observe a more simple excitation spectrum for SBP : Eu^{2+} at relatively higher energy ($\sim 500\,cm^{-1}$ higher) than that for the case of SCAP : Eu^{2+}. Now the question pertains to the anomaly observed in the splitting pattern of the $4f^65d$ level of Eu^{2+} as reflected in the excitation spectra. To rationalize this, invoking the concept of preferred orientation of d-orbital(s) would be in order. We have from the recent work by Poort and Blasse [18] on several Eu^{2+}-doped compounds which suggests that a long wavelength emission with a large Stoke's shift can be observed for Eu^{2+} emission when present in host lattices having linear cationic chains formed by large cation(s). Divalent europium when occupying these chains will experience a positive charge in the chain direction thus enabling a preferred orientation of d-orbital of Eu^{2+} in the chain direction. The negative charges due to the anionic neighbors will further facilitate this resulting in the lowering of its energy. Hence this leads to a long wavelength emission. On the other hand we encounter the opposite situation for Eu^{2+} in the SBP matrix. Here Eu^{2+} occupies an irregular nine coordinated large polyhedron occurring in tortuous vertical columns formed by $(BO_4)^{3-}$ and $(PO_4)^{3-}$ tetrahedra with columns interconnected by a 3_1 screw axes. The irregular columnar arrangement of cationic polyhedra with a 3_1 screw inter-chain symmetry cannot effectively push the 5d level of Eu^{2+} to lower energy due to averaging effect. This we consider quite unfavorable for the preferred orientation of d-orbital of Eu^{2+} thereby explaining the occurrence of the Eu^{2+} emission in such a short wavelength as in the present investigation.

3.3. Photostimulated luminescence of Eu^{2+} in $SrBPO_5$

Storage phosphors working on the principle of photostimulated luminescence have become indispensible for application in radiography. Especially the digital radiography in medicine has become so popular that the photographic film-based conventional methods have become obsolete. $BaFBr:Eu^{2+}$ phosphor system is extensively used in digital X-ray radiography. Various spectral features of this system such as blue-violet emission (in the region where photo-multiplier having maximum sensitivity) and fast luminescence decay time (to facilitate fast read-out) etc are highly favorable for radiographic imaging application.

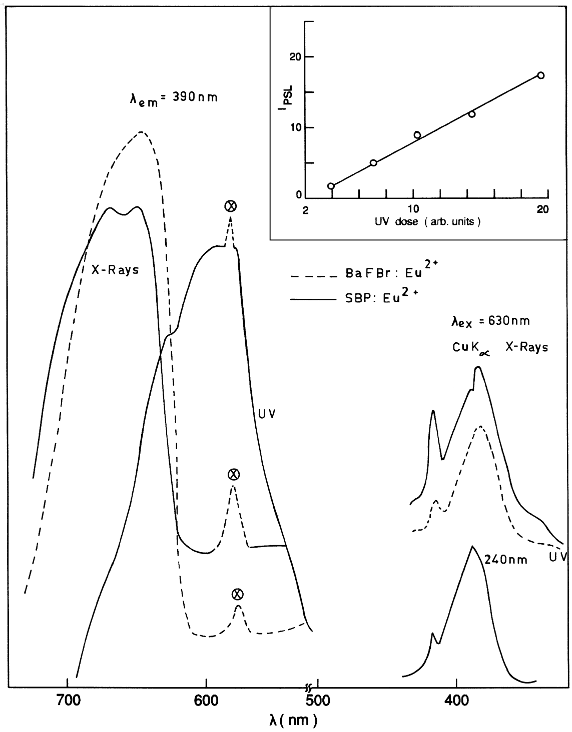

Fig. 6. Photostimulated luminescence emission and excitation spectra of Eu^{2+} (1%) doped SBP (solid line) compared with $BaFBr:Eu^{2+}$ (1%) (dashed line) for UV (240 nm, 10 mins) and X-ray (Cu K_α, 40 kV, 25 mA, 10 mins). Inset: dose versus response (PSL intensity) of $SBP:Eu^{2+}$ sample for different UV doses. X denotes instrumental artifact.

In the present investigation we have found that $SrBPO_5:Eu^{2+}$, a new luminescent system showing intense PSL with the other properties comparable with $BaFBr:Eu^{2+}$ (Fig. 6). In order to evaluate the suitability of this new system we compare various features concerning its prospects for radiography application (Table 1). In all fairness it appears to us

Table 1
Comparison of $SrBPO_5:Eu^{2+}$ with $BaFBr:Eu^{2+}$ systems

Property	$BaFBr:Eu^{2+}$	$SrBPO_5:Eu^{2+}$	Comments
Crystal structure	Tetragonal	Hexagonal	
Crystal-morphology	Plate like (conventional synthesis) Spherical (spray dried)	Polyhedral	Favorable
Stability	Hygroscopic	Non-hygroscopic	Ideal
X-ray absorption	Ba-K_α	Sr-K_α	Favorable
Density (g/cm^3)	5.18	3.19	Lower
Emission max (nm)	390	390	Ideal
PSL excitation max (nm)	640	640	Ideal

that this material has all the features favorable for X-ray storage phosphor application. Further we note that in the BaFBr : Eu^{2+} system, electrons are stored in F-centers due to the halogen vacancies and the holes are trapped in the vicinity of the impurity center. The same analogy can be extended for the SBP : Eu^{2+} system too except that instead of halogen vacancies, oxygen vacancies are the precursors for F center formation as dictated by the crystal chemistry of the system. Also it should be noted that there is considerable difference in the stimulated excitation spectra between UV- and X-ray exposed samples (Fig. 6). This points to the complexity of the multiple photo-stimulable centers involved. Since this is a preliminary report more detailed studies are necessary to assess the exact potential of this new luminescent system.

4. Conclusions

The unusually low wavelength emission of Eu^{2+} in $SrBPO_5$, observed can be attributed to the absence of preferred orientation of d-orbital of Eu^{2+} as determined by the crystal chemistry effects. The most important aspect of this investigation is the nearly identical photostimulated luminescence properties with that of BaFBr : Eu^{2+}, the currently used system in the industry.

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