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Luminescence properties of Eu^{3+}-doped $Al_2(WO_4)_3$

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Emission spectra of $Al_2(WO_4)_3$ doped with Eu^{3+} were recorded at room temperature (orthorhombic phase) and at 10 K (monoclinic phase). The luminescence excitation spectra and luminescence decay profiles were recorded for both structural modifications at RT and LN_2T, and the luminescence lifetimes of Eu^{3+} have been estimated. Two-site behaviour of the optically active ions in both phases has been revealed in the luminescence studies. However, the emission decay profiles give one lifetime of the $^5D_2$ level, equal to 1.8 ms and 848.4 μs at room temperature and liquid nitrogen temperature, respectively. The results obtained have been explained in terms of an unusual location of Eu^{3+} ions inside the crystal tunnels, parallel to the *c*-axis.

Key words: *aluminium tungstate; luminescence; excitation; optical properties*

1. Introduction

This paper reports on the luminescence properties of $Al_2(WO_4)_3$ tungstate doped with Eu^{3+} ions. $Al_2(WO_4)_3$ belongs to the $A_2(BO_4)_3$ group of compounds (A = Cr, Al, Sc, In; B = Mo, W), which have been extensively investigated due to their unusual chemical and physical properties. These compounds exhibit a ferroelastic phase transition, from an orthorhombic *Pnca* (D_{2h}^{14}) to a monoclinic $P2_1/a$ (C_{2h}^{5}) structure [1–3]. The orthorhombic phase exhibits a negative thermal expansion [2–6]. High trivalent ion conduction has been discovered in these crystals [7–10]. A pressure-induced amorphization has been recently described in scandium molybdate and tungstate at moderate pressures [10–12]. Finally, these crystals can serve as crystal hosts for transition metal or lanthanide ion doping. For the above reasons, the tungstates

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and molybdates of this family have been applied in fuel cell electrolytes [13], gas sensors [13], laser materials [14], optoelectronics [6], and as catalysts support [6].

The effect of pressure on the resistivity and compressibility of $Al_2(WO_4)_3$ has been investigated [15]. It was shown that the resistance of the crystal is strongly frequency -dependent and an anomalous change appears at about 5 kbar. Both the resistance and compressibility prove the occurrence of a reversible phase transition at this pressure.

High-pressure Raman studies of the $Al_2(WO_4)_3$ crystal have been performed by us, showing the onset of two reversible phase transitions at 0.35 and 2.9 GPa [16]. These transitions have been explained to be the result of a reorientation of the tungstate tetrahedra. The phase in the range 0.35–2.9 GPa is consistent with the low-temperature monoclinic phase $P2_1/a$.

In the present paper, we report the luminescence properties of Eu^{3+} ions in the $Al_2(WO_4)_3$ host. In the previous paper, we studied this crystal doped with Cr^{3+} ions [14]. It was stated that the activator substitutes the 8d position occupied by aluminium(III) ions. Since the ionic radii of Al^{3+} and Cr^{3+} ions in this coordination are equal to 0.535 and 0.615 Å, respectively, the mutual substitution of these ions was easily done [14]. In the present study, we have tried to introduce Eu^{3+} ions into the $Al_2(WO_4)_3$ crystal despite the fact that the ionic radius of such an ion is significantly larger (0.947 Å). It is expected that a positive result of this substitution will allow a new laser material containing lanthanide ions to be obtained.

2. Experimental

The synthesis of $Al_2(WO_4)_3$:Eu single crystals was carried out using the flux method described in [14, 16].

Emission experiments were performed using a dye laser with a 467 nm excitation wavelength. The emission was detected with a cooled R 5108 photomultiplier (λ = 400–1200 nm). A low temperature (10 K) was obtained by mounting the sample into a Leybold temperature-controlled closed-cycle cryostat.

Lifetime measurements were performed with an optical parametric oscillator as the excitation source. The 21 410 cm^{-1} line was chosen for the excitation. The emitted light was detected by a photomultiplier connected to a Tektronix TDS 3052 oscilloscope. Measurements were performed at 300 and 77 K.

We tried to measure electronic absorption spectra of the crystals at room temperature using a Cary 5 spectrometer. These spectra could not be recorded due to a small concentration of Eu^{3+} ions. For this reason, the excitation spectra were measured. They were recorded using a SSF 01 Spectrofluorimeter equipped with a 160 W Xe lamp with a sapphire window and an Al-coated parabolic reflector. For low-temperature measurements (7 K), a continuous flow helium cryostat (Oxford model) equipped with a temperature controller was used.

3. Results and discussion

Structural properties. The structure of $Al_2(WO_4)_3$ has been determined by us using low-temperature X-ray equipment [14]. In the 210–300 K temperature range this crystal is orthorhombic with the space group *Pbcn* (D_{2h}^{14}) and four formula units per unit cell. The lattice parameters at 293 K are: $a = 12.571$, $b = 9.046$ and $c = 9.129$ Å. Low-temperature X-ray studies revealed the presence of a first-order phase transition around 210 K. The phase stable below 210 K is monoclinic with the space group $P2_1$ ($P2_1/n$). Its lattice parameters at 160 K are: $a = 8.962$, $b = 9.080$, $c = 12.587$ Å and $\beta = 90.06°$. In the orthorhombic phase, the active ions are located in a slightly distorted octahedral arrangement of the oxygen atoms. The site symmetry of Al^{3+} ions is C_1, but its local symmetry can be regarded as close to the tetragonal C_{4v} because one Al–O distance significantly differs from the others. On the other hand, the monoclinic phase showed the presence of four different Cr^{3+} sites in the crystal [14]. The Eu^{3+} ions in the sample could replace the Al^{3+} ions, in a similar way as Cr^{3+} ions. However, another effect cannot be excluded. As the structure of the $Al_2(WO_4)_3$ host contains two tunnels of different sizes (Fig. 1) and the difference between the ionic radii of Eu^{3+} and Al^{3+} ions is very large, it is very likely that the active ions occupy these tunnels instead of the Al^{3+} sites. The tunnels are directed parallel to the *c*-axis of the orthorhombic phase and the *b*-axis of the monoclinic phase.

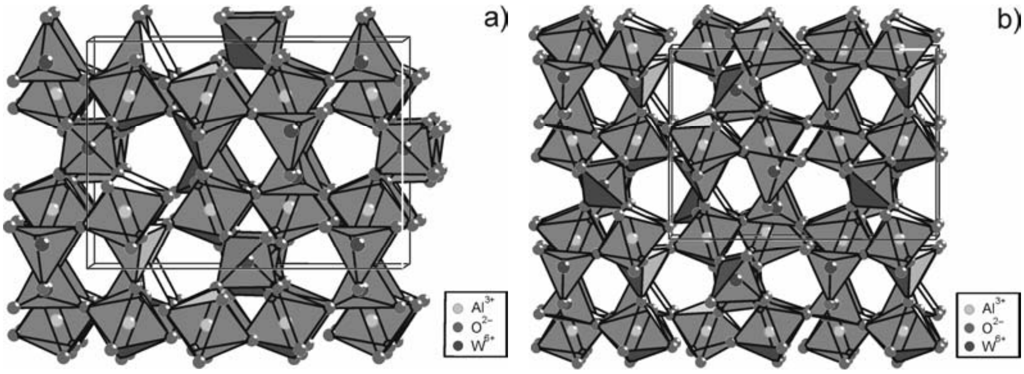

Fig. 1. Crystal structure of the $Al_2(WO_4)_3$ host in two phases: a) high-temperature (orthorhombic) phase and b) low-temperature (monoclinic) phase

Luminescence spectra. The luminescence spectra of the $Al_2(WO_4)_3$:Eu crystal recorded at 300 and 10 K are shown in Fig. 2. Table 1 lists the wavenumbers of the electronic transitions observed in the visible region. The presence of $^5D_0 \rightarrow {}^7F_{0-4}$ transitions and $^7F_{1,2}$ *J*-degeneracy prove that the site symmetry of Eu^{3+} ions both in the orthorhombic and monoclinic phases could be described by low-symmetry point groups: C_1, C_2, C_s or C_{2v} [17, 18]. The excitation spectra (Fig. 3) measured at 300 and 7 K confirm this conclusion. Because at room temperature the population of the $^7F_1$

level is about 27%, a transition from this level to $^5D_1$ is observed. The same situation is not observed at low temperature due to a dramatic decrease in the $^7F_1$ level population. From the luminescence and excitation spectra recorded at low temperatures, the Stark level components of electronic multiplets were calculated. Comparing the number of the theoretical and experimental multiplet components, we can say that the site symmetry of Eu^{3+} ions is low. The number of some components is higher than expected from the selection rules for monoclinic symmetry. We can, therefore, say that Eu^{3+} ions occupy two sites in two structural modifications of the crystal and their excitation and emission properties are the same (Table 2).

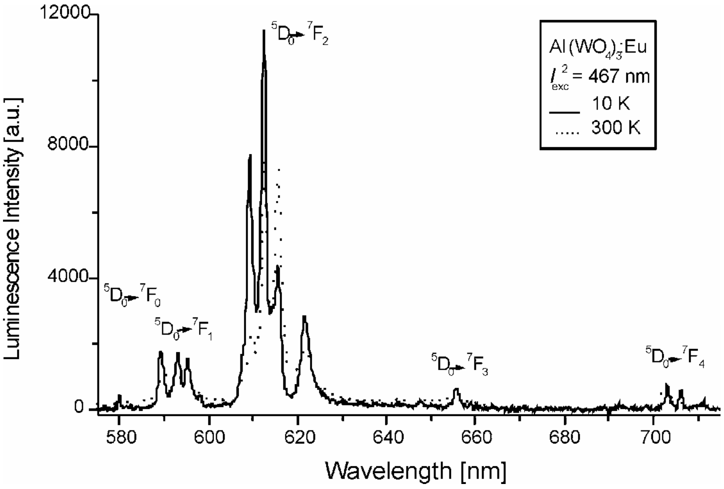

Fig. 2. Emission spectra obtained from the Eu^{3+} co-doped $Al_2(WO_4)_3$ crystal at 300 and 10 K. The excitation wavelength was 467 nm

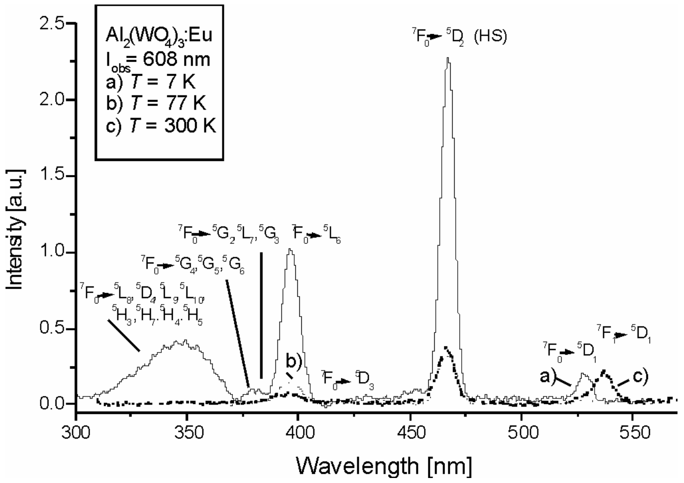

Fig. 3. Excitation spectra obtained for the $Al_2(WO_4)_3$:Eu crystal at 300, 77 and 7 K; λ_{obs} = 608 nm

Table 1. Energy of the Eu(III) emission bands measured for the $Al_2(WO_4)_3$:Eu crystal[*]

Transition	T = 10 K		T = 300 K	
	[cm^{-1}]	[nm]	[cm^{-1}]	[nm]
$^5D_0 \rightarrow {}^7F_0$	17 253	579.6 sh		
	17 241	580	17 244	579.9
$^5D_0 \rightarrow {}^7F_1$	16 969	589.3		
	16 883	592.3 sh	16 915	591.2 b
	16 861	593.1		
	16 812	594.8 sh	16 798	595.3
	16 798	595.3		
	16 711	598.4		
$^5D_0 \rightarrow {}^7F_2$	16 458	607.6 sh		
	16 415	609.2	16 404	609.6
	16 329	612.4	16 324	612.6
	16 281	614.2 sh		
	16 247	615.5	16 244	615.6
	16 088	621.6	16 090	621.5
$^5D_0 \rightarrow {}^7F_3$	15 439	647.7		
	15 284	654.3 sh	15 344	651.7
	15 253	655.6		
	15 211	657.4 sh	15 265	655.1
$^5D_0 \rightarrow {}^7F_4$	14 438	692.6	14 424	693.3
	14 316	698.5	14 316	698.5
	14 245	702 sh	14 243	702.1
	14 221	703.2	14 225	703
	14 203	704.1 sh	14 192	704.6 sh
	14 158	706.3	14 162	706.1
	14 063	711.1	14 069	710.8

[*] b – broad band, sh –shoulder.

The intensity of the $^5D_0 \rightarrow {}^7F_0$ band transition is very weak although it is clearly seen that its bandwidth is large (24.3 and 26.7 cm^{-1} at room and low temperature, respectively). This band could be deconvoluted into two components, which also suggests the existence of two sites occupied by Eu^{3+} ions.

Optical transitions typical of Eu^{3+} ions in a crystal correspond mainly to intra f^N transitions of predominantly electric dipole character. On the other hand, electric dipole transitions between states of the same configurations are strictly parity forbidden and the spectra observed result from mixing states of opposite parity during non-centrosymmetric interactions. The f-f transitions are allowed as the magnetic-dipole ones that obey the selection rule $\Delta J = 0, \pm 1$. The $^5D_0 \rightarrow {}^7F_2$ transition is electric dipole in character, in contrast to the $^5D_0 \rightarrow {}^7F_1$ one, which is purely magnetic dipole allowed. Fluorescence spectra are known to be very sensitive to perturbations of the first coordination sphere. The ratio between the integrated intensities of the transitions: $I(^5D_0 \rightarrow {}^7F_2) : I(^5D_0 \rightarrow {}^7F_1) = I_{0\text{-}2} : I_{0\text{-}1}$ was related to the covalency of the Eu^{3+} ion surroundings via short-range effects [18–26]. Comparing our results, it is seen that the $I_{0\text{-}2} : I_{0\text{-}1}$ ratio is almost the same at both room and low temperature and equals 5.5, meaning that the covalent nature of the local Eu^{3+} ion sites is the same.

Table 2. Stark level components of electronic multiplets of Eu^{3+} ions in $Al_2(WO_4)_3$ crystal

(S, L, J) multiplet	Energy of Stark levels [cm^{-1}]	The number of Stark levels		ΔE [cm^{-1}]
		Theoretical	Experimental	
$^7F_0$	0, 12	1	2	12
$^7F_1$	272, 358, 380, 429, 443, 530	3	6	258
$^7F_2$	783, 826, 912, 960, 994, 1153	5	6	370
$^7F_3$	1802, 1957, 1988, 2030	7	4	228
$^7F_4$	2803, 2925, 2996, 3020, 3038, 3083, 3178	9	7	375
$^5D_1$	18818, 18889, 18954	3	3	136
$^5D_2$	21286, 21413, 21542	5	3	256
$^5D_3$	24378, 24462	7	2	84
$^5L_6$	24740, 25151, 25240, 25549, 25733	13	5	993

Lifetime measurements. Lifetime measurements of the $^1D_2$ level were carried out with a 467 nm excitation. The emission decay profiles measured at 300 and 77 K are shown in Fig. 4. We have found that the data can be well fitted by a single exponential profile both at high and low temperatures.

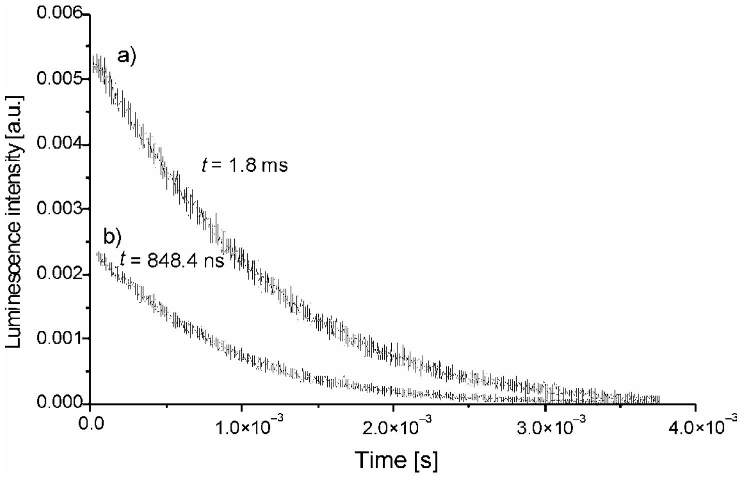

Fig. 4. Room-temperature (a) and liquid nitrogen-temperature (b) time dependence of Eu^{3+} emission obtained for the $Al_2(WO_4)_3$:Eu crystal. The excitation wavelength was 467 nm

The lifetime of the $^5D_2$ level in the material studied is 1.8 ms at 300 K and 848.4 μs at 77 K. These results do not agree with X-ray data, which predict a one-site structure of the orthorhombic phase and a two-site behaviour of the monoclinic phase. The presence of only one component in the decay profile at 77 K suggests that the two different Eu^{3+} sites of the monoclinic phase have nearly the same lifetimes of $^5D_2$ luminescence.

4. Conclusions

Eu^{3+} ions do not replace the aluminium(III) sites in the $Al_2(WO_4)_3$ crystal, as observed for Cr^{3+} ions [14]. The concentration of the active ions in this sample is very low. The Eu^{3+} ions are located inside the tunnels that run parallel to the *c*-axis of orthorhombic phase and are also present in the monoclinic phase. Luminescence spectra indicate that Eu^{3+} ions occupy two sites, both in the orthorhombic and monoclinic phase. The coordination shells of the both sites have nearly the same degree of covalency and probably very close bond lengths. This is the reason for their optical similarity, i.e. very similar optical transition energies and excited state lifetimes. The present study therefore shows that the results obtained for the Eu^{3+} doped $Al_2(WO_4)_3$ crystal are different from those obtained for the Cr^{3+} doped sample. The main conclusion of the present study is that the crystal studied is a prospective host for transition metal ions [14], but cannot be applied for f-electron elements.

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