A Comparison between the Gd^{3+} Emission in the Scheelite Structure and the M'–$YTaO_4$ Structure

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The X-ray excited emission spectra of $CaMoO_4$:Gd, $CaWO_4$:Gd, M'–$YTaO_4$:Gd, and M'–$LuTaO_4$:Gd are reported and compared. The rate of energy transfer from the host lattice to Gd^{3+} varies strongly. The vibronic features in the Gd^{3+} emission are similar. Their intensities are compared with those for Eu^{3+} in the same lattice and discussed in terms of Judd's theory on vibronic transitions on rare-earth ions. © 1989 Academic Press, Inc.

1. Introduction

The scheelite and fergusonite host lattices, as well as the different M'–$YTaO_4$ host lattice, have frequently been used to obtain efficient luminescent materials (*1–3*). Part of these play an eminent role in the field of X-ray phosphors (*4*). Recently, M'–$LuTaO_4$ has also drawn attention for this purpose, in view of its very high density (9.75 g ml^{-1}) and despite the high price of lutetium oxide (*5*).

In the course of our studies of X-ray excited Gd^{3+} luminescence (*6, 7*) it seemed interesting to investigate the Gd^{3+} luminescence in these hosts and to compare the results. This is the purpose of the present paper. Emphasis will be upon the energy transfer from the host lattice to the Gd^{3+} ion and on the vibronic features in the Gd^{3+} emission spectra.

2. Experimental

Samples were prepared using techniques described elsewhere (*2, 3*). They were checked by X-ray powder diffraction. The way in which the optical measurements were performed has been described before (*8*).

3. Results

The following samples were investigated: $CaMoO_4$:Gd, $CaWO_4$:Gd, M'–$YTaO_4$:
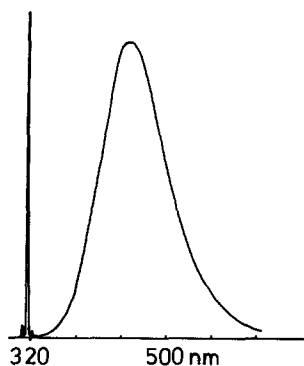
FIG. 1. X-ray excited emission spectrum of Ca-WO$_4$: Na,Gd. Broadband due to tungstate, sharp lines to Gd^{3+}.

Gd, and M'–LuTaO$_4$: Gd. The gadolinium concentrations were 5, 5, 1, and 1 at.%, respectively. Charge compensation in the former two samples was achieved by the addition of sodium.

The X-ray excited emission spectra consist of a broadband due to the host lattice groups (MoO$_4^{2-}$ or WO$_4^{2-}$ or tantalate (1) and a variable amount of sharp-line Gd^{3+} emission. The emission intensity under X-ray excitation is high. Figures 1 and 2 give two representative examples of these spectra, viz., CaWO$_4$: Na,Gd and M'–YTa O$_4$: Gd. For CaMoO$_4$: Gd no Gd^{3+} emission

TABLE I

RELATIVE INTEGRATED INTENSITIES OF THE Gd^{3+} AND HOST LATTICE GROUP EMISSIONS UNDER X-RAY EXCITATION AT 300 K

Composition	at.% Gd	Relative intensities	
		Host lattice group	Gd^{3+}
CaMoO$_4$: Na,Gd	5	100	0
CaWO$_4$: Na,Gd	5	98	2
M'–YTaO$_4$: Gd	1	81	19
M'–LuTaO$_4$: Gd	1	88	12

could be observed. Table I presents the relative integrated intensities of the Gd^{3+} emission and the host lattice group emission at room temperature.

The Gd^{3+} emission in Figs. 1 and 2 is due to the $^6P \rightarrow {}^8S$ transition. In case of the tantalates there is also a very small amount of $^6I \rightarrow {}^8S$ emission present (see Fig. 3). The relative intensity is a few tenths of a percent of the $^6P \rightarrow {}^8S$ emission. The assignment is as follows: 281.50 nm: $^6I_{7/2} \rightarrow {}^8S$, 278.25 nm: $^6I_{9/2,17/2} \rightarrow {}^8S$, 276.25 nm: $^6I_{11/2,15/2,13/2} \rightarrow {}^8S$.

Table II shows the vibronic features belonging to the $^6P \rightarrow {}^8S$ emission of YTaO$_4$: Gd and CaWO$_4$: Na,Gd together with an assignment. The integrated intensity of the vibronic features is about 8% rel-
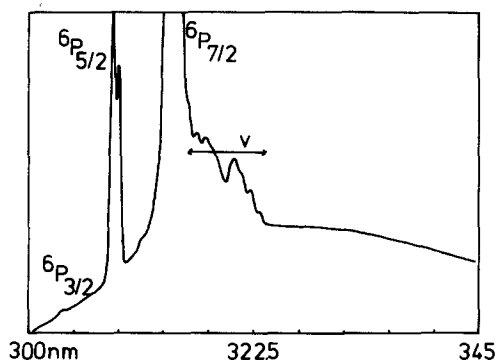

FIG. 2. X-ray excited emission spectrum of YTaO$_4$: Gd. Broadband due to tantalate, sharp lines to Gd^{3+}. (v) indicates the vibronic lines.

FIG. 3. The $^6I \rightarrow {}^8S$ line emission of Gd^{3+} in YTaO$_4$: Gd at the onset of the tantalate emission band.

TABLE II

ASSIGNMENT OF THE VIBRONIC FEATURES IN THE $^6P \to {}^8S$ EMISSION OF Gd^{3+} IN M'–$YTaO_4$ AND $CaWO_4$

$YTaO_4$: Gd	Assignment[a]		
31.850	$^6P_{7/2} \to {}^8S$ (e_1)		
31.765	$^6P_{7/2} \to {}^8S$ (e_2)		
31.645	e_1–205	} Gd vs tantalate	
31.565	e_2–200	} lattice vibration	(9)
31.475	e_1–325	ν_2 (tantalate)	(9)
31.410	e_2–355; e_1–440		
31.340	e_2–425	ν_4 (tantalate)	(9)
31.200	e_1–650	}	
31.135	e_2–630	} ν_3 (tantalate)	(9)
31.035	e_1–815	}	
30.950	e_2–815	} ν_1 (tantalate)	(9)
$CaWO_4$: Na,Gd			
31.960	$^6P_{7/2} \to {}^8S$ (e)		
31.575	e–385	ν_4 (tungstate)	(10)
31.190	e–770	ν_3 (tungstate)	(10)
31.060	e–900	ν_1 (tungstate)	(10)

Note. All values in cm^{-1}.
[a] e indicates electronic origin.

ative to that of the $^6P_{7/2} \to {}^8S$ electronic line. This value is host-lattice independent within the experimental accuracy.

4. Discussion

4.1. Relative Intensities in the Emission Spectra

For the overall interpretation of the emission spectra we assume that the mechanism of the X-ray excitation proceeds as follows: the greater part of the created charge carriers are trapped by the host lattice groups; subsequently, radiative recombination occurs on the host lattice groups, or energy transfer takes place to nearby Gd^{3+} ions, followed by Gd^{3+} emission. This mechanism is supported by several arguments:

(i) the host lattice groups can change their valency more easily than the Gd^{3+} ions;

(ii) undoped $CaWO_4$ and the two undoped tantalates are very efficient X-ray

phosphors with emission from the intrinsic host lattice groups (3–5, 8);

(iii) this mechanism is able to explain the difference in energy transfer rates in case of $LuTaO_4$ with several activators (5).

This model is also able to explain the results in Table I. If the transfer rate to Gd^{3+} exceeds the radiative rate of the host lattice group in the presence of nearest-neighbor Gd^{3+} ions, the relative amount of host lattice group emission is $(1 - x)^8$, where x is the Gd^{3+} concentration and 8 the number of cation sites nearest to a host lattice group. This results in 40% Gd^{3+} emission for $x = 0.05$, and 8% Gd^{3+} emission for $x = 0.01$. The tantalates show somewhat more Gd^{3+} emission than anticipated, indicating that the transfer to Gd^{3+} occurs also to Gd^{3+} ions in the next shell of cation neighbors. Therefore this simple model accounts reasonably well for the tantalates, but not at all for $CaWO_4$ and $CaMoO_4$.

The reason for this is rather obvious. The tantalate emission has its maximum close to the position of the ^6P level of the Gd^{3+} ion. This implies a favorable spectral overlap in the expression for the energy transfer rate. The critical distances for transfer of this type is slightly larger than the Ta–Gd distance (10). This implies that a model in which tantalate–Gd^{3+} transfer occurs over nearest, and possibly next-nearest, neighbors is expected to be a realistic one.

In the case of $CaMoO_4$: Na,Gd this spectral overlap has completely vanished. Whereas the ^6P level is at about 313 nm, the molybdate emission becomes observable only for $\lambda > 380$ nm. In the absence of molybdate–Gd^{3+} transfer, no Gd^{3+} emission can be expected.

In the case of $CaWO_4$: Na,Gd the spectral overlap is small, but not zero, leading to a low amount of Gd^{3+} emission. A quantitative evaluation seems impossible, since it is not known how the excess charge of

TABLE III

RATIO OF INTEGRATED INTENSITIES OF VIBRONIC LINES AND ELECTRONIC LINES FOR Gd^{3+} AND Eu^{3+} IN $CaWO_4$ AND $LuTaO_4$

	$\dfrac{^6P_{7/2}-^8S\ (v)}{^6P_{7/2}-^8S\ (e)}$		Ref.
$CaWO_4$: Na,Gd	0.09		This work
$LuTaO_4$: Gd	0.09		This work
	$\dfrac{^7F_0-^5D_2\ (v)}{^7F_0-^5D_2\ (e)}$	$\dfrac{^7F_0-^5D_2\ (v)}{^7F_0-^5D_1\ (e)}$	
$CaWO_4$: Na,Eu	0.26	0.92	(11)
$LuTaO_4$: Eu	0.25	1.0	(12)

the Gd^{3+} ion influences the energy levels of the neighboring tungstate groups.

The rate of tungstate → Gd^{3+} (^6P) transfer is comparable to the rate of tantalate →Gd^{3+} (^6I) transfer because the ^6I levels are also situated on the edge of the tantalate emission band. This explains the presence of weak ^6I emission in the tantalates, whereas it is absent in the other hosts.

4.2. The Vibronic Gd^{3+} Spectra

The emission of the Gd^{3+} ion in the 305–325-nm region consists of the dominant $^6P_{7/2} \rightarrow \,^8S$ emission, the thermally activated $^6P_{5/2} \rightarrow \,^8S$ emission on its shorter wavelength side, and vibronic features on its longer wavelength side. Their intensity is only one order of magnitude less than that of the electronic $^6P_{7/2} \rightarrow \,^8S$ transition. The $^6P_{5/2} \rightarrow \,^8S$ emission disappears if the temperature is lowered.

The $^6P_{7/2} \rightarrow \,^8S$ emission is ideal for studying the vibronic features, because the spectrum has no electronic lines at lower energies. The relative intensity of the vibronic lines seems to be independent of the hosts used in this study. It is interesting to note that the same is true for Eu^{3+}. Relevant data are compiled in Table III. In the case of Eu^{3+} the $^7F_0-^5D_2$ excitation lines are as favorable for vibronic studies as the $^6P_{7/2} \rightarrow \,^8S$ emission lines of Gd^{3+} for the same reason.

According to Judd (13) the intensity of a given vibronic line is determined by, among other things, the factor $(g + 6\alpha R^{-3})^2$, where g is the charge of the ligands, α their polarizibility, and R the rare-earth-ion-to-ligand distance. It turns out that g and $6\alpha R^{-3}$ are of the same order of magnitude. In the present host lattices R will be roughly equal, and $g = 2$ for the tungstate and $g = 3$ for the tantalate. The polarizibility α is approximately by the classical expression $\alpha = e^2m^{-1}\ (\omega_0^2 - \omega^2)^{-1}$ (14), where e and m are the electronic charge and mass, respectively. Further ω_0 is the resonance absorption frequency and ω the frequency involved. The quantum-mechanical expression is more complicated and contains the oscillator strength which, however, is about equal for the host lattice groups involved.

Using the values of the frequency of the vibronic lines involved, and the frequencies of the relevant absorption transitions, i.e. ~40.000 cm⁻¹ for the tungstate group and ~45.000 cm⁻¹ for the tantalate group, we arrive at the result that α is about a factor 1.5 higher for the tungstate than for the tantalate group. Since g is a factor 1.5 higher for the tantalate, and both factors are equally important, this shows that the vibronic intensities should also be equal.

This consideration leads to an interesting prediction. If the absorption of the host lattice group shifts to lower energies, the vibronic intensities should increase. This is what has been observed by one of us (12). The most extreme situation is reached for $SrTiO_3: Eu^{3+}$. The titanate absorption is at about 25.000 cm⁻¹. This implies that α is one order of magnitude higher than in the tungstate group. This explains nicely the very strong vibronic lines in the emission spectrum of $SrTiO_3: Eu^{3+}$, an old observation which has not yet found an explanation (15).

The assignment of the vibronic features is not discussed here. It parallels that de-

scribed in other studies (*11, 16, 17*). In conclusion, the comparison of the emission spectra obtained points to different rates of transfer to Gd^{3+} and to equal intensities of the vibronic features. These observations are explained in terms of existing theories.

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