

THE LUMINESCENCE OF DOPED AND UNDOPED $\text{BaLn}_2(\text{MoO}_4)_4$ (Ln = La, Gd)

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ABSTRACT

The luminescence of nominally pure $\text{BaLn}_2(\text{MoO}_4)_4$ (Ln = La, Gd) is reported. Below 300 K molybdate emission is observed. The following activators were investigated: Eu^{3+} , Tb^{3+} , Pb^{2+} and Bi^{3+} . The two lanthanide ions show their characteristic emission, the two s^2 configuration ions give an emission in which the host-lattice group as well as the activator is involved. The luminescence properties of these compositions are discussed and compared with those of related materials.

INTRODUCTION

The luminescence of the scheelites CaMoO_4 and CaWO_4 is well known for a long time [1,2]. The latter has been used as an X-ray phosphor for some 70 years [3]. The host lattice groups MoO_4^{2-} and WO_4^{2-} are the luminescent centres; the optical transitions involved are of the charge-transfer type. These compounds have also been used as host lattices for laser materials [4]. The luminescence of scheelite-type compounds $\text{M}^+\text{M}^{3+}(\text{WO}_4)_2$ has also been described in the literature [5,6].

Some years ago other binary molybdates and tungstates were reported in the literature [7-9]. Their structure was found to be different from the scheelite structure.

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It was established that compounds of composition $\text{BaLn}_2(\text{MoO}_4)_4$ are formed with $\text{Ln}=\text{Nd-Tm}$, including Y. However, $\text{BaLa}_2(\text{MoO}_4)_4$ has the scheelite structure [8]. The crystal structure of $\text{BaNd}_2(\text{MoO}_4)_4$ [7] contains MoO_4^{2-} tetrahedra, Nd^{3+} ions in an irregular eight coordination, and Ba^{2+} ions in a tenfold coordination. The Ba^{2+} ions lie between the layers formed by the Mo^{6+} and Nd^{3+} polyhedra.

For the tungstates another composition has been reported, *viz.* $\text{MLn}_4(\text{WO}_4)_7$ ($\text{M}=\text{Ca,Sr}$) [9]. Its crystal structure is unknown as far as we are aware. In view of the technically important properties of scheelite-type molybdates and tungstates it seemed interesting to investigate the luminescence properties of doped and undoped compositions $\text{BaLn}_2(\text{MoO}_4)_4$. In this paper we report the more interesting results.

EXPERIMENTAL

Powder samples were prepared from high-purity starting materials using techniques and conditions as described in the literature [8,9]. As activators we used Eu^{3+} , Tb^{3+} , Pb^{2+} and Bi^{3+} . Their concentrations amount to some 5 mole per cent and are specified below as far as necessary. All samples were checked by X-ray powder diffraction, using $\text{CuK}\alpha$ radiation.

The optical measurements were performed on Perkin-Elmer spectrofluorometers MPF equipped with a Xe lamp. By using an Oxford flow cryostat the temperature could be lowered to $\sim 5\text{K}$. Decay times were measured using a nitrogen-laser pumped dye laser (Molelectron). For further details we refer to earlier publications [10,11].

RESULTS AND DISCUSSION

$\text{BaLa}_2(\text{MoO}_4)_4$

The La compound in the series $\text{BaLn}_2(\text{MoO}_4)_4$ has still a scheelite structure [8]. This means that the Ca-sublattice of CaMoO_4 is occupied by a statistical mixture of 1Ba^{2+} , 2La^{3+} and 1 vacancy, *i.e.* the structure of $\text{BaLa}_2(\text{MoO}_4)_4$ is highly disordered. This is reflected by the diffuse reflection spectrum which shows a very long tail into the visible region (Fig. 1). The optical absorption is due to the charge-transfer transition of the molybdate group [2]. The position of the corresponding absorption band depends strongly on the surroundings of the molybdate group, so that the disorder results in an enormous inhomogeneous broadening of the molybdate absorption.

At 5 K the compound $\text{BaLa}_2(\text{MoO}_4)_4$ shows an orange-red emission of medium intensity. The main emission band has its maximum at 620 nm. The corresponding excitation band has its maximum at 295 nm. The Stokes shift is about $18 \times 10^3 \text{ cm}^{-1}$. The luminescence intensity decreases gradually with increasing temperature. At 85 K it has decreased to 50%, at 160 K it is nearly quenched.

Upon excitation with $\lambda > 300$ nm the emission maximum shifts to longer wavelengths, e.g. 650 nm for 310 nm excitation, and 680 nm for 330 nm excitation. Figure 1 shows also the excitation spectrum for 700 nm emission.

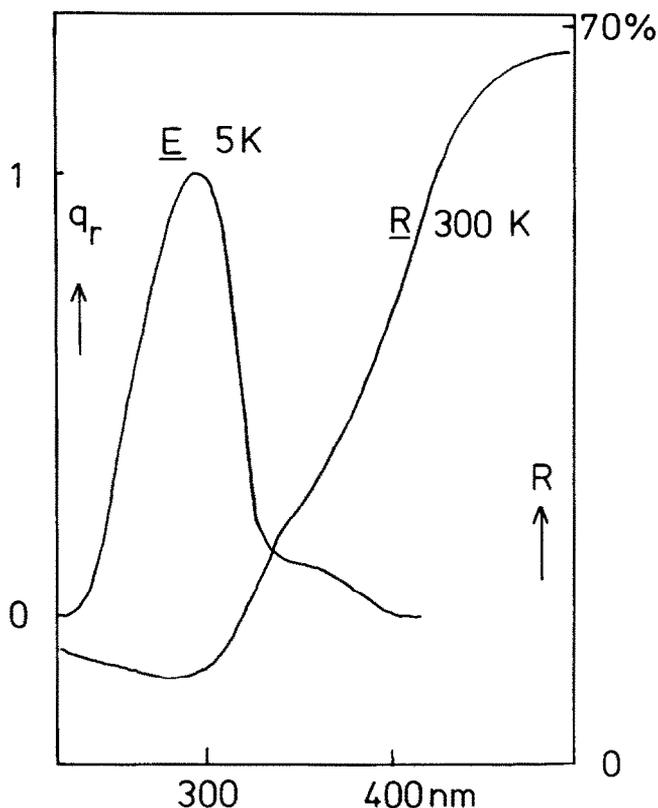


Fig. 1. Diffuse reflection spectrum of $\text{BaLa}_2(\text{MoO}_4)_4$ at 300 K (R), and excitation spectrum of the 700 nm emission of $\text{BaLa}_2(\text{MoO}_4)_4$ at 5K. q_r denotes the relative quantum output in arbitrary units.

In addition to the main band at 295 nm, it shows a shoulder at some 340 nm. This shows also that the molybdate groups have varying surroundings. From a comparison between the diffuse reflection spectrum and the excitation spectrum (Fig. 1) it is clear that the molybdate groups with the lowest absorption bands do not luminesce at all, not even at 5K.

The main spectral features of $\text{BaLa}_2(\text{MoO}_4)_4$ are rather similar to those of SrMoO_4 (excitation maximum ~ 290 nm, Stokes shift $\sim 17 \times 10^3 \text{ cm}^{-1}$ and quenching temperature 170 K, [1]). Since we may assume that the molybdate groups surrounded by one or more vacancies have the lowest charge-transfer energies [2,12], the main emission of $\text{BaLa}_2(\text{MoO}_4)_4$ is most probably due to molybdate groups surrounded by Ba^{2+} and La^{3+} ions. This seems to be equivalent to a

complete Sr^{2+} coordination. The higher charge of the La^{3+} ion seems to compensate for the larger radius of the Ba^{2+} ion [2,12].

The molybdate groups with lower charge-transfer energy show weaker or no luminescence. This is in good agreement with the configurational coordinate model which predicts lower quenching temperatures if the absorption transition moves to lower energy [13,14]. The compound $\text{BaLa}_2(\text{MoO}_4)_4$ illustrates clearly within one and the same composition what has been shown before for a whole series of molybdates, *viz.* if the absorption transition is at low energy, no luminescence of importance can be expected. The medium intensity of the 620 nm emission, together with its rapid quenching with increasing temperature, indicates that this emission has not even a high quantum efficiency at 5 K. The nonradiative transitions involved are of the fast bottom-crossover type [13,15].

$\text{BaGd}_2(\text{MoO}_4)_4$

The undoped compound

At 5 K $\text{BaGd}_2(\text{MoO}_4)_4$ shows an orange-red molybdate emission. The main emission band has its maximum at 580 nm. The corresponding excitation band has its maximum at 275 nm. The Stokes shift is very large, *viz.* $20 \times 10^3 \text{ cm}^{-1}$. The efficiency is low and decreases regularly with increasing temperature. At $\sim 180 \text{ K}$ the luminescence is quenched.

In addition there is a much weaker excitation maximum at about 320 nm. Excitation into this band gives a slightly different emission maximum, *viz.* 590 nm. The Stokes shift is much smaller, *viz.* $15 \times 10^3 \text{ cm}^{-1}$.

The intrinsic molybdate groups are considered to be the main luminescent centre with the 580 nm emission band. The Stokes shift is very large; CaMoO_4 , for example, has only $16 \times 10^3 \text{ cm}^{-1}$ [2]. This large Stokes shift is responsible for the low efficiency, even at 4.2 K [13,14]. A large Stokes shift indicates a strong relaxation of the excited state, *i.e.* a pronounced expansion relative to the ground state. In the crystal structure of $\text{BaGd}_2(\text{MoO}_4)_4$ the molybdate groups are surrounded on one side by Gd^{3+} ions and on the other side by Ba^{2+} ions [7]. The soft Ba^{2+} -ion layer will not counteract the expansion of the molybdate group very much. Therefore, we ascribe the large Stokes shift to the presence of Ba^{2+} ions on one side of the molybdate group.

The additional emission is more puzzling. It is well known that tungstates and molybdates show additional emissions [2]. These are usually ascribed to extrinsic tungstate and molybdate groups. In CaMoO_4 (CaWO_4) these are $\text{MoO}_3(\text{WO}_3)$ groups, *i.e.* tetrahedra in which one of the four oxygen positions is vacant [2]. Another possibility is disorder in the crystal structure. An early example is Ba_2MgWO_6 [16]. An outspoken example is $\text{BaLa}_2(\text{MoO}_4)_4$ which was discussed above.

As indicated in Table I, the Stokes shift of the additional emission is smaller than that of the intrinsic emission. Therefore we ascribe this emission to a molybdate group which has as a neighbour on the barium sites a Gd^{3+} ion (*i.e.* we assume a slight disorder between the Ba^{2+} and Gd^{3+} ions). This reduces the relaxation of the excited state, and therefore the Stokes shift.

Table I. Some luminescence characteristics of the broad-band emissions of doped and undoped $BaGd_2(MoO_4)_4$ at 5 K.

Composition	Maximum emission band(nm)	Maximum excitation band(nm)	Stokes shift ($10^3 cm^{-1}$)	Quenching temperature (T_q, K)	Assignment*
$BaGd_2(MoO_4)_4$	580	275	20	180	$(MoO_4^{2-})_i$
	590	320	15		$(MoO_4^{2-})_e$
$BaGd_2(MoO_4)_4-Eu^{3+}$	Eu^{3+}	275	-	-	$(MoO_4^{2-})_i$
		310	-	-	$(Eu^{3+}-O^{2-})_{CT}$
$BaGd_2(MoO_4)_4-Tb^{3+}$	Tb^{3+}	275	-	-	$(MoO_4^{2-})_i$
		315	-	-	$(Tb^{3+}-Mo^{6+})_{CT}$
$BaGd_2(MoO_4)_4-Bi^{3+}$	Bi^{3+}	610	-	250	$(MoO_4^{2-})_i$
		620	320	15	250
$BaGd_2(MoO_4)_4-Pb^{2+}$	Pb^{2+}	580	-	-	$(MoO_4^{2-})_i$
		560	330	12.5	250

* i: intrinsic, e: extrinsic, CT: charge-transfer

Since the broad emission bands of the intrinsic and extrinsic centres nearly coincide, it is very hard to investigate this proposal in more detail. The addition of 1 mole % of extra Gd_2O_3 to the starting materials resulted in a slight increase of the extrinsic excitation band which seems to confirm our proposal. The diffuse reflection spectra of

BaGd₂(MoO₄)₄ samples show only a few percent of absorption in the region of the extrinsic excitation band. This implies that the Ba²⁺/Gd³⁺ disorder is 1% or less, so that it cannot be observed during the X-ray determination of the crystal structure.

BaGd₂(MoO₄)₄-Eu³⁺

A sample of this composition shows at room temperature and below a red emission under ultraviolet excitation. Figure 2 shows part of the Eu³⁺ emission spectrum. The ⁵D₀ - ⁷F₂ emission dominates.

The Gd³⁺ site in this structure has no symmetry elements [7]. The Eu³⁺ emission spectrum suggests the presence of pseudo-symmetry elements. The crystal structure [7] shows that the Gd³⁺-ion coordination can be approximated by a square antiprism, *i.e.* C_{4v} site symmetry. This symmetry predicts the following number of lines: ⁵D₀ - ⁷F₀ 1 (1), ⁵D₀ - ⁷F₁ 2 (2), ⁵D₀ - ⁷F₂ 2 (2), ⁵D₀ - ⁷F₃ 2 (2), ⁵D₀ - ⁷F₄ 4 (4). The numbers between brackets indicate the number of lines observed experimentally, if we neglect some very weak features. This is a surprising good agreement.

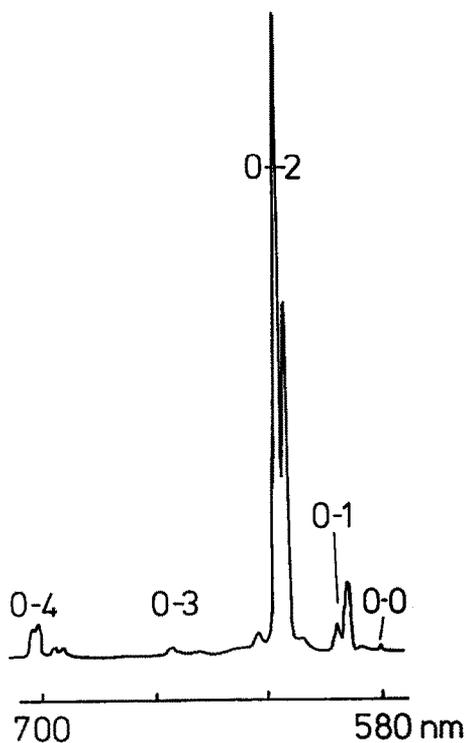


Fig. 2. Emission spectrum of BaGd_{1.82}Eu_{0.18}(MoO₄)₄ at 5 K under 310 nm excitation. The notation J - J' denotes the transitions ⁵D_J → ⁷F_{J'}.

Weak features on the long wavelength side of the $^5D_0 - ^7F_2$ emission lines can be ascribed to coupling with molybdate vibrations ($\sim 400 \text{ cm}^{-1}$, $\sim 800 \text{ cm}^{-1}$). The same is observed in the excitation spectrum on the short wavelength side of the $^7F_0 - ^5D_0$ and $^7F_0 - ^5D_2$ transitions. This has been observed and discussed before for the compounds $M^+Eu^{3+}W_2O_8$, $M^+Eu^{3+}Mo_2O_8$ [6], and for $CaWO_4 - Eu^{3+}$ [17].

The excitation spectrum of the Eu^{3+} emission shows a very broad band in the ultraviolet region. At 300 K there is a maximum at about 310 nm. This band is ascribed to the Eu^{3+} charge-transfer transition. At 5 K there is an additional maximum at 275 nm, corresponding to the host lattice. Excitation with this wavelength at 5 K yields mainly Eu^{3+} emission. The amount of molybdate emission is 5% or less for a Eu^{3+} concentration of 9 mole %.

This shows that energy transfer from the molybdate group to Eu^{3+} occurs. Using the formula $R_c^6 = 0.6 \times 10^{28} \times 4.8 \times 10^{-16} \times f_{Eu} \times E^{-4} \times SO$ [18], where f_{Eu} is the oscillator strength of the Eu^{3+} lines, E the energy of maximal spectral overlap and SO the spectral overlap, we find $R_c = 3 \text{ \AA}$ for an electric dipole-dipole interaction. This distance is shorter than the shortest Eu-Mo distance, so that we can conclude that exchange interaction yields also a certain contribution. For this we need wavefunction overlap between the orbitals of Eu^{3+} ($4f$) and the MoO_4^{2-} group. This overlap is not necessarily vanishing as has been shown before for $Eu_2(MoO_4)_3$ [19].

At 5 K the host lattice excitation band is more pronounced than at 300 K. This is not surprising since the nonradiative rate within the molybdate group increases with temperature. The relatively low efficiency for host-lattice excitation is ascribed to the presence of this nonradiative decay channel. That for charge-transfer excitation is ascribed to a nonradiative return to the ground state via the charge-transfer state [20].

Upon excitation into the 5D_1 level with the dye laser, the decay time of the Eu^{3+} emission was measured. The decay curves are all exponential. The decay time is temperature independent and amounts to 0.53 ms. This is a relatively short value. It agrees with data reported for other molybdates and vanadates, *i.e.* compounds which also show an optical absorption edge at relatively low energy [21]. The emission spectrum of the Eu^{3+} ion with its dominating $^5D_0 - ^7F_2$ lines, together with the short decay time, points to a strong influence of hypersensitivity on the $^5D_0 - ^7F_2$ transition of Eu^{3+} in $BaGd_2(MoO_4)_4$. In a covalent surroundings such an effect is not surprising.

In the system $\text{BaGd}_{2-x}\text{Eu}_x(\text{MoO}_4)_4$ the intensity of the Eu^{3+} emission increases with x up to $x=0.7$, i.e. 35 mole % of Eu^{3+} . This is the critical concentration (x_c) for quenching. According to $x_c = 2/N$ where N is the number of sites to which transfer can occur [22], N is about 6. From the crystal structure [7] it is found that each Gd^{3+} site has five Gd^{3+} neighbour sites within 6\AA . In view of the uncertainty in the x_c value, the agreement is considered to be good. This implies that the concentration quenching of the Eu^{3+} emission is due to energy migration over the Eu^{3+} ions to quenching sites.

$\text{BaGd}_2(\text{MoO}_4)_4 - \text{Tb}^{3+}$

The luminescence of Tb^{3+} in $\text{BaGd}_2(\text{MoO}_4)_4$ has a rather low efficiency independent of temperature. The emission spectrum consists of the well-known emission transitions from the $^5\text{D}_4$ level. The excitation spectrum consists at 5 K of intra - $4f^8$ Tb^{3+} lines, a band with a maximum at 315 nm and one at 275 nm. At 300 K the former one has disappeared. We assume that a considerable amount of quenching can be ascribed to $\text{Tb}^{3+} - \text{Mo}^{6+}$ electron transfer [20]. The 315 nm band may be ascribed to the corresponding electron-transfer band or to a $4f-5d$ transition on Tb^{3+} . The latter possibility does not seem very probable in view of the low energy position of this band.

In conclusion, 315 nm excitation yields only (weak) Tb^{3+} emission at low temperatures. The electron transfer quenching has obviously a thermally activated component. On the other hand, 275 nm excitation results in energy transfer from the molybdate group to Tb^{3+} . In view of the position of the molybdate emission band, only the $^5\text{D}_4$ level can be populated in this way. Therefore, we have skipped the electron-transfer state, and the 275 nm excitation band persists up till room temperature. However, a large amount of Tb^{3+} luminescence is still quenched due to the presence of the electron-transfer state.

$\text{BaGd}_2(\text{MoO}_4)_4 - \text{Bi}^{3+}$

As has been discussed at length elsewhere [2,23,24], the presence of ions with s^2 configuration, e.g. Bi^{3+} , Pb^{2+} , in molybdates and tungstates induces the presence of additional emission and excitation bands with sometimes higher quenching temperatures than the intrinsic emission. In the case of $\text{CaWO}_4\text{-Pb}$ this leads to an important technical application [1]. For this reason we investigated Bi^{3+} and Pb^{2+} in $\text{BaGd}_2(\text{MoO}_4)_4$.

The Bi^{3+} ion induces in $\text{BaGd}_2(\text{MoO}_4)_4$ a strong additional excitation band at 320 nm. The emission maximum is at about 620 nm. The host lattice band is also observed in the excitation spectrum (see Table I). The efficiency of the emission is higher than for the undoped molybdate. The quenching temperature has increased to 250 K. The Stokes shift ($15 \times 10^3 \text{ cm}^{-1}$) is smaller than for the molybdate.

These results agree with the earlier observations. The additional bands are ascribed to charge-transfer transitions of the type $\text{Bi}^{3+} - \text{Mo}^{6+}$. In view of the antibonding character of the $6s^2$ electrons, the relaxation in the excited state is less and the Stokes shift smaller than for the molybdate group [2]. Consequently the efficiency and the quenching temperature go up.

$\text{BaGd}_2(\text{MoO}_4)_4 - \text{Pb}^{2+}$

Similar observations as for Bi^{3+} in $\text{BaGd}_2(\text{MoO}_4)_4$ were made for the Pb^{2+} ion (see Table I). The Stokes shift of the additional emission is surprisingly small ($12.5 \times 10^3 \text{ cm}^{-1}$). The relevant values are not far off from those for PbMoO_4 [1,2].

CONCLUSION

We have investigated the luminescence of doped and undoped $\text{BaGd}_2(\text{MoO}_4)_4$. The results can be explained in terms of theories proposed before. In all cases the quenching temperature is at relatively low temperatures and the luminescence efficiencies are not better than moderate

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