

JAHN–TELLER EFFECT IN THE Sb^{3+} EMISSION IN ZIRCON-STRUCTURED PHOSPHATES

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The luminescence of the Sb^{3+} ion in YPO_4 , LuPO_4 and ScPO_4 consists of two emission bands. The intensity ratio of these bands depends strongly on temperature. The observed phenomena are satisfactorily explained by assuming a dynamical Jahn–Teller effect to be operative in the radiative excited state of the Sb^{3+} ion.

1. Introduction

The phosphates ScPO_4 , LuPO_4 and YPO_4 form an interesting host lattice to study the luminescence properties of trivalent antimony. These phosphates have the tetragonal zircon structure, in which only one crystallographic position is available for the trivalent ions which are coordinated by eight O^{2-} ions (site symmetry D_{2d}).

Grafmeyer et al. [1,2] investigated the luminescence of YPO_4 doped with Sb^{3+} . They found two emission bands with maxima at 300 nm (the UV band) and 395 nm (the visible band). Below 40 K, mainly UV emission was observed. At 25 K the intensity of the UV band decreased rapidly while at the same time the intensity of the visible band increased, leaving only visible emission from 40–160 K. Finally above 160 K, both emissions were observed. No definite explanation for the observed phenomena was presented. We reinvestigated the luminescence properties of $\text{YPO}_4\text{—Sb}^{3+}$. In addition, we investigated two isostructural compounds viz. $\text{LuPO}_4\text{—Sb}^{3+}$ and $\text{ScPO}_4\text{—Sb}^{3+}$.

2. Experimental

$\text{YPO}_4\text{—Sb}^{3+}$ was prepared as follows: Y_2O_3 (Highways 99.99%) and Sb_2O_3 (Merck p.a.) were dissolved in diluted HCl and precipitated with ammonia. After firing the precipitate for 3 h at 500°C we obtained

$(\text{Y,Sb})_2\text{O}_3$. This oxide mixture was ground with $(\text{NH}_4)_2\text{HPO}_4$ (Merck p.a., excess 15%) and then fired at 900°C during 5 h, followed by a 30 h firing period at 1200°C.

For $\text{LuPO}_4\text{—Sb}^{3+}$ and $\text{ScPO}_4\text{—Sb}^{3+}$ a different preparation method had to be used since it turned out that no antimony had been incorporated after the long firing period at 1200°C. Therefore LuPO_4 was prepared by grinding Lu_2O_3 (Highways 99.999%) with ammonium phosphate (excess 15%) and firing the mixture for 3 h at 900°C followed by 20 h firing at 1200°C. Then a mixture of Sb_2O_3 and ammonium phosphate (excess 15%) was added to the obtained LuPO_4 ; after grinding the mixture was fired during 12 h at 900°C followed by a 5 h firing period at 1200°C. Similarly, $\text{ScPO}_4\text{—Sb}^{3+}$ was prepared starting from Sc_2O_3 (Highways 99.99%).

All samples were checked by X-ray powder diffraction using $\text{CuK}\alpha$ radiation. Only a small part of the starting amount of antimony is really built into the lattice, especially in the case of $\text{ScPO}_4\text{—Sb}^{3+}$ as indicated by the diffuse reflectance spectra.

Luminescence spectra were recorded using a Perkin–Elmer MPF-3A spectrofluorimeter equipped with an Oxford CF-100 continuous flow cryostat. Reflectance spectra were recorded at room temperature using a Perkin–Elmer EPS-3T spectrophotometer.

3. Results

The reflectance spectra of $\text{YPO}_4\text{--Sb}^{3+}$, $\text{LuPO}_4\text{--Sb}^{3+}$ and $\text{ScPO}_4\text{--Sb}^{3+}$ were obtained from 210 to 360 nm. They show a doublet-type absorption band between 220 and 255 nm. Since the pure phosphates have no absorption in this region, this confirms that the samples indeed contain Sb^{3+} . Moreover, since no other absorption bands are observed, the activator occupies only one crystallographic position in agreement with the structure of the host lattice.

Due to instrumental limitations all emission spectra were obtained by excitation in the long-wavelength component of the absorption doublet, viz. $\lambda_{\text{exc}} = 245$ nm (see table 1). For the samples two emission bands were observed, one in the UV region (the UV band), the other (mainly) in the visible region (the visible band). The maxima of these bands shift slightly with temperature. In table 1 these maxima at 8 K and at room temperature are given.

The intensity ratio of the visible and UV band is strongly temperature dependent as shown in fig. 1 for the case of $\text{YPO}_4\text{--Sb}^{3+}$. At low temperature ($T < 25$ K), emission is mainly UV. Between 25 and 40 K, the intensity of the UV emission decreases rapidly while that of the visible emission increases. At $T > 50$ K only the visible band is observed. At 180 K, however, the UV band reappears. At higher temperatures the visible emission decreases and the UV band increases. In fig. 2, the UV and visible emission intensities for each of the three compositions are plotted against temperature.

Inspection of fig. 2 clearly reveals that the UV-visible intensity ratio depends on both temperature and host lattice. Furthermore, we note that tempera-

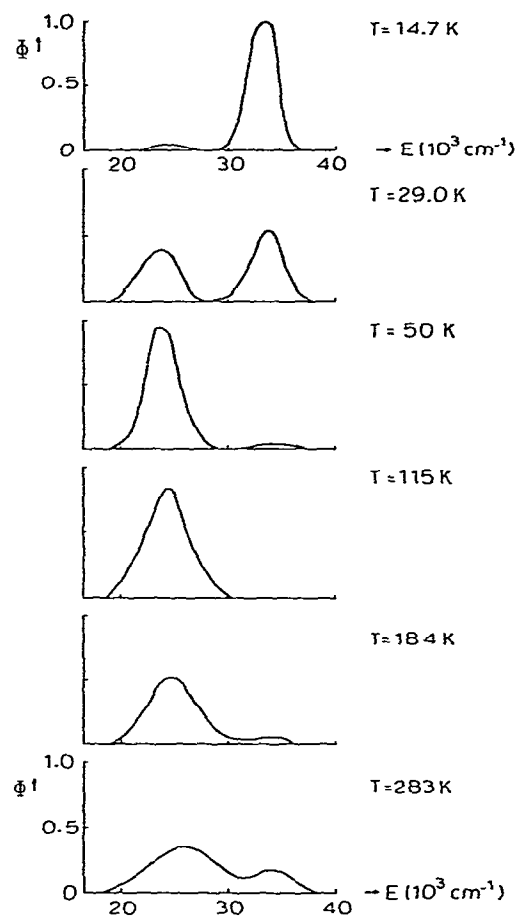


Fig. 1. Emission spectra of $\text{YPO}_4\text{--Sb}^{3+}$ at different temperatures. $\lambda_{\text{exc}} = 245$ nm.

ture quenching occurs at higher temperatures for all three compositions, the extent of quenching increasing in the order $\text{YPO}_4 < \text{LuPO}_4 < \text{ScPO}_4$ (see fig. 2).

Finally, the emission spectra obtained from samples with a varying antimony content show the UV-visible intensity ratio to be independent of the Sb^{3+} concentration.

4. Discussion

The Sb^{3+} ion has an electron configuration $5s^2$, which corresponds to a 1S_0 ground state. The first excited configuration is $5s5p$ giving a triplet state

Table 1
Positions of the maxima of the emission bands of the Sb^{3+} ion in zircon-type phosphates at room temperature (RT) and at $T = 8$ K (all values in nm)

Composition	Excitation wavelength	Emission maxima			
		visible band		UV band	
		8 K	RT	8 K	RT
$\text{YPO}_4\text{--Sb}^{3+}$	245	415	395	290	295
$\text{LuPO}_4\text{--Sb}^{3+}$	245	400	380	290	295
$\text{ScPO}_4\text{--Sb}^{3+}$	240	365	350	—	300

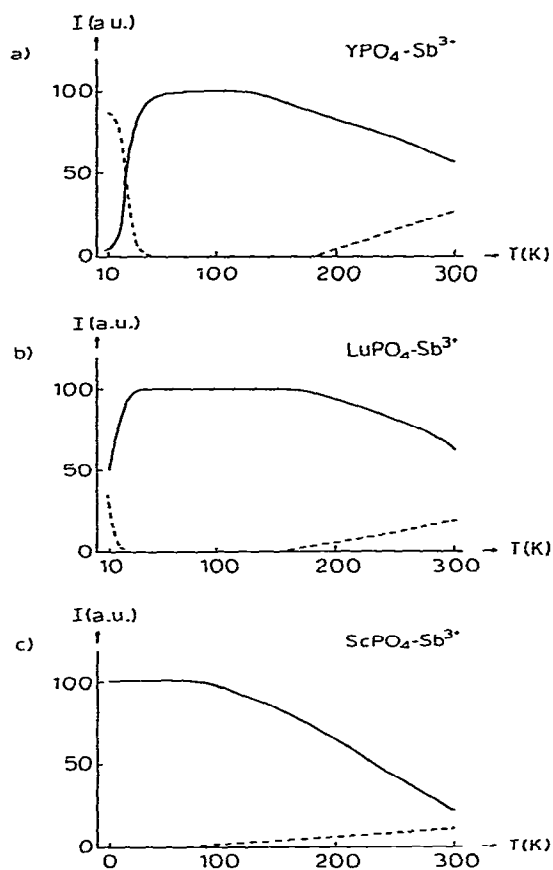


Fig. 2. Emission intensity versus temperature for the visible band (full line) and the UV band (broken line) of $\text{YPO}_4\text{-Sb}^{3+}$ (a), $\text{LuPO}_4\text{-Sb}^{3+}$ (b) and $\text{ScPO}_4\text{-Sb}^{3+}$ (c).

3P_0 , 3P_1 , 3P_2 and a singlet state 1P_1 . The $^1S_0\text{--}^1P_1$ transition (usually designated as the "C band") is allowed; the $^1S_0\text{--}^3P_1$ transition is spin forbidden, but spin-orbit coupling relaxes this selection rule. The other two transitions are strictly forbidden. The $^1S_0\text{--}^3P_1$ transition ("A band") is the transition with the lower energy.

In the reflectance spectra we observed for all three compositions only one absorption band with a doublet character which must be ascribed to the A band transition. The splitting of the A band is a well known phenomenon for s^2 ions in which the 3P_1 state is perturbed by the Jahn-Teller effect [3]. Therefore, we must conclude that excitation took place in the 3P_1 level, implying that the emission originates from the

same level (or the underlying 3P_0 trap level).

It is important to note that the two emission bands are obtained by one and the same excitation wavelength and that their intensity ratio is independent of the Sb^{3+} concentration. This leads to the conclusion that we are not dealing with two different luminescent centres (which might be connected by energy transfer), but that both emissions originate from one and the same Sb^{3+} ion, in line with the fact that only one crystallographic site is available for the cations in the host lattice. The observation of two emissions from one centre is not uncommon for s^2 ions and has been observed for example for the monovalent s^2 ions in the alkali halides [3,4].

The only way to explain satisfactorily the observed temperature dependence of the intensity ratio of the two emissions shown in fig. 2 is to assume that we are dealing with a dynamical Jahn-Teller effect, working on the 3P_1 adiabatic potential energy surface (APES). In alkali halides doped with Ti^+ -like ions, the APES of the $^3T_{1u}$ (3P_1) relaxed excited state shows two minima, arising from the Jahn-Teller coupling of the orbital triplet state to the e_g and t_{2g} lattice modes. These minima are labeled X and T and give rise to two different emission bands: the A_T band at higher energy

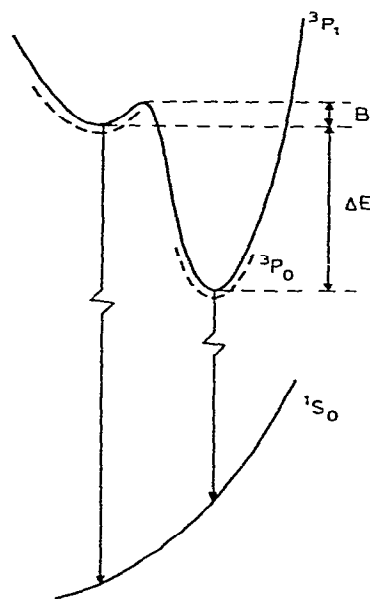


Fig. 3. Schematic configurational coordinate diagram for $\text{LnPO}_4\text{-Sb}^{3+}$ ($\text{Ln} = \text{Y, Sc, Lu}$). See also text.

Table 2
APES parameter values^{a)} for the 3P_1 relaxed excited state of Sb^{3+} ions in zircon-type phosphates

Composition	Ionic radius ^{b)} (Å)	ΔE (cm ⁻¹)	B (cm ⁻¹)
YPO ₄ -Sb ³⁺	$r(Y^{3+}) = 1.015$	1040 ± 80	80 ± 10
LuPO ₄ -Sb ³⁺	$r(Lu^{3+}) = 0.97$	800 ± 40	40 ± 8
ScPO ₄ -Sb ³⁺	$r(Sc^{3+}) = 0.87$	600 ± 70	<20

^{a)} See fig. 3 for the definition of ΔE and B .

^{b)} See ref. [5].

and the A_X band at lower energy. Correspondingly, the visible emission band in the present phosphates may be identified as the A_{vis} band, and the UV band as the A_{UV} band.

Fig. 3 gives a schematic picture of the relevant configurational coordinate diagram showing the two minima vis and UV. These minima are separated by an energy barrier, denoted as B , while the energy difference between the vis and UV minima is denoted as ΔE . The values of B and ΔE can be derived from the observed temperature dependence of the emission intensities (e.g. ref. [14]).

With the present experimental data on the UV-visible intensity ratios for all three compositions we calculated provisional values for B and ΔE . For ScPO₄-Sb³⁺ no B value could be calculated since no UV emission is observed at 8 K. However, the barrier height in ScPO₄-Sb³⁺ must have a finite value, because we observe two emission bands at higher temperatures. Furthermore, since at 8 K only visible emission is observed, the B value must be lower than 20 cm^{-1} . The calculated values for B and ΔE are given

in table 2. The cationic radii for the three host lattices are also included in table 2.

Comparison of cationic radii with the calculated values for ΔE and B suggests a relation between the radius of the host-lattice cation and the value of ΔE and B : the larger the space available for the Sb^{3+} ion, the larger the values of ΔE and B . Additional experiments are in preparation to obtain more accurate data over a wider temperature range, allowing a more detailed discussion of the present results.

In conclusion we remark that a preliminary explanation of the emission spectra of LnPO₄ (Ln = Y, Lu, Sc) is possible by assuming a dynamical Jahn-Teller effect working on the APES of the 3P_1 relaxed excited state of Sb^{3+} . The observed temperature behaviour of the UV and visible emission bands can be understood by assuming two minima in the APES of the 3P_1 relaxed excited state. The relative depths of these minima seem to depend on the radius of the host-lattice cation.

References

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