The Luminescence of the Scheelite NaBi(MoO₄)₂

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The luminescent properties of the scheelite $NaBi(MoO_4)_2$ are reported. Below 50 K an efficient, red emission occurs. The results agree with those for other bismuth molybdates. The decay measurements indicate an energy level structure of the emitting state which is very similar to that in $PbMoO_4$. The distribution of the Na^+ and Bi^{3+} ions is probably short-range ordered. © 1987 Academic Press, Inc.

Introduction

Tungstates and molybdates with scheelite structure are well known for their luminescence *(1, 2)*. Among these $CaWO_4$ and $CaMoO_4$ should be mentioned first, the former having been used as an applied X-ray phosphor for a long time. The optical transitions take place in the tungstate and molybdate groups and are of the charge-transfer type *(2)*.

It is also known that ions with s^2 configuration, like Pb^{2+} and Bi^{3+}, can influence the luminescent properties of the tungstates and molybdates considerably *(1, 2)*. In connection with the scheelite structure, $PbWO_4$ and $PbMoO_4$ should be mentioned *(3)*. These compounds have their optical absorption edge and the maximum of their green emission band at longer wavelengths than do the corresponding alkaline earth compounds. Bismuth tungstates and molybdates show emission at even longer wavelength, viz., in the red spectral region *(4)*. However, these bismuth compounds do not have the scheelite structure.

In this paper we wish to report on the luminescence of single-crystal NaBi-$(MoO_4)_2$, which has the scheelite structure *(5)*; i.e., it is isomorphous with $CaMoO_4$ with a statistical distribution of the Na^+ and Bi^{3+} ions on the Ca^{2+} sites. From an electronic point of view there is a great similarity between $PbMoO_4$ and $NaBi(MoO_4)_2$, since the Pb^{2+} and Bi^{3+} ions are isoelectronic.

The present study was performed on single crystals. This was also the case for the lead scheelites *(3)*. The bismuth molybdates and tungstates, however, were investigated on powder samples. It will be shown that all data fit together nicely.

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Experimental

Crystals of NaBi(MoO₄)₂ were grown from the melt (congruent melting temperature ca. 1140 K) by the Czochralski method. Stoichiometric mixtures of the chemically pure starting materials Na_2CO_3, Bi_2O_3, and MoO_3 were prefired at 975 K for 24 hr. In most cases the pulling direction was parallel to the crystallographic c-axis, sometimes to the a-axis. Suitable pulling rates ranged from 4 to 8 mm/hr with a rotation of 15 rpm. The crystals obtained have optical quality and exhibited amber color; their lengths reached up to 60 mm, with diameters up to 25 mm (6). Similar growth conditions and results have been reported by Akimov et al. (7).

One of the crystals was cut and polished to dimensions of $7 \times 7 \times 2.5$ mm³.

The optical instrumentation consists of a spectrofluorometer MPF 44B equipped with an Oxford helium flow cryostat. Decay times were measured using a photon counting system (EG and G). The excitation source is a N₂-flash lamp (8). Absorption measurements were performed at room temperature on a Perkin–Elmer Lambda 7 spectrophotometer.

Results

Below 100 K the scheelite NaBi(MoO₄)₂ shows a red emission under long-wavelength ultraviolet excitation. Figure 1 shows the emission and excitation spectra of this luminescence at 4.2 K. The emission band shows a maximum at 600 nm, the corresponding excitation maximum is 385 nm. Upon 395 nm excitation (i.e., near the onset of the excitation spectrum) the emission maximum is slightly shifted to about 610 nm.

Optical absorption spectra on single crystals show an intense absorption for $\lambda < 400$ nm. Diffuse reflection spectra on powdered samples show the maximum of the first ab-
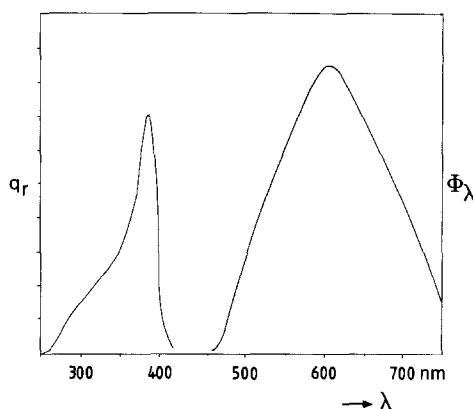

FIG. 1. Emission and excitation spectra at 4.2 K of the luminescence of a NaBi(MoO₄)₂ single crystal. Emission spectrum recorded for excitation at 385 nm. Excitation spectrum recorded for emission 600 nm. q_r gives the relative quantum output in arbitrary units. Φ_λ gives the spectral radiant power per constant wavelength interval in arbitrary units.

sorption band at about 370 nm at 300 K. Assuming that the thermal shift of this maximum is similar to that observed for Pb-MoO₄ (3), we estimate the position of the first absorption band of NaBi(MoO₄)₂ at 4.2 K at about 360 nm. This is a strikingly different value from the excitation maximum (385 nm), so that the latter cannot be considered to correspond to an absorption maximum. This is due to the well-known phenomenon that in strongly absorbing crystals excitation into the absorption maximum is not very effective, because the excitation cannot enter the crystal and considerable radiationless losses occur in the surface layer.

From the emission and absorption maximum we derive a value of 12,000 cm⁻¹ for the Stokes shift of the luminescence.

In Figure 2 the temperature dependence of the luminescence intensity is given. Quenching occurs above 20 K. The intensity has dropped to 50% at about 40 K. This figure shows also the temperature dependence of the decay time of the luminescence. All decay curves are purely exponential. At the lowest temperatures there is
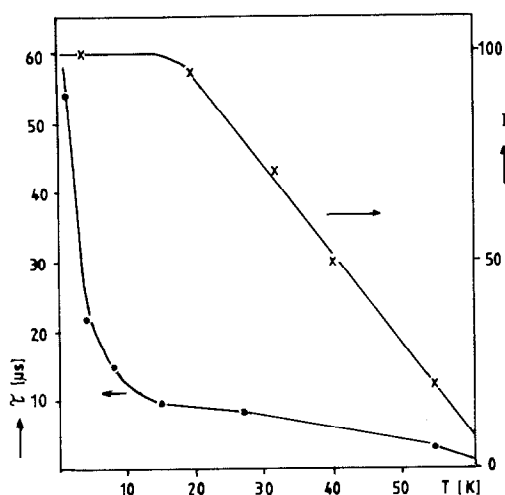
FIG. 2. Decay times of the 600-nm emission of NaBi-$(MoO_4)_2$ as a function of temperature (black points). The line indicated by crosses gives the relative emission intensity (I).

a rapid increase of the decay time for decreasing temperature. Even at 1.5 K no plateau value has been attained. This indicates the presence of a very shallow optical trap. Exactly the same has been observed for $PbMoO_4$. The trap depth is of the order of a few wavenumbers. For higher temperatures there is a continuous decrease of the value of the decay time. Since temperature quenching occurs already above 20 K, we did not analyze the temperature dependence of the decay time any further.

Discussion

In Ref. (4) it was shown that the luminescence of bismuth molybdates is in the red spectral region. The Stokes shift in these compounds amounts to ~11,000 cm^{-1} for molybdate tetrahedra and ~9,000 cm^{-1} for molybdate octahedra. The value of 12,000 cm^{-1} for the red emission of $NaBi(MoO_4)_2$ fits into the series of results, the scheelite-structure containing tetrahedral molybdate groups. Actually the luminescence properties of γ'-Bi_2MoO_6, $Bi_2Mo_2O_9$, and Bi_2

$(MoO_4)_3$, all with tetrahedral coordination (3), are very similar to those of NaBi-$(MoO_4)_2$.

The precise nature of the optical transitions involved is not clear, but they have a considerable metal-to-metal charge-transfer character, i.e., $Bi^{3+} \rightarrow Mo^{6+}$. The optical transitions of the molybdate group and of the Bi^{3+} ion, when separated from each other, are situated at higher energy than the transitions under discussion (2).

The emission of $NaBi(MoO_4)_2$ seems to consist of one band only. By exciting into the tail of the absorption it was possible to observe an emission at slightly longer wavelength. This would be a surprising result if the distribution of Na^+ and Bi^{3+} ions on the larger cation sublattice of the scheelite structure were completely random. In that case the molybdate groups would have a variable number of Bi^{3+} ions around them, so that several emission bands are to be expected. Our result suggests that the Na^+ and Bi^{3+} ions, which according to X-ray diffraction are not long-range ordered, are short-range ordered. This confirms an early prediction by Van Santen (9). Also, the vibrational spectra of scheelites $M^+M^{3+}(MoO_4)_2$ have shown that there must be a considerable amount of short-range order in these compounds (10). The additional emission excited in the absorption tail is then ascribed to a molybdate group with more than the average number of Bi^{3+} ions around it.

The low quenching temperature of the luminescence of $NaBi(MoO_4)_2$ has also been observed for the other bismuth molybdates. The configurational coordinate model shows clearly that broadband red emissions are not expected to have high quenching temperatures (11).

There is a striking analogy between the decay times of $PbMoO_4$ (3) and those of $NaBi(MoO_4)_2$ in the temperature region where temperature quenching is of no importance. This shows that the energy level

structure of the emitting state in these compounds must be similar. This result is not unexpected in view of the similarity in electronic configuration. The energy level structure is not easy to unravel nor to account for. It has been suggested (2) that the molybdate emission is due to a triplet–singlet transition. This has been confirmed by Van der Waals et al. (12). However, the heavy s^2 ions form a disturbing factor and will increase the influence of spin–orbit coupling. It cannot be excluded that the level splitting of a few wavenumbers, which follows from the temperature dependence of the decay time, is due to a splitting of the triplet as observed in more simple systems (12). This warrants further research.

Acknowledgment

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