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Luminescence Properties of Alkali Europium Double Tungstates and Molybdates $AEuM_2O_8$

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The luminescence properties of $AEuW_2O_8$ and $AEuMo_2O_8$ (A^+ = alkali metal ion) are reported. These properties depend on the crystal structure type. Vibronic coupling between the electronic transitions of the Eu^{3+} ion and the vibrational transitions of the tungstate or molybdate group is observed. The concentration quenching of the Eu^{3+} luminescence is weak. The analysis of the Eu^{3+} decay curves points to energy migration and shows the two-dimensionality of the Eu^{3+} sublattice in $KEuMo_2O_8$ and the one-dimensionality of the Eu^{3+} sublattice in $KEuW_2O_8$ and $RbEuW_2O_8$.

1. Introduction

The scheelite lattice of compounds such as $CaWO_4$ has often been used as a host for rare-earth ions, for fundamental studies as well as applications (*1*). In this paper we report on the Eu^{3+} luminescence of alkali europium double molybdates and tungstates. Some of these compounds have a scheelite-related crystal structure, but others have a completely different structure. A marked property of these systems is the fact that they do not show clear concentration quenching.

In recent years the crystal structures of the compounds $ALnW_2O_8$ and $ALnMo_2O_8$ (A^+ = alkali metal ion, Ln^{3+} = rare-earth ion) have been determined (see, e.g., Refs. (*2–5*) and references therein). The crystal structure and luminescence properties of $CsLnW_2O_8$ ($Ln = Eu^{3+}, Tb^{3+}$) have recently been studied in our laboratories (*2*). Now we report on the luminescence of $AEuW_2O_8$ ($A = Li^+, Na^+, K^+$, and Rb^+) and AEu Mo_2O_8 ($A = Li^+, Na^+, K^+, Rb^+$, and Cs^+). Since these compounds have different crystal structures, it was interesting to investigate the extent to which the luminescence is determined by the structure.

From structural data it is known that in some of the investigated compounds the Eu^{3+} sublattice has a dimensionality lower than three, i.e., the ions are ordered in planes or in chains. The energy migration characteristics of Eu^{3+} compounds with two- or one-dimensional sublattices have been studied extensively in the Utrecht laboratory (*6–11*). Theoretical models for

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the time dependence of the Eu^{3+} donor luminescence in such systems are described in Refs. (*12–14*). We investigated whether these models can be applied to the experimentally measured decay curves of the Eu^{3+} emission of the above-mentioned compounds.

2. Experimental

The powder samples of $AEuW_2O_8$ and $AEuMo_2O_8$ were prepared following methods described in Ref. (*2*), the latter at slightly lower temperatures than the former. Some of the samples showed a faint coloring.

The equipment for the diffuse reflectance, luminescence, and decay curve measurements was described previously (*6, 15*). The measurements were performed at room temperature and 4.2 K.

3. Results

All samples show an intense red Eu^{3+} luminescence upon broad band UV excitation. The amount of concentration quenching is obviously small, in agreement with early reports by Van Uitert (*1*). The diffuse reflectance spectra of all compounds, recorded at room temperature, contain the sharp absorption lines corresponding to the transitions within the $4f^6$ shell of the Eu^{3+}. The optical absorption edge for the molybdate spectra lies at 300 ± 10 nm and for the tungstates at 280 ± 10 nm. This absorption is due to the charge transfer transition in the molybdate or tungstate group. The broad band tails into the visible, which accounts for the color of the samples.

Figure 1 presents the excitation spectrum of the Eu^{3+} emission of $CsEuMo_2O_8$ as a typical example of the excitation spectra of all compounds. It consists of the sharp lines due to the transitions within the $4f^6$ shell of the Eu^{3+} and a broad band in the UV. On the high energy side of the $^7F_0 \rightarrow {}^5D_{0,1,2}$ excitations some vibronic features can be seen.

Figure 2 presents the emission spectrum of the Eu^{3+} ion in $CsEuMo_2O_8$. The elec-

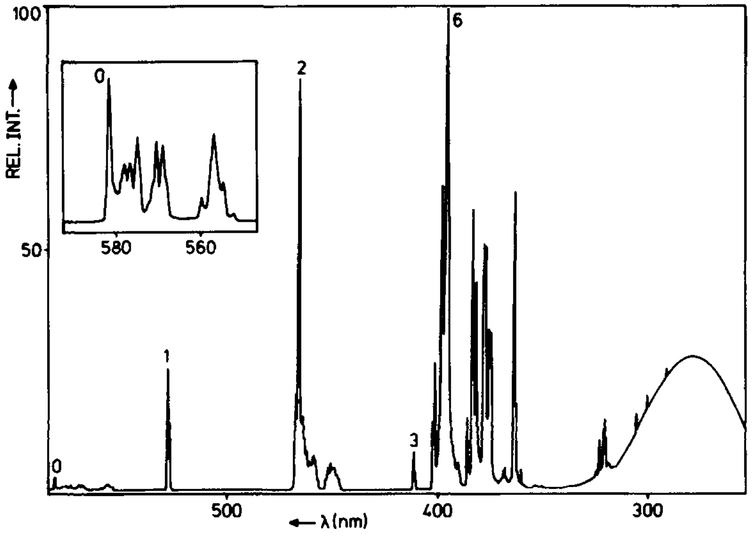

FIG. 1. Excitation spectrum of the Eu^{3+} emission of $CsEuMo_2O_8$, recorded at 4.2 K; $\lambda_{em} = 614$ nm. The numbers 0, 1, 2, 3, and 6 denote the $^7F_0 \rightarrow {}^5D_{0,1,2,3}$ and $^5L_6$ transitions. The inset shows the vibronic lines coupled with the $^7F_0 \rightarrow {}^5D_0$ electronic transition enlarged.

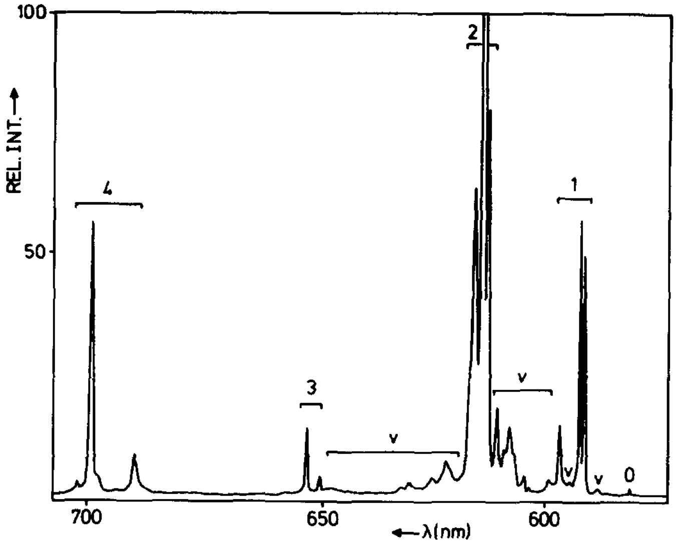

FIG. 2. Emission spectrum of $CsEuMo_2O_8$, recorded at 4.2 K; $\lambda_{exc} = 396$ nm. The numbers 0, 1, 2, 3, and 4 denote the $^5D_0 \rightarrow {}^7F_{0,1,2,3,4}$ transitions; v, vibronic transition.

tronic transitions $^5D_0 \rightarrow {}^7F_{0,1,2,3,4}$ are clearly visible. The emission of higher ^5D_J levels is quenched. The emission spectra of all compounds are dominated by the $^5D_0 \rightarrow {}^7F_2$ transition. Considering the number and the relative intensity of the lines in the emission transitions, the spectra can be divided into four groups (see also Fig. 3):

(1) $LiEuMo_2O_8$, $LiEuW_2O_8$, $NaEuMo_2O_8$, and $KEuMo_2O_8$;

(2) $KEuW_2O_8$;

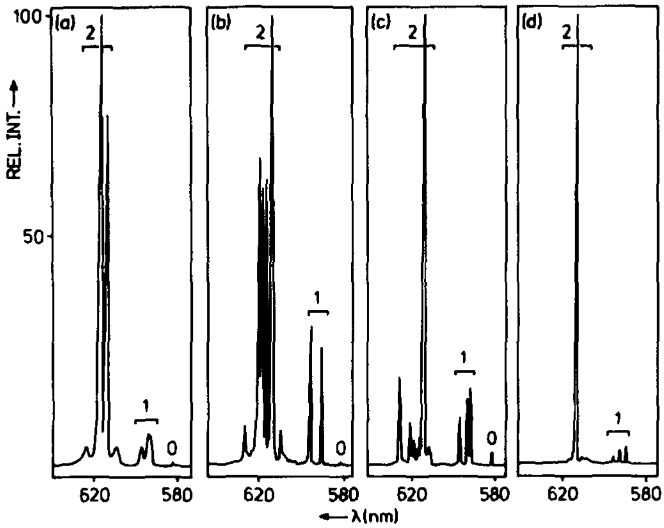

FIG. 3. Spectra of the $^5D_0 \rightarrow {}^7F_{0,1,2}$ emission lines, denoted 0, 1, and 2, recorded at 4.2 K; $\lambda_{exc} = 396$ nm. (a) $LiEuW_2O_8$, (b) $KEuW_2O_8$, (c) $RbEuW_2O_8$, and (d) $RbEuMo_2O_8$.

(3) $RbEuW_2O_8$;
(4) $RbEuMo_2O_8$ and $CsEuMo_2O_8$.

The lines in the spectra of group 1 are relatively broad. Furthermore, all spectra contain vibronic emission lines. In some cases we observed also tungstate emission. This was most significant for $LiEuW_2O_8$. Therefore this compound was studied in more detail. The tungstate emission consists of a broad band in the region 320–650 nm with a maximum at about 450 nm. The band shows small dips due to radiative transfer to Eu^{3+}. At 4.2 K the amount of tungstate emission is about 20% of the total emission. Similar observations have been made before for $NaEuW_2O_8$ (*16*).

The decay curves of the Eu^{3+} emission of the compounds $KEuW_2O_8$, $KEuMo_2O_8$, and $RbEuW_2O_8$ were measured. At 4.2 K the curves are exponential, with decay times of 490, 590, and 1180 μsec, respectively. At room temperature the curves are nonexponential. Figure 4 shows a semilogarithmic plot of the decay curves of $KEuMo_2O_8$ as a representative example.

4. Discussion

4.1. Host Lattice Excitation and Energy Transfer

The broad band in the UV region of the excitation spectra of the Eu^{3+} emission indicates efficient energy transfer from the molybdate or tungstate group to Eu^{3+}, as discussed before (*2*). In the case of $LiEuW_2O_8$ this transfer is not complete, and tungstate luminescence is observed. At this point we will discuss the energy transfer process of the tungstate group to Eu^{3+}. The critical distance R_c of energy transfer from the excited tungstate group to an Eu^{3+} ion is defined as the distance for which the probability of transfer equals the probability of radiative relaxation. We can estimate R_c in the case of electric dipole–dipole interaction with the formula (*17*):

$$R_c^6 = 0.6 \times 10^{28} \times \frac{4.8 \times 10^{-16}}{E^4} \times f \times \mathrm{SO}. \tag{1}$$

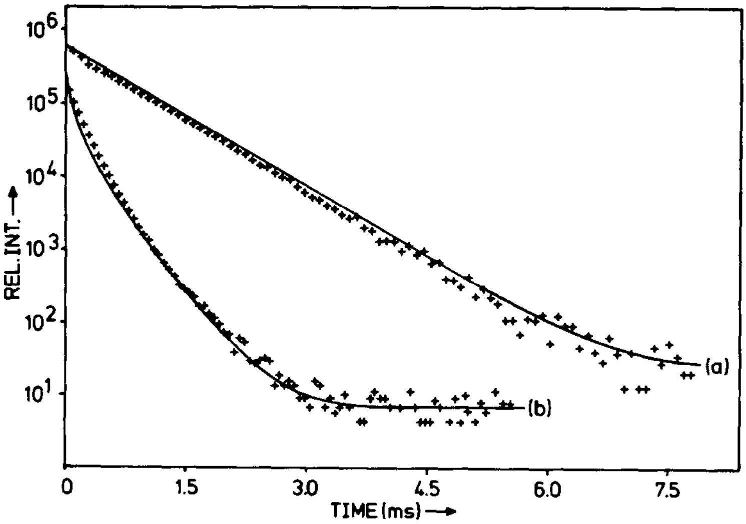

FIG. 4. Decay curves of the Eu^{3+} emission intensity in $KEuMo_2O_8$; $\lambda_{exc} = 527.75$ nm; $\lambda_{em} = 613.00$ nm. (a) $T = 4.2$ K, the solid line represents a fit to an exponential function; (b) $T = 300$ K, the solid line is a fit to Eq. (4) with $d = 2$.

TABLE I

VIBRONIC LINES IN THE LUMINESCENCE SPECTRA OF $CsEuMo_2O_8$ AT 4.2 K

Excitation spectrum[a]	Emission spectrum		Assignment vibrational mode
$^7F_0 \rightarrow {}^5D_0$: 17,190	$^5D_0 \rightarrow {}^7F_0$: 17,190	$^5D_0 \rightarrow {}^5F_2$: 16,290	
$^7F_0 \rightarrow {}^5D_0$: +120			Eu–O
$^7F_0 \rightarrow {}^5D_0$: +150			Eu–O
$^7F_0 \rightarrow {}^5D_0$: +210	$^5D_0 \rightarrow {}^7F_0$: −210	$^5D_0 \rightarrow {}^7F_2$: −210	Eu–O
$^7F_0 \rightarrow {}^5D_0$: +330		$^5D_0 \rightarrow {}^7F_2$: −290	Molybdate bending
$^7F_0 \rightarrow {}^5D_0$: +360			
$^7F_0 \rightarrow {}^5D_0$: +390	$^5D_0 \rightarrow {}^7F_0$: −380		
$^7F_0 \rightarrow {}^5D_0$: +420		$^5D_0 \rightarrow {}^7F_2$: −410	
$^7F_0 \rightarrow {}^5D_0$: +680	$^5D_0 \rightarrow {}^7F_0$: −660		Molybdate stretching
$^7F_0 \rightarrow {}^5D_0$: +770	$^5D_0 \rightarrow {}^7F_0$: −770	$^5D_0 \rightarrow {}^5F_2$: −760	
$^7F_0 \rightarrow {}^5D_0$: +870	$^5D_0 \rightarrow {}^7F_0$: −850	$^5D_0 \rightarrow {}^5F_2$: −850	
$^7F_0 \rightarrow {}^5D_0$: +930			

Note. All values in cm^{-1}.

[a] For the $^7F_0 \rightarrow {}^5D_2$ transition the vibronic spectrum is similar but more complicated due to the splitting of the $^5D_2$ level.

Here f is the oscillator strength of the $^7F_0 \rightarrow {}^5D_2$ transition of the Eu^{3+} ion which we estimate to be 10^{-7}, E is the energy of maximum spectral overlap ($\approx$2.5 eV), and SO is the normalized spectral overlap, which we estimate from our spectra to be about 1 eV^{-1}. This yields a value of R_c of 4.4 Å. This is about equal to the distance between the tungsten ion and its eight nearest cation neighbors ($\approx$4 Å), so that the transfer rate between an excited tungstate group and an Eu^{3+} nearest neighbor equals roughly the tungstate radiative rate. The compound $LiEuW_2O_8$ is a disordered scheelite, in which the Li^+ and Eu^{3+} ions are randomly distributed over the cation sites. The fraction of tungstate groups with n nearest Eu^{3+} neighbors is given by:

$$X_n = \binom{8}{8-n} \times (0.5)^8. \qquad (2)$$

Neglecting nonradiative processes, the relative amount of radiative emission from the tungstate group (A_W) is then given by the expression:

$$A_W = \sum_{0}^{n=8} X_n \times \left(\frac{1}{n+1}\right). \qquad (3)$$

In this way we calculate A_W to be 23%, which is in good agreement with the experimentally observed 20% tungstate emission. Therefore, we may conclude that electric dipole–dipole interactions are predominant in this system, and that any possible exchange interaction between the tungstate group and Eu^{3+} is only minor. The results also confirm that the Li^+ and Eu^{3+} ions are disordered. In ordered systems Eqs. (2) and (3) lead to A_W of 6%, because now only the terms with $n = 4$ are relevant.

4.2. Eu^{3+} Emission Spectra

The vibronic transitions of the Eu^{3+} ion in tungstate scheelites were investigated by Yamada and Shionoya (*16*). In Table I a comparison is made of the vibrational frequencies in the $CsEuMo_2O_8$ lattice, determined from our excitation and emission spectra. The lattice does not have the scheelite structure, but nevertheless the coupling with molybdate bending and stretching modes is here also clearly observable. The mode frequencies were estimated from data given in Ref. (*18*).

The differences observed in the emission spectra of the various compounds can be explained by differences in crystal structure. The Li and Na compounds of group 1 have the scheelite structure with cation disorder. This accounts for the broadening of the lines in the spectra. According to Ref. (*3*) $KEuMo_2O_8$ has an ordered scheelite structure which is triclinic. The Eu^{3+} polyhedra are ordered in sheets, forming a two-dimensional sublattice. The Eu^{3+} site symmetry is C_1. The number of lines in the $^5D_0 \rightarrow {}^7F_{0,1,2}$ transitions agrees with this site symmetry, but these lines are only slightly narrower than the lines in the spectra of the disordered scheelites. This suggests that $KEuMo_2O_8$ is also slightly disordered. This follows also from the vibrational spectra (*19*).

The structure of $KEuW_2O_8$ is isomorphous with that of α-KYW_2O_8 (*4, 20*) and contains WO_6 double chains. The Ln site symmetry is C_2. The emission spectrum is consistent with this symmetry, but the $^7F_1$ level is split in such a way that two levels are nearly degenerate. The sublattice of Eu^{3+} polyhedra is essentially one-dimensional.

The structure of $RbEuW_2O_8$ is monoclinic (*2*). The Eu^{3+} polyhedra form a one-dimensional sublattice, with *Ln* site symmetry C_1, consistent with the emission spectrum. The tungstate groups in this crystal structure occur in clusters of four.

Finally, the crystal structures of $RbEuMo_2O_8$ and $CsEuMo_2O_8$ are not yet known. The sharp emission lines and the threefold splitting of the $^7F_1$ level indicate that there is only one *Ln* site with low symmetry present in this lattice. However, it must be stressed that one should be careful in deriving site symmetries from Eu^{3+} emission spectra (*21*).

4.3 Concentration Quenching

The concentration quenching of the Eu^{3+} luminescence in the compounds under consideration in this paper was shown to be weak by Van Uitert (*1*), who diluted the Eu^{3+} sublattice with Y^{3+}. This indicates that energy migration in the concentrated compounds over the Eu^{3+} sublattice to acceptor sites is an inefficient process. At low temperatures migration has to take place via the $^7F_0$–$^5D_0$ transition on the Eu^{3+} ion. This transition has a very low intensity in these compounds (see Fig. 3), which makes the probability for transfer by multipole–multipole interaction very low. For short Eu–Eu distances energy transfer by exchange might have a reasonable rate (*8*). This distance varies from 4 to 5 Å in these compounds. Either transfer by exchange is not very probable in these compounds or the number of acceptors is low.

At higher temperatures the $^7F_1$ level of the Eu^{3+} ion becomes thermally populated and energy migration can occur via the transition $^7F_1$–$^5D_0$ (*15*). This is not a very efficient process, as must be concluded from the fact that the emission intensity of the Eu^{3+} luminescence in the investigated compounds decreases only by a factor of 3 to 4 going from 4.2 K to room temperature. In $EuAl_3B_4O_{12}$ this transfer process is reasonably efficient (*22*). However, in the present compounds the coordination of Eu^{3+} forbids a strong admixture of electric dipole–dipole character into the $^5D_0$–$^7F_1$ magnetic dipole transition, as was argued elsewhere (*23*).

With the structural data in mind, we have tried to analyze the decay curves of $RbEuW_2O_8$, $KEuW_2O_8$, and $KEuMo_2O_8$. The exponential curves at 4.2 K confirm that at this temperature only radiative relaxation of the Eu^{3+} ions occurs. The radiative decay times τ_0 are comparable to what has been found before for Eu^{3+} ions in oxidic lattices with charge transfer states at relatively low energies (*6–9, 15*). The nonexponentiality of the decay curves at room temperature implies that at this temperature energy migration takes place. In the case of one- and two-dimensional systems an expression was derived for the long-time donor intensity (in this case Eu^{3+}), using the theory of a random walk of the excitation energy over the donor sublattice to randomly distributed quenching sites (acceptors) (*14*):

$$I(t) = I(0)\exp[-^{t}/\tau_0 - Bt^{d/(d+2)}], \quad (4)$$

in which B is a constant depending on acceptor concentration and donor–donor transfer probability and d is the dimensionality of the system. In this model it is assumed that the acceptor sites trap the migrating energy at the first encounter. This assumption is valid in this case, since the acceptors are quenchers which do not allow back transfer. The room temperature decay curves of the three compounds could be fitted very well to Eq. (4) in which the appropriate value of d was substituted (see also Fig. 4). If we take $d = 1$ for $KEuMo_2O_8$ and $d = 2$ for $RbEuW_2O_8$ and $KEuW_2O_8$, the fit quality decreases, although not drastically. We conclude that the energy migration in these three compounds has a dimensionality lower than three, in agreement with the structural data. The best theoretical fit to the experiment is obtained for the dimensionality prescribed by the cyrstal structure data.

Acknowledgments

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