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BRIEF COMMUNICATIONS

Luminescence in the Pentaborate $LiBa_2B_5O_{10}$

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The luminescence of Eu^{2+} and Pb^{2+} in the pentaborate $LiBa_2B_5O_{10}$ is reported. Both ions show efficient emission with large Stokes shift. The emission maximum of the Eu^{2+} ion is at unusually long wavelength, viz., 620 mm.

Introduction

Recently Smith and Keszler (*1*) reported the crystal structure of $LiBa_2B_5O_{10}$ (*1*). This is a unique structure; the strontium analog does not exist. The structure contains a one-dimensional polyborate anion built from BO_3 and BO_4 groups. The Li^+ ions are in tetrahedral coordination, the Ba^{2+} ions in an irregular eight coordination. The average Ba^{2+}–O^{2-} distance is relatively long, 2.84 Å vs the expected 2.80 Å. The individual distances range from 2.64 to 3.02 Å, the shorter distances being on one side of the Ba^{2+} ion.

Since borates are suitable host lattices for luminescent materials (for example, the pentaborate $MgGdB_5O_{10}$ (*2, 3*)), and in view of the peculiar Ba^{2+} coordination, we were tempted to investigate the luminescence of divalent ions on barium sites. For this purpose we selected Eu^{2+} and Pb^{2+}. Indeed the luminescence obtained shows some peculiar characteristics.

Experimental

The preparation procedure is the same as described in Ref. (*1*). Activator concentrations vary from 0.5 to 1.0 mole%. The firing atmosphere was N_2/H_2 (20/1) in the case of Eu^{2+} activation, and air in the case of Pb^{2+} activation. The resulting products were checked by X-ray powder diffraction. The diffractograms could be indexed as indicated in Ref. (*1*).

Optical measurements were performed down to 4.2 K using a Perkin–Elmer MPF 3 spectrofluorometer equipped with a helium cryostat as described in Ref. (*3*). Diffuse reflection spectra were measured at room temperature using a Perkin–Elmer Lambda 7 spectrometer.

Results

A. $LiBa_2B_5O_{10}$:Eu^{2+}

This composition shows an intense orange emission under ultraviolet excitation. Upon cooling to 4.2 K the intensity does not increase markedly, indicating that thermal quenching occurs only above room temperature. Figure 1 shows emission and excitation spectra at 4.2 K. At room temperature the structure in the excitation band has disappeared and the bands have broadened.

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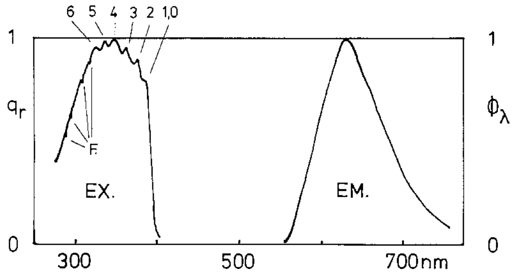

FIG. 1. Emission and excitation spectra of the luminescence of $LiBa_{1.98}Eu_{0.02}B_5O_{10}$ at 4.2 K. The relative quantum output (q_r) and the spectral radiant power per constant wavelength interval (Φ_λ) are given in arbitrary units. Fano antiresonances are indicated by F. The figures on top indicate the J values of the ^7F_J components of the lowest level of the $4f^65d$ configuration. The position (in 10^3 cm^{-1}) are as follows: 1,0 26,2; 2 26,8; 3 27,6; 4 28,8; 5 29,7; 6 30,7.

This broadening amounts to some 25% from which the frequency of the phonon involved can be estimated to be 320 cm^{-1} using a graph given by Curie (*4*). This seems a reasonable value for a Eu^{2+}–O^{2-} vibration.

The position of the emission band is at spectacularly long wavelength, 630 nm. It is clear that this is not due to a low-energy position of the first excited state, since the absorption is in the ultraviolet, as observed usually for the Eu^{2+} ion. However, the Stokes shift of the Eu^{2+} emission is unusually large, viz., some 11.000 cm^{-1}. A representative value is a few thousand wavenumbers (*5*).

The fine structure in the excitation band can be analyzed in terms of the splitting of the $4f^6$ configuration in the $4f^65d$ excited state into seven ^7F_J levels. This runs parallel to the analysis given before for BaB_5O_9Br:Eu^{2+} (*6*). The line on the long-wavelength side was used to calculate the Stokes shift of the emission. Dips due to Fano antiresonance were also observed (see Refs. (*6*, *7*)). Finally we note that the excitation band corresponds to an absorption band in the reflection spectrum.

b. $LiBa_2B_5O_{10}$:Pb^{2+}

This composition also shows a temperature-independent, efficient luminescence under short-wavelength ultraviolet excitation. Spectra at 4.2 K are given in Fig. 2. The excitation band is at the limit of the instrumental setup. Its maximum is estimated to be about 245 nm. This band appears also in the reflection spectrum. The emission is in the blue with a maximum at 430 nm. This implies again a formidable Stokes shift of some 18.000 cm^{-1} (see also Ref. (*8*)).

Simultaneously we observed at 4.2 K a broad emission band around 475 nm with an excitation band around 310 nm. These maxima depend on the excitation wavelength and the monitored emission wavelength, respectively. These bands are much broader than the ones in Fig. 2. They are, therefore, ascribed to Pb^{2+} in a glassy second phase, probably a borate glass. At room temperature this emission has disappeared. It is well known that strongly Stokes-shifted emissions quench easily in glass modifications (*9*, *10*).

Discussion

The nature of the optical transitions involved is well known. In case of Eu^{2+} we are dealing with $4f$–$5d$ transitions, in the

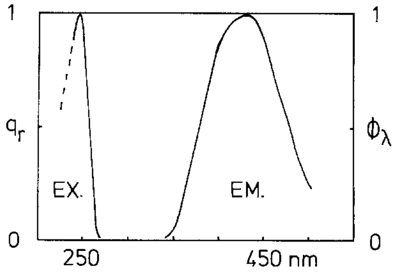

FIG. 2. Emission and excitation spectra of the luminescence of $LiBa_{1.99}Pb_{0.01}B_5O_{10}$ at 4.2 K. See also Fig. 1.

case of Pb^{2+} with $^1S_0$–$^3P_{1,0}$ transitions (see, e.g., Ref. (*8*)). Therefore we will not discuss the spectroscopy any further.

The striking result of this study is the large Stokes shift in this stiff borate host lattice. Large Stokes shifts are expected to imply low quenching temperatures of the luminescence (*8*). However, this is certainly not the case here. It is obvious to relate these peculiar luminescence characteristics to the nature of the barium site in $LiBa_2B_5O_{10}$.

It is important to consider that the barium site is irregular with too long Ba–O distances and the shorter ones among these on one side of the Ba^{2+} ion. This is a favorable site for ions with s^2 configuration like Pb^{2+} which prefer one-sided coordination. In that case these ions show an intense luminescence with large Stokes shift as has been demonstrated and discussed before (*8, 11*). In fact the Pb^{2+} luminescence characteristics are very similar to those of, for example, $PbAl_2O_4$ (*11*). Although an exact explanation is lacking, the pseudo-Jahn–Teller effect has been used to describe these properties: whereas the ground state corresponds to an asymmetrical coordination, the excited state corresponds to a more symmetrical (or less off-center) position of the central metal ion.

The luminescence properties of Eu^{2+} in $LiBa_2B_5O_{10}$ are even more unique. In view of the noble gas electron configuration of the Eu^{2+} ($4f^7$) ion, it is hard to imagine an explanation on the basis of electron configuration like in the case of Pb^{2+} ($6s^2$). However, a size effect seems to play a role, since the larger Ba^{2+} ion is already too small for the barium site in $LiBa_2B_5O_{10}$.

In view of the data on the Ba^{2+} polyhedron in $LiBa_2B_5O_{10}$ it is easy to imagine that the Eu^{2+} ion in barium sites is situated off-center. Then it cannot be excluded that the potential energy surface of the ground state shows, next to the equilibrium minimum, still another minimum, so that the usually applied harmonic approximation of the configurational coordinate model (*4, 8*) is no longer valid. If the Eu^{2+} ion occupies in the excited state a more symmetrical position, the large Stokes shift has been accounted for, because the reorganization must be large. In view of the potential energy surface of the ground state this is not necessarily accompanied by a low thermal quenching temperature like that required in the single configurational coordinate model in the harmonic approximation. This implies, peculiarly enough, a strong analogy between the Pb^{2+} and the Eu^{2+} ion, although the physical background is different for the two ions (electron configuration vs size, respectively).

On the other hand it cannot be excluded that the emission of $LiBa_2B_2O_{10}$:Eu^{2+} is due to a completely different mechanism, viz., radiative decay of an impurity-trapped exciton as proposed by McClure and Pedrini (*12*).

In conclusion, the luminescence characteristics of Pb^{2+} and especially Eu^{2+} in Li $Ba_2B_5O_{10}$ are remarkable.

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