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The VO_4^{3-} and Eu^{3+} Luminescence in Oxides with Ordered β-K_2SO_4 Structure

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The VO_4^{3-} and Eu^{3+} luminescence in compounds with ordered β-K_2SO_4 structure is reported. The ratio of the Eu^{3+} and vanadate emission intensity depends on the excitation energy.

Introduction

Recently Salmon *et al.* (*1*) have described compounds of the type $Na_3La(PO_4)_2$ and $Na_3La(VO_4)_2$ with a superstructure of β-K_2SO_4. We have investigated the luminescence of the vanadate group and the Eu^{3+} ion in this lattice. The luminescences of $Na_3La(VO_4)_2$, $Na_3La(PO_4)_{1.9}(VO_4)_{0.1}$, and $Na_3La_{0.98}Eu_{0.02}(VO_4)_2$ are reported.

Experimental

The samples were prepared by firing an intimate mixture of the starting materials at a temperature of 1050°C in air. Starting materials were Na_2CO_3, NH_4VO_3, $(NH_4)_2HPO_4$ (all Merck, p.a.), La_2O_3 (Koch Light 99.9%), and Eu_2O_3 (Fluka SG, puriss). Samples were checked by X-ray analysis using a Philips diffractometer with Cu$K\alpha$ radiation. Emission and excitation spectra were measured for all compounds. Furthermore, the quenching temperature and the decay time of the luminescence of $Na_3La(VO_4)_2$ were determined. The performance of the optical measurements has been described elsewhere (*2*).

Results

At 77°K, $Na_3La(VO_4)_2$ and $Na_3La(PO_4)_{1.9}(VO_4)_{0.1}$ show a yellow luminescence of medium intensity. At room temperature this luminescence is quenched. $Na_3La_{0.98}Eu_{0.02}(VO_4)_2$ shows an orange luminescence of medium intensity at 77°K, whereas at room temperature a weak red luminescence is observed. In Fig. 1 we present the emission and excitation spectra of $Na_3La(PO_4)_{1.9}(VO_4)_{0.1}$, as recorded at 5°K. For $Na_3La(VO_4)_2$ similar emission and excitation spectra were found. The excitation spectra clearly consist of two excitation bands (around 3.7 and 4.8 eV). The emission contains two overlapping subbands. Apparently the low-energy excitation band corresponds to the low-energy emission band and the high-energy excitation band corresponds to the high energy emission band. Under the same experimental conditions the emission spectra of $Na_3La(PO_4)_{1.9}(VO_4)_{0.1}$ show relatively more low-energy emission than those of $Na_3La(VO_4)_2$. For $Na_3La(VO_4)_2$ a decay time of 800 μsec was found at 10°K and the quenching temperature, as defined by Kröger (*3*), was 120°K. Both the decay time and the quenching temperature were determined with an excitation of 3.9 eV.

The emission spectrum of $Na_3La_{0.98}Eu_{0.02}(VO_4)_2$ (Fig. 2), measured at 77°K, shows VO_4^{3-} emission as well as Eu^{3+} emission from the $^5D_0$ level. The ratio of the intensities of the Eu^{3+} and the VO_4^{3-} emission depends on the excitation energy. This ratio is about 25% under 4.9-eV excitation and 50% under 4.1-eV

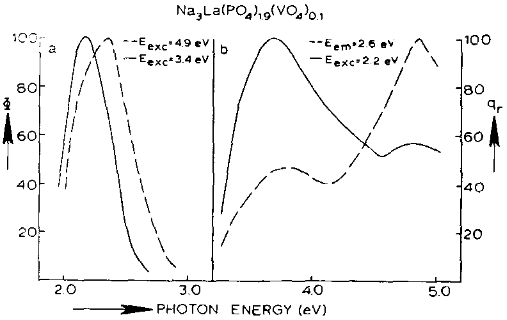

FIG. 1. (a) Spectral energy distribution of the emission of $Na_3La(PO_4)_{1.9}(VO_4)_{0.1}$ at 5°K for different excitation energies. Φ denotes the spectral radiant power per unit energy in arbitrary units. (b) Relative excitation spectra of the emission of $Na_3La(PO_4)_{1.9}(VO_4)_{0.1}$ at 5°K for different emission energies. q_r is the relative quantum output.

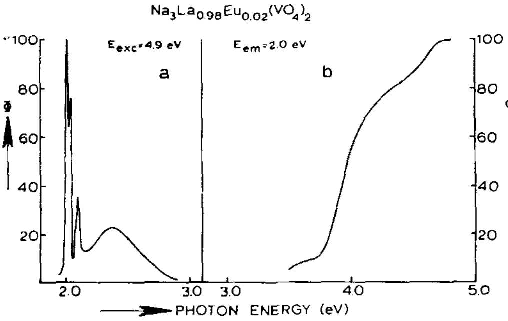

FIG. 2. (a) Spectral energy distribution of the emission of $Na_3La_{0.98}Eu_{0.02}(VO_4)_2$ at 77°K. Recording this spectrum the slit width was chosen so that the spectral resolving power became too small to observe the fine structure of the Eu^{3+} emission. Other spectra did show this fine structure. (b) Relative excitation spectrum of the Eu^{3+} emission of $Na_3La_{0.98}Eu_{0.02}(VO_4)_2$ at 77°K.

excitation, but when excited with 3.4 eV, the Eu^{3+} emission is almost absent.

Discussion

In $Na_3La(VO_4)_2$ and $Na_3La(PO_4)_{1.9}(VO_4)_{0.1}$ the excitation and emission transitions can be ascribed to transitions within the VO_4^{3-} group. Referring to the results of earlier work on the vanadates (*2*), we use the following energy level scheme for the VO_4^{3-} group: the configuration $t_1{}^6$ gives rise to a $^1A_1$ ground state and the first excited configuration $t_1{}^5e$ gives rise to four levels with the order $^3T_1$, $^3T_2 < {}^1T_1 < {}^1T_2$. The emission corresponds to a transition from one of the triplet states ($^3T_1$, $^3T_2$) to the ground state $^1A_1$. The long decay time is in accordance with this assignment. The fact that $Na_3La(VO_4)_2$ shows efficient luminescence at lower temperatures indicates that the excitation energy is not mobile in this temperature region, as has been argued for YVO_4 (*4*). The fact that actually two emission bands are observed can be ascribed to crystallographically different vanadate groups, in accordance with the crystal structure. All the vanadate groups have three Ln^{3+} neighbors; 25% of these groups contain one oxygen that has no Ln^{3+} neighbors. We shall denote these groups by type 1 and the other 75% by type 2. In the groups of type 1, the V–O charge transfer energy is assumed to be low due to a destabilization of the ground state. This is a consequence of the fact that one of the oxygens is surrounded by Na^+ ions only, so that locally there is no complete charge compensation (*5*). It is obvious, then, that the low-energy excitation and emission transitions take place in groups of type 1, whereas the type 2 groups give rise to the high-energy excitation and emission band. This assignment also explains why $Na_3La(PO_4)_{1.9}(VO_4)_{0.1}$ shows relatively more emission in the lower-energy region than the pure vanadate: Since the V^{5+} ion is larger than the P^{5+} ion ($r^{IV}_{V^{5+}} = 0.36$, $r^{IV}_{P^{5+}} = 0.17$ Å (*6*)), vanadium will prefer the type 1 sites, where one of the oxygens (bound to Na^+ only) can expand easily.

In the case of $Na_3La_{0.98}Eu_{0.02}(VO_4)_2$ the excitation takes place in the vanadate group. The presence of the red Eu^{3+} emission can be explained by the occurrence of energy transfer from the VO_4^{3-} group to the Eu^{3+} ion. This transfer has been studied well in other systems; it occurs via exchange interaction and can only take place over a short distance (*5*). It has not been observed before that the ratio of the Eu^{3+} and the VO_4^{3-} emission intensity of Eu^{3+}-activated vanadates depends markedly on the excitation energy. There is no energy transfer when the excitation energy is low, i.e., when the excitation takes place in the type 1 groups only. Since the charge distribution of the lowest excited level is for the main part located on the vanadium and the oxygen that has no Ln^{3+} neighbors, the wavefunction overlap of the electrons of the vanadate group in this level and the $4f$ electrons of the Eu^{3+} ion will be relatively small and so will the energy transfer probability. If the excitation energy increases, the ratio of the Eu^{3+} and the VO_4^{3-} emission intensity increases to 50%. For higher excitation energies the vanadate groups of type 2 are also excited. These groups can transfer their excitation energy to neighboring Eu^{3+} ions.

If we neglect vanadate–vanadate energy transfer and consider short-range vanadate–Eu^{3+} energy transfer only, the calculated value of this ratio is 6%. In this calculation we have used the fact that each VO_4^{3-} group has three Ln^{3+} neighbors and that the Eu^{3+} concentration is 2%. The larger experimental value points to the presence of a restricted contribution of vanadate–vanadate transfer to the total energy transport mechanism.

Furthermore, the Eu^{3+} emission lines are sharp and their number is restricted, but one or two are larger than the maximum permitted value (three for ${}^5D_0 \rightarrow {}^7F_1$, five for ${}^5D_0 \rightarrow {}^7F_2$). This indicates that there is long-range order between the Ln^{3+} and Na^+ ions with crystallographically different Ln^{3+} ions, in fair agreement with the crystallographic data (*1*).

The presence of an exceptional V–O bond in the model presented above can also be deduced from the infrared spectrum of $Na_3La(VO_4)_2$. This spectrum shows, apart from a broad absorption band around 800 cm^{-1}, which is also observed in other vanadates (*7*), two weak bands at 930 and 950 cm^{-1}. This is a very high value for the V–O stretching frequency (compare Ref. *7*). It is therefore ascribed to the V–O bond in which the oxygen is surrounded by Na^+ ions only.

In conclusion, the present system is too complicated for detailed analysis, but the dependence of the emission spectra upon excitation energy makes it worthwhile for them to be reported.

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