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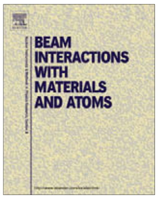

Radiation induced defects in $BaBPO_5$:Ce and their role in thermally stimulated luminescence reactions: EPR and TSL investigations

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ABSTRACT

Defect centers induced by gamma irradiation in Ce doped $BaBPO_5$ were investigated using EPR spectroscopy. From EPR studies, three phosphorous centered radicals were characterized on the basis of observed ^{31}P hyperfine splitting and g values as PO_4^{2-}, PO_2^{2-} and PO_4^{4-} radicals. In addition to this, two types of boron oxygen hole centers (BOHC) and O^- were also formed at room temperature. An intense broad signal in sample annealed in argon ($g_\perp = 1.9258$ and $g_\parallel = 1.8839$) was assigned to Ce^{3+} ions associated with the electron trapped at anion vacancy or nearby lattice defect. TSL studies showed two glow peaks, a relatively weaker one at 425 K and an intense one at 575 K. Spectral studies of the TSL glow peaks have shown that Ce^{3+} ion acts as emission center. From the temperature dependence of the EPR spectra of gamma irradiated samples, the glow peaks at 425 K and 575 K were attributed to thermal destruction of PO_4^{2-}/O^- and BOHC, respectively, by trapping of electrons from elsewhere. The energy released in electron hole recombination process is used for the excitation of Ce^{3+} ions resulting in these glow peaks at 425 K and 575 K. The spectral studies of the TSL glow peaks have shown emission at 330 nm indicating Ce^{3+} acts as the luminescent centre. The trap depth and the frequency factor for the 425 K and 575 K peaks were determined using different heating rates method.

1. Introduction

X-ray storage phosphors are materials capable of storing images produced by the absorption of X-ray radiation. Upon X-ray irradiation of the phosphor, radiation induced defects are generated, which must be stable at room temperature (at least for few minutes) for practical use. It is generally believed that electron and hole trap centers are involved in the image formation. For read out process, usually the electron centers such as F centers (electron trapped at anion vacancies) are photo excited. The excitation induces a recombination with the hole trap centers and the energy freed in the recombination process is transferred to an activator (in many cases rare earth ions). This process is called photo stimulated luminescence (PSL). Advantage of X-ray storage phosphors over conventional X-ray films are their high sensitivity, the large dynamic range and the fact that the X-ray image is in the digital form. The main disadvantage, however, is the lower spatial resolution (~5 line pairs/mm) compared to best X-ray film. The low resolution power is to a large extent, the result of light scattering during the readout system.

The best known X-ray storage phosphor and only one, which is used commercially is BaFBr:Eu. Alkaline earth borophosphates $SrBPO_5$ doped with Eu^{2+} have been identified as new luminescent materials, which show intense photo stimulated luminescence upon UV and X-ray irradiations with potential applications in medical diagnosis and digital radiography [1,2]. $MBPO_5$ is suggested to be a excellent host for accommodating luminescent ions viz rare-earth ions and extensive studies have been carried out on the luminescence properties of rare earth ions doped in this matrix. In this host lattice most of the trivalent lanthanide ions RE^{3+} (RE = Ce, Tb, Sm) are stabilized at M^{2+} site in $MBPO_5$ (M = Ba, Sr and Ca), while Eu stabilized as Eu^{2+}. The UV-excited blue emission of $MBPO_5$:Eu^{2+} (M = Ca, Sr, Ba) phosphors prepared in H_2/N_2 reducing atmosphere have been reported by Blasse et al. [3]. The luminescence processes of europium in crystalline and glass modifications of $CaBPO_5$ were investigated [4–6] and reports also exist on preparation of $SrBPO_5$:Eu^{2+}, an X-ray storage and neutron imaging phosphor. Karthikeyani and Jagannathan [1] depicted X-ray storage property of $SrBPO_5$:Eu^{2+}, which showed similar spectral features to the commonly used BaFBr:Eu^{2+}. Moreover, the phosphor $SrBPO_5$:Eu^{2+} showed efficient photo-stimulated luminescence at 390 nm by illuminating with laser light, after neutron irradiation, revealing its utility as neutron imaging material. BaFBr:Eu^{2+} phosphor system is extensively used in digital X-ray radiography. However,

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barium fluoro-halide:Eu^{2+} phosphor has some limitations like its plate like morphological features resulting in light piping and hygroscopic nature limiting its stability [7,8]. Therefore, $SrBPO_5$:Eu^{2+} and $BaBPO_5$:Eu^{2+} can be considered as suitable alternatives for Eu^{2+} doped barium fluoro-halides. The luminescence properties of Ce^{3+} ions doped in the alkaline earth (Sr, Ba) borophosphates have also been reported [9–12]. Ce^{3+} ions show allowed optical transitions, in absorption and emission, which are of the 4f–5d type. It was seen that the Ce^{3+} ion in $CaBPO_5$ shows an efficient 5d–4f luminescence with maximum at 320 and 340 nm. The decay time of the emission was very short (19.5 ns). Since the decay time of Ce^{3+} emission in a crystal is shorter than that of Eu^{2+} emission (typically 20 ns versus ~0.8 μs), a screen containing Ce^{3+}-doped phosphor can read faster, enabling high speed imaging. Lu et al. investigated the effect of co-doping of Tb^{3+} and Ce^{3+} on the photoluminescence properties of $BaBPO_5$, wherein the energy transfer from Ce^{3+} ions to Tb^{3+} ions was found to increase with an increase in Ce^{3+} content [13]. X-ray excited luminescence, optical transmission and TSL were conducted recently by Weifeng et al. [14]. They suggested that the thermal bleaching of colour centers in undoped samples are mainly responsible for the observed TSL peak at 403 K. However, detailed mechanism about the TSL is not fully understood.

Though, extensive work on luminescence properties of the borophosphates have been reported in literature, practically little literature data exists on the TSL studies in these phosphors. To augment the process taking place in thermally stimulated luminescence (TSL), extensive work has been reported from our laboratory on several inorganic phosphors doped with lanthanide/actinide ion, by carrying out electron paramagnetic resonance (EPR) and/or and photo acoustic spectroscopy (PAS), wherever feasible [15–18]. In case of $SrBPO_5$:Eu^{2+}, it was suggested [1] that the recombination between the trapped electrons at anion vacancies (F centers) and the hole trapped centers in the vicinity of the impurity center (Eu^{2+}) are mainly responsible for the photo stimulated luminescence emission at 390 nm;, however, the electrons and hole trapped were not identified in these studies. In the present work, we have identified the defects/radical ions formed on gamma irradiation in $BaBPO_5$:Ce as well as the role of electron hole recombination reactions on TSL process, using EPR. Finally based on EPR results we have suggested most probable mechanism for the observed TSL peaks.

2. Experimental

Polycrystalline samples of $BaBPO_5$ doped with 0.5% of Ce^{3+} were prepared using solid state reaction technique. Stoichiometric mixtures of analytical grade purity $BaCO_3$ (Analytical Reagent, BDH, England), H_3BO_3 (excess of 3 mol% to compensate the losses occurred during heating process, A.R. Grade, Fluka, Germany), $NH_4H_2PO_4$ (Analytical Reagent, BDH, England) and 99.9% purity CeO_2 (Johnson Matthey, England) were calcined at 1275 K for 4–8 h (before calcinations, the mixtures were preheated at 675 K for 4 h). The samples thus prepared were annealed in argon atmosphere (**S_1**) and air atmosphere (**S_2**). The X-ray diffraction patterns of the samples were recorded using Cu Kα radiation ($\lambda = 1.5418$ Å) employing a Philips X-ray diffractometer (model PW 1710, Netherlands) fitted with graphite crystal monochromator. The X-ray diffraction patterns at room temperature were collected in the range 10–90° with a 2θ steps of 0.05°. The samples **S_1** and **S_2** were analyzed for trace metal impurities by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) using 46P Panorama, polyscan atomic emission spectrometer operated at 40.68 MHz; Jobin Yvon, France. TSL glow curve were recorded using home made PC adapted TSL unit in the range of 300–700 K. EPR studies were carried out using a Bruker ESP-300 spectrometer (Germany) operated at X-band frequency (9.5 GHz) with 100 kHz modulation frequency. Di phenyl picryl hydrazyl (DPPH) was used for calibration of g-values of free radicals. The temperature dependence of the EPR spectra were studied in the range 300–600 K using Eurotherm B VT 2000 accessory. $BaBPO_5$:Ce^{3+} samples were irradiated in a ^{60}Co gamma source (dose rate 3.0 kGy/h) prior to TSL and EPR experiments. Photoluminescence measurements were carried out on PL- Hitachi F-2000, Fluorescence Spectrometer).

3. Results and discussion

3.1. Chemical and physical characterization of synthesized $BaBPO_5$:Ce^{3+} polycrystalline samples

The observed X-ray data of $BaBPO_5$:Ce^{3+} was found to be in agreement with those given in JCPDS 19-0096. The crystal structure of $BaBPO_5$ has been investigated in detail [19–21]. The diffraction pattern of the product obtained by solid state reaction indicated that $BaBPO_5$:Ce^{3+} crystallizes in the hexagonal structure, space group $P3_121$, with three formula units per unit cell, M^{2+} ions are 10-fold coordinated by O^{2-} ions in the form of C_2 symmetry. The anionic units of BO_4^{5-} (BO bond distances, 1.0439–1.523 Å) and PO_4^{3-} (PO bond distances, 1.578–1.497 Å) tetrahedral are connected by common corners. The arrangements of BO_4^{5-} and PO_4^{3-} are loop–branched chains. The central three signal chains of BO_4 tetrahedra run parallel to [0 0 1] and the BO_4 units are linked to terminal PO_4 tetrahedra. The observed lattice parameters were found to be in good agreement with those reported in the literature ($a = 6.85$ Å, $c = 6.70$ Å). This structure is suggested to be a excellent host for accommodating luminescent ions viz. rare-earth ions. Absence of metallic impurities in samples at ultra-trace level (μg/g) was confirmed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

3.2. TSL studies

Prior to gamma irradiation no glow peaks were observed in undoped $BaBPO_5$ and $BaBPO_5$ doped with Ce^{3+} samples. Upon gamma irradiation to a dose of 1 kGy, two glow peaks were observed in $BaPO_5$:Ce at 425 K and 575 K (heating rate = 2.5 K/s), of which the peak at 575 K was found to be more intense (Fig. 1). It may be noted that the TSL yield in samples prepared in argon atmosphere (**S_1**) is five times more as compared to samples prepared in air atmosphere (**S_2**). The ratio of the relative intensities of the high temperature peak (575 K) to the low temperature peak (425 K) are 3.5 and 1.3, respectively, for the sample **S_1** and **S_2**. Systematic gamma dose dependence studies of the glow peaks showed the TSL yield to be maximum at a gamma dose of 1 kGy. To determine the trap parameters, viz, trap depth (E) and frequency factor (s), the glow curves were recorded at different heating rates (0.5, 1, 1.5, 2.5 and 3 K/s). A plot of $\ln(T_m^2/\beta)$ versus $1/T_m$ (where β represents heating rate and T_m represents glow peak temperature) was obtained and a least square fit programme was employed to get the best fit for E and s factors. The trap depth and the frequency factor for the 425 K and 575 K peaks were determined (for 425 K, $E = 0.98 \pm 0.03$ eV, $s = 1.42 \times 10^9$/s and for 575 K, $E = 1.6 \pm 0.03$ eV $s = 1.86 \times 10^8$/s). Isothermal decay experiments carried out with TSL have revealed the high temperature peak at 575 K to obey second order kinetics. Spectral studies of TSL glows, obtained using narrow band interference and transmittance filters, showed an intense emission around 330 nm, which is typical of emission of Ce^{3+} ion. This is further confirmed by photoluminescence studies wherein an emission around 340–345 nm characteristic of Ce^{3+} was observed for excitation with 270 nm wavelength. This is shown in Fig. 2. The luminescence properties of $MBPO_5$:Ce^{3+} (M = Sr, Ba) solid solutions has been reported previously. The most