High-frequency EPR investigation of X-ray storage SrBPO$_5$:Eu phosphor

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Abstract

High-frequency EPR (HFEPR) spectra of the SrBPO$_5$:Eu with stillwellite structure, which was prepared using EuCl$_3$.6H$_2$O as a dopant, have been examined in order to clarify the Eu sites in it. They showed an intense doublet at 3.3 T corresponding to $g = 2.0$ as is expected for the ^{8}S state ions. Also, weak satellites were observed on both sides of the central doublet signal symmetrically. This means that microwave energy at 90 GHz is sufficiently larger than the zero-field splitting. Taking into account the crystal structure of stillwellite and the earlier PL investigation, a single Eu^{2+} site was assumed for the HFEPR simulation. As a result, it was found that HFEPR spectrum simulated using $g = 1.98161$, $|D| = 0.130$ T and $\lambda = |E/D| = 0.06$ reasonably agrees well with the experimental one, supporting that the Eu^{2+} occupies the Sr site. The large $|D|$ value small λ value obtained implies that the crystal field surrounding Eu^{2+} has a strong axial field with weak rhombic distortion.
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1. Introduction

X-ray storage phosphors are practically useful for digital radiography in the medical diagnosis field. Recently, two of the authors have examined Eu^{2+}-doped phosphor SrBPO$_5$:Eu with an emission at 390 nm by means of X-ray crystallography, X-band EPR spectroscopy and photoluminescence spectroscopy [1]. According to them, at low

loadings of Eu^{2+} the X-band EPR spectra showed 12 lines centred around $g = 2.0$, which suggests that Eu^{2+} occupies a high-symmetry site. At higher loadings, however, very complicated EPR resonance, which is not simply assigned to Eu^{2+} in a single site, was observed, implying that some Eu^{2+} occupy low-symmetry site(s).

Previously we have succeeded in identifying low-symmetry Eu^{2+} which is doped in alkaline earth aluminate phosphors by means of high-frequency EPR (HFEPR) spectroscopy [2–5], and confirmed that the HFEPR has advantage over X-band EPR

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for the investigation of metal ions with a large zero-field splitting. In this paper, therefore, we report the results of the HFEPR investigation of the $SrBPO_5$:Eu phosphor.

2. Experimental

Eu^{2+}-doped samples were prepared by conventional solid-state reaction with $SrCO_3$, H_3BO_3, $(NH_4)HPO_4$ and $EuCl_3.6H_2O$ (or Eu_2O_3) under mild reducing atmosphere. Eu^{2+} concentration was adjusted to 1 mol%, because in the previous study the optimum europium(II) concentration for photoluminescence and photo-stimulated luminescence is 1 mol% [1]. The preparation procedure was described elsewhere [1]. HFEPR measurements at 90 GHz were carried out at room temperature using a novel quasi-optical induction mode spectrometer that was designed and built at the University of St. Andrews, UK.

3. Results and discussion

Fig. 1 shows the X-band EPR spectrum of the $SrBPO_5$:Eu prepared with a $EuCl_3$ of 1.0 mol%. The same spectral pattern was obtained when
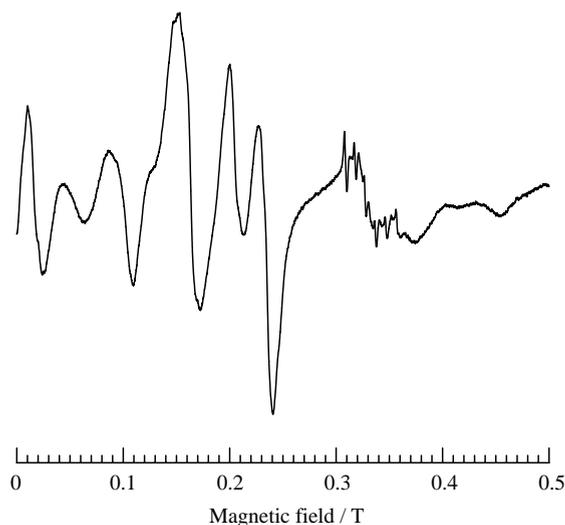
Eu_2O_3 was used as a dopant, implying that the chloride ion rarely affects the environment surrounding Eu^{2+}. Also, it was confirmed that the EPR spectrum obtained in this study is fundamentally the same as those reported by one of the authors earlier, although the resonance attributed to Eu^{2+} in a high-symmetry site is not obvious because of the intense hyperfine lines due to Mn^{2+} impurity.

It is seen that several broad signals appear over the wide range of magnetic field. Amongst them the signals appearing in the magnetic field in the range of 0–0.25 T are stronger than those observed at about 0.33 T although the g-value of ^8S state ions without orbital angular momentum should be close to 2.0. Such X-band EPR spectrum is a typical pattern for the Eu^{2+} with a large zero-field splitting, which results in the mixing of the wave functions. In other words, Eu^{2+} occupies low-symmetry site(s) [2–5].

Fig. 2(a) shows the 90 GHz HFEPR spectrum of the $SrBPO_5$:Eu prepared using $EuCl_3 \cdot 6H_2O$ as a

Fig. 1. X-band EPR spectrum of the $SrBPO_5$:Eu with stillwellite structure recorded at room temperature.
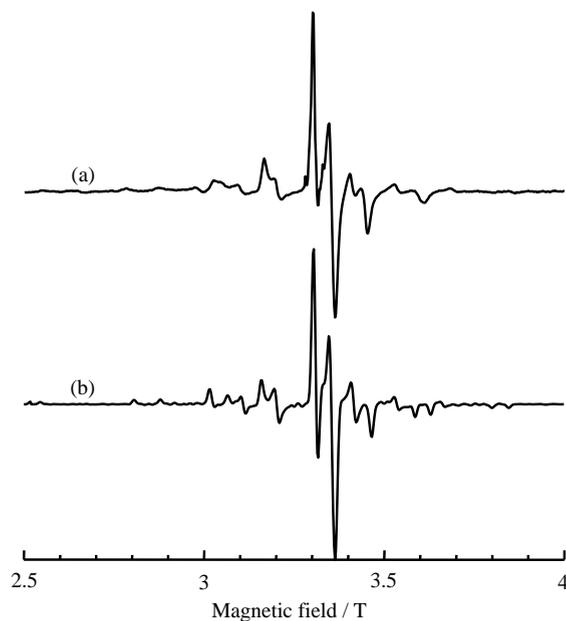

Fig. 2. Room-temperature 90 GHz EPR spectra of the $SrBPO_5$:Eu with stillwellite structure: (a) experimental spectrum and (b) simulated spectrum with $g = 1.9816$, $|D| = 0.130$ T and $\lambda = |E/D| = 0.06$. Lorentzian line shape with a peak-to-peak width of $\Delta H = 0.0075$ T was assumed.

dopant. It is immediately noticed that the obtained HFEPR spectral pattern is different from that measured at X-band. An intense doublet signal appears at 3.3 T corresponding to $g = 2$ as is expected for the ^{8}S state ions. Also, weak satellites are observed on both sides of the doublet signal symmetrically. When the HFEPR spectrum is measured under the condition satisfying Zeeman energy $\gg$ zero-field splitting energy, it consists of seven fine structure lines for $\Delta M_S = \pm 1$. This means that microwave energy at 90 GHz is large enough compared with the zero-field splitting.

Based on the crystal structure of stillwellite [6] and the results of the photoluminescence investigation reported earlier [1] a single Eu^{2+} site is assumed for the HFEPR simulation. EPR parameters were roughly estimated as follows: g-value was calculated using $g = h\nu/\beta H$ with the magnetic field where the central intense signal crossovers zero in intensity. From the satellites appearing at 3.19 and 3.45 T next to the intense doublet the $|D|$ value is 0.15 T. For the $|E/D|$ $(= \lambda)$ an initial value of 0.1 was used. This is because three absorption-like satellites at $\lambda = \frac{1}{3}$ should be expected on both sides of the central signal, while three absorption-like and three derivative-like satellites at $\lambda = 0$. Observed HFEPR spectrum implies that the λ value is in between.

Simulated HFEPR spectrum, which was carried out using the equation derived using the second perturbation theory [7,8], is shown in Fig. 2(b). The parameters used were $g = 1.9816$, $|D| = 0.130$ T and $\lambda = |E/D| = 0.06$. It is obvious that the simulated HFEPR spectrum reasonably agrees well with the experimental one, supporting that the Eu^{2+} occupies the strontium site since there is only a single site in the unit cell of stillwellite. The obtained $|D|$ value is very large, while the λ value is small, implying that the crystal field surrounding Eu^{2+} has a strong axial field with weak rhombic distortion.

From the photoluminescence studies [1], we observe that the stillwellite-type $SrBPO_5$ system, for low levels of Eu^{2+} doping ($\sim 0.01\%$) shows a weak emission band around 350 nm while for moderate level of Eu^{2+} doping (1–5%) an intense narrow band around 390 nm is observed. These two emission bands might suggest two kinds of

cationic site(s) occupied by Eu^{2+} in this system. The absence of 350 nm emission band for higher levels of Eu^{2+} doping may be explained in terms of intersite energy transfer in favour of 390 nm emission band having profound dependence on Eu^{2+} concentration. For all practical purposes, the intense 390 nm emission band due to Eu^{2+} centre in $SrBPO_5$ can be considered to represent Eu^{2+} emission in $SrBPO_5$. The band emission from Eu^{2+} centre(s) can be assigned to $4f^65d \rightarrow {}^8S_{7/2}$ (an allowed f–d type) transition. The occurrence of band emission due to parity allowed 'f–d' transition that is possible irrespective of whether the cationic site(s) occupied by Eu^{2+} has an inversion centre or not and hence symmetry independent.

The narrow band emission observed from Eu^{2+} centre(s) clearly point out that the lowest excited state is $4f^65d$ state. The 5d orbital of Eu^{2+} can undergo considerable crystal filed splitting determined by the symmetry and the chemical coordination of the cationic site(s) it occupies.

In conclusion, it is found that for the $SrBPO_5$:Eu the Eu^{2+} occupies the strontium site which has strong axial crystal field with weak rhombic distortion. This explains the PL behaviour as follows: A simple comparison of the excitation spectrum of $SrBPO_5$:Eu^{2+} in relation to cubic KCl:Eu^{2+} readily reveals that the excitation spectrum due to the splitting of the 5d orbital in $SrBPO_5$ is more complex and broader by approximately 20%. This suggests that the axial field parameter $|D| = B_2^0$ is much larger in $SrBPO_5$. Further, the complex excitation spectrum of $SrBPO_5$:Eu^{2+} implies that this cationic site can have weak rhombic field too (low value for E). These results are possible for Eu^{2+} occupying a 9 or 10 coordinated sites due to the fact that Sr^{2+} has no symmetry elements [9,10]. These results are in good agreement with the conclusions deduced from the HFEPR studies on $SrBPO_5$:Eu^{2+}.

References

[1] A. Karthikeyani, R. Jagannathan, J. Lumin. 86 (2000) 79.

[2] T. Nakamura, K. Kaiya, N. Takahashi, T. Matsuzawa, C.C. Rowlands, V. Beltran-Lopez, G.M. Smith, P.C. Riedi, J. Chem. Soc. Faraday Trans. 94 (1998) 3009.

[3] T. Nakamura, K. Kaiya, N. Takahashi, T. Matsuzawa, C.C. Rowlands, V. Beltran-Lopez, G.M. Smith, P.C. Riedi, Phys. Chem. Chem. Phys. 1 (1999) 4011.

[4] T. Nakamura, K. Kaiya, N. Takahashi, T. Matsuzawa, C.C. Rowlands, V. Beltran-Lopez, G.M. Smith, P.C. Riedi, J. Mater. Chem. 10 (2000) 2566.

[5] T. Nakamura, K. Kaiya, N. Takahashi, T. Matsuzawa, M. Ohta, C.C. Rowlands, G.M. Smith, P.C. Riedi, Phys. Chem. Chem. Phys. 3 (2001) 1721.

[6] A.A. Voronkov, Yu.A. Pyatenko, Sov. Phys. Cryst. 12 (1967) 214.

[7] J.R. Pilbrow, Transition Ion Electron Paramangetic Resonance, Clarendon Press, Oxford, 1990, p. 614.

[8] T. Takeyama, T. Nakamura, T. Takahashi, V. Beltran-Lopez, C.C. Rowlands, in: A. Kawamori, J. Yamauchi, H. Ohta (Eds.), EPR in the 21st Century, Elsevier Science B.V., Netherlands, 2001, 63pp.

[9] Y. Ono, K. Takayanama, T. Kajitani, J. Phys. Soc. Jpn. 65 (1996) 3224.

[10] A.A. Voronkov, Yu.A. Pyatenko, Kristallografiya 12 (1967) 135.