ON THE LUMINESCENCE OF BISMUTH ALUMINATE ($Bi_2Al_4O_9$)

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The luminescence of Eu^{3+} and Tb^{3+} in $Bi_2Al_4O_9$ is reported. It is shown that the Bi^{3+} excitation energy does not migrate through the lattice. The Cr^{3+} ion shows 704.5 nm line emission in this host lattice.

1. Introduction

Bismuth aluminate, $Bi_2Al_4O_9$, has recently been reported to show efficient, green luminescence at room temperature [1]. The isomorphous compound $Bi_2Ga_4O_9$ did not luminescence. Luminescence at room temperature is a rare phenomenon for bismuth compounds. Other examples are $Bi_4Si_3O_{12}$ [2] and $Bi_4Ge_3O_{12}$ [3].

The crystal structure of $Bi_2Al_4O_9$ is known [4]. The Al^{3+} ions are in equal amounts in tetrahedral and octahedral coordination. The Bi^{3+} ion has only three near oxygen neighbours at one side.

Since the shortest Bi–Bi distance amounts to only 4 Å, energy migration through the host lattice is easy conceivable. We tried to study this by using rare earth ions as trap centres. Further it seemed tempting to investigate the reasons why $Bi_2Ga_4O_9$ does not luminesce at room temperature.

2. Experimental

Samples were prepared as described in ref. [1]. All products were fluxed with NaCl. After washing the products were shown to be single-phase by X-ray analysis. The performance of the optical measurements has been described before [5].

3. Results

Our samples $Bi_2Al_4O_9$ show the same luminescence characteristics as described before [1]: a broad emission band peaking at 490 nm and a broad excitation band

peaking at 285 nm. The position of these bands is practically temperature independent down to liquid helium temperature. We tried to dope this compound with Tb^{3+} and Eu^{3+} in concentrations up to one atomic per cent. In the doped samples the rare earth emission could be directly excited in the characteristic rare earth bands. If excitation was into the host lattice, this emission could hardly be detected on the broad host lattice emission band. This was independent of temperature up to 300 K. We conclude that the excitation energy does not migrate through the lattice.

All aluminate samples showed in addition a red emission band peaking at about 700 nm with a corresponding excitation band with a maximum at 380 nm. This emission is absent at room temperature, but is present at liquid nitrogen temperature. We assume that it is due to an impurity. This might be, for example, Fe^{3+} [6], although the value of the decay time is too short (see below). Another possibility is the presence of a small amount of a second phase of the sillenite type [7,8]. Compounds of this type (like $Bi_{12}SiO_{20}$ and $Bi_{12}GeO_{20}$) are known to luminesce [9] and have optical properties that are very similar to the ones we observed. This additional emission will not be discussed further.

The $Bi_2Ga_4O_9$ sample showed luminescence below room temperature. The results are comparable with those for $Bi_2Al_4O_9$. The maxima of the emission and
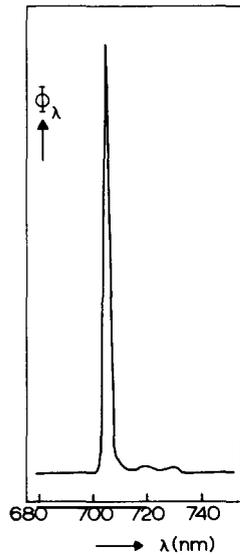

Fig. 1. Spectral energy distribution of the Cr^{3+} emission of $Bi_2Al_4O_9 : Cr^{3+}$ at liquid helium temperature under host lattice excitation. Φ_λ presents the spectral radiant power per unit wavelength interval in arbitrary units.
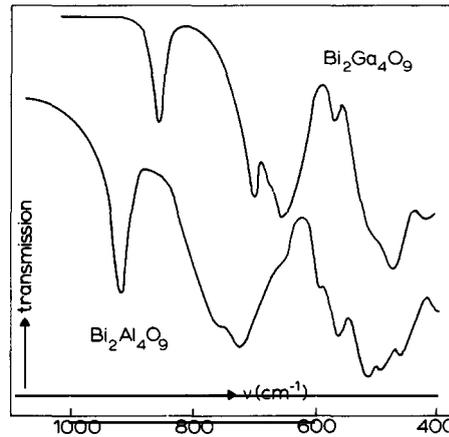
Fig. 2. Infrared spectra of $Bi_2Al_4O_9$ and $Bi_2Ga_4O_9$ at room temperature.

excitation band are 530 and 285 nm, respectively (values at liquid nitrogen temperature).

The Cr^{3+} ion changes the luminescence behavior of $Bi_2Al_4O_9$ more drastically than the rare earth ions. For a Cr^{3+} concentration of 0.5 at.% about 30% of the emission originates from the Cr^{3+} ion and 70% from the host lattice itself (values at 4.2 K under host lattice excitation). The Cr^{3+} emission at this temperature consists of a narrow emission line peaking at 704.5 nm followed by some weak vibronic features at about 300 and 500 cm^{-1} (fig. 1).

The infrared spectra down to 400 cm^{-1} are presented in fig. 2 (KBr-pellets). The bands at 910 cm^{-1} and about 750 cm^{-1} in the case of the aluminate are at much higher frequencies than the corresponding beands in the case of the gallate indicating that they have mainly Al–O character. In the 500 cm^{-1} region the differences are less outspoken indicating a certain Bi–O character.

Finally we performed decay time measurements on the $Bi_2Al_4O_9$ sample. The 490 nm emission band has at 10 K a decay time of 14 μs. The value decreases slowly to 4 μs at 100 K. The corresponding values for the red, additional emission are 26 μs and 4 μs.

4. Discussion

The luminescence of the Bi^{3+} ion is well known and reasonably understood [10,11]. The emission is ascribed to the $^3P_1 - {}^1S_0$ transition. Below the emitting $^3P_1$ level the $^3P_0$ level is acting as an optical trap [11]. Following Brixner [1] we ascribe the excitation band of $Bi_2Al_4O_9$ to the $^1S_0 - {}^3P_1$ transition on the Bi^{3+} ion. The emission at room temperature is due to the $^3P_1 \rightarrow {}^1S_0$ transition. From the short decay time at low temperature we have to conclude that even at these temperatures the emission is still mainly from the $^3P_1$ level, since the radiative decay time from $^3P_0$ amounts to several hundreds of microseconds. This points to a very small energy difference between the $^3P_0$ and $^3P_1$ level as has been discussed elsewhere [12].

The Stokes shift of the Bi^{3+} emission in $Bi_2Al_4O_9$ amounts to 15 000 cm^{-1} which is large [12]. As a consequence the luminescent centre relaxes considerably after excitation. As a consequence the energy migration between Bi^{3+} ions mutually has a large thermal activation energy [13,14]. Since the Bi^{3+} excitation energy is not transferred to rare earth ions in the lattice, we conclude that even at room temperature the relaxation cannot be counteracted by thermal activation and that the excitation energy does not migrate through the host lattice. As a consequence no concentration quenching occurs and $Bi_2Al_4O_9$ emits at room temperature in spite of its high Bi^{3+} concentration.

The Stokes shift in the case of $Bi_2Ga_4O_9$ is still larger, viz. 16 500 cm^{-1}. This makes energy migration even more improbable, so that the lower quenching temperature of the luminescence of $Bi_2Ga_4O_9$ in comparison with that of $Bi_2Al_4O_9$

is due to the larger offset of the excited state parabola in the case of the gallate.

Let us finally consider the results for $Bi_2Al_4O_9$: Cr^{3+}. Since the Bi^{3+} excitation energy is not mobile, the energy transfer mechanism between the Bi^{3+} and Cr^{3+} ions consists of a one-step energy transfer process. From the ratio of the Bi^{3+} and the Cr^{3+} emission intensity and the cell parameters of $Bi_2Al_4O_9$ [4], the critical distance for this transfer is estimated to be 9 Å at liquid helium temperature. The $^3P_1 - {}^1S_0$ emission of the Bi^{3+} ion overlaps mainly with the $^4A_2 \rightarrow {}^4T_1(F)$ absorption band of the Cr^{3+} ion. In view of the reaonable absorption strength of both transitions the value of 9 Å is not unreasonable for energy transfer by electric dipole interaction.

The emission of the Cr^{3+} ion at 704.5 nm originates from the ^2E level in view of its sharp line character [15]. The ^2E level is, therefore, situated below the $^4T_2$ level. The maximum of the $^4A_2 \rightarrow {}^4T_2$ absorption band is in fact found at much higher energies, viz. at 620 nm. The vibronic features at 300 and 500 cm^{-1} are ascribed to coupling with vibrations which have mainly Bi—O character (see above).

In the near future we hope to perform measurements at very low temperatures on the undoped bismuth compounds.

References

[1] L.-H. Brixner, Mat. Res. Bull. 13 (1978) 563.
[2] G. Blasse, Philips Res. Repts. 23 (1968) 344.
[3] M.J. Weber and R.R. Monchamp, J. App. Phys. 44 (1973) 5495.
[4] N. Niizeki and M. Wachi, Z. Kristallogr. 127 (1968) 173;
    R. Arpe and Hk. Müller-Buschbaum, J. Inorg. Nucl. Chem. 39 (1977) 233.
[5] H. Ronde and G. Blasse, J. Inorg. Nucl. Chem. 40 (1978) 215.
[6] N.T. Melamed, P.J. Viccaro, J.O. Artman and F. de S. Barros, J. Luminescence 1/2 (1970) 348.
[7] E.M. Levin and R.S. Roth, J. Res. Natl. Bur. Std. 68A (1964) 197.
[8] S.C. Abrahams, P.B. Jamieson and J.L. Bernstein, J. Chem. Phys. 47 (1967) 4034.
[9] R.B. Lauer, Appl. Phys. Lett. 17 (1970) 178.
[10] G. Blasse and A. Bril, J. Chem. Phys. 48 (1968) 217.
[11] G. Boulon, J. de Phys. 32 (1971) 333;
     G. Boulon, C. Pédrini, M. Guidoni and Ch. Pannel, J. de Phys. 36 (1975) 267.
[12] G. Blasse and A.C. van der Steen, Solid States Commun. 31 (1979) 993.
[13] W.H. Fonger and C.W. Struck, J. Luminescence 17 (1978) 241.
[14] C. Hsu and R.C. Powell, J. Luminescence 10 (1975) 273.
[15] G.F. Imbusch, in: Luminescence of Inorganic Solids, ed. B. di Bartolo (Plenum Press, New York, 1978) p. 115.