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Luminescence of alkaline-earth borate-phosphates activated with divalent europium

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BAUER[1] has reported the existence of two alkaline-earth borate-phosphates, viz. CaBPO₅ and SrBPO₅. Their X-ray diagrams can be indexed on the basis of a hexagonal unit cell; their crystal structure is not known at the moment. In the course of our investigations on the luminescence of the Eu^{2+} ion in mixed metal oxides [2-5] Eu^{2+} -activation of these borate-phosphates has been studied.

EXPERIMENTAL

Samples were prepared by firing intimate mixtures of $CaCO_3$, $SrCO_3$, $BaCO_3$, Eu_2O_3 , H_3BO_3 and $(NH_4)_2HPO_4$ in the required proportions for 4 hr at temperatures between 400 and 600°C and after a milling procedure for another 4 hr between 800 and 900°C. The firing atmosphere consisted of nitrogen containing a few per cent of hydrogen. Samples were checked by X-ray analysis. The performance of the optical measurements has been described previously [6, 7].

RESULTS AND DISCUSSION

The X-ray diagrams of the Eu^{2+} -activated alkaline-earth borate-phosphates are similar to those reported by Bauer[1]. BaBPO₅ is isomorphous with CaBPO₅ and SrBPO₅. Lattice parameters are given in Table 1.

| Composition | Hexagonal lattice parameters (Å)* | | Reflection (%, 254 nm) | Quantum efficiency (%) 254 nm maximum value | | Energy conversion factor for cathode-ray excitation (% 20 kV) |
|--------------------------------------|--------------------------------------|-------|---------------------------|--|----|---|
| | а | с | | | | |
| CaPBO ₅ -Eu ²⁺ | 6.69 | 13.33 | 13 | 12 | 15 | 0.5 |
| SrPBO ₅ -Eu ²⁺ | 6.86 | 13.66 | 20 | 55 | 60 | 4.0 |
| BaPBO ₅ -Eu ²⁺ | 7.06 | 13.93 | 20 | 65 | 70 | 3.5 |

Table 1. Lattice parameters and efficiencies of Eu^{2+} -activated alkaline-earth borate phosphates (Eu^{2+} concentration 1 at. per cent)

*Values for the unactivated host lattices.

The Eu²⁺-activated alkaline-earth borate-phosphates show a deep-blue luminescence under excitation with long- and short-wave u.v. radiation and cathode-rays. The spectral energy distribution of the emissions is given in Fig. 1. With increasing ionic radius of the alkaline-earth ion of the host lattice the emission shifts to shorter wavelengths. The excitation spectrum of the emission and the diffuse reflection spectrum of BaBPO₅-Eu²⁺ is presented in Fig. 2. For CaBPO₅-Eu²⁺ and SrBPO₅-Eu²⁺ these spectra are nearly identical. Because the unactivated borate-phosphates do not absorb in the u.v. region, the strong and broad absorption band in the short-wavelength u.v. region must be due to the

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Notes



Fig. 1. Spectral energy distribution of the emission of $Me_{0.99}Eu_{0.01}BPO_5$ (Me = Ca, Sr, Ba). 254 nm excitation. Along the ordinate the radiant power per constant wavelength interval (I) has been plotted in arbitrary units.



Fig. 2. Relative excitation spectrum of the emission (drawn line) and diffuse reflection spectrum (broken line) of Ba_{0.99}Eu_{0.01}BPO₅.

 Eu^{2+} ion (4*f*-5*d* transition, see [3]). With this absorption band corresponds a strong excitation band. In view of the position of this band the phosphor BaBPO₅-Eu²⁺ is excited efficiently with 254 nm radiation.

Table 1 shows some data on the efficiency of the luminescence of the phosphors. For the Sr- and Ba-phosphor the efficiencies are high, for the Ca-phosphor they are considerably lower. The reason for this follows from Fig. 3, where the temperature dependence of the intensity of the luminescence under 254 nm excitation is given. The luminescence of the Ca-phosphor is for the greater part thermally quenched at room temperature. The low-temperature efficiency of this phosphor is high. Figure 3 illustrates a rule mentioned previously by us [3]: in a series of isomorphous alkaline-earth compounds activated with Eu²⁺ the quenching temperature of the luminescence of BaBPO₅-Eu²⁺ is even extremely high: the intensity of the emission has decreased to 50 per cent of the low-temperature value at 570°K. For other efficient and temperature-persistent Eu²⁺ phosphors this temperature is lower: 475° K for Sr_{0.8}Mg_{1.2}P₂O₇-Eu[8], 520°K for BaAl₁₂O₁₉-Eu[4] and 500°K for BaB₈O₁₃-Eu[5].

Concentration quenching of the Eu^{2+} luminescence was studied for the barium host lattice. From Table 2 it follows that the critical concentration for concentration quenching is about 2 to 3 at. per cent

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Fig. 3. Temperature dependence of the intensity of the emission of $Me_{0.99}Eu_{0.01}BPO_5$ (Me = Ca, Sr, Ba) under 254 nm excitation.

Table 2. Concentration dependence of the efficiency of the luminescence of BaBPO₅-Eu²⁺

| <i>x</i> in Ba _{1-x} Eu _x BPO ₅ | Reflection (%, 254 nm) | Quantum efficiency (%, 254 nm excitation) | Energy conversion factor for cathode-ray excitation (%, 20 kV) |
|---|---------------------------|--|---|
| 0.005 | 30 | 60 | 2.5 |
| 0.01 | 20 | 65 | 3.5 |
| 0.02 | 13 | 70 | 3.5 |
| 0.03 | 10 | 65 | 2.5 |
| 0.05 | 8 | 60 | 2.0 |
| 0.07 | 5 | 50 | 1.5 |
| 0.10 | 4 | 45 | 1.0 |

of europium. For this concentration the average distance between neighbouring europium centres is about equal to the critical distance for energy transfer between these centres [9–11]. Using the fact that the unit cell contains three formula units[1], the average Eu-Eu distance can be found from the value of the critical concentration for concentration quenching. This distance is about 20 Å. This value agrees satisfactorily with the value estimated theoretically by Dexter for transfer between centres with overlapping, allowed electric-dipole transitions, viz. 25 Å[12]. In the case of Eu²⁺ we are also dealing with transitions of this type.

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