JOURNAL OF MATERIALS SCIENCE 26 (1991) 1069–1072

Eu^{2+} luminescence in alkali sulphate lattices

V. S. KISHAN KUMAR, B. S. V. S. R. ACHARYULU, S. B. S. SASTRY*
Department of Physics, Indian Institute of Technology, Madras 600 036, India

Results of optical absorption and fluorescence studies on europium-doped sulphates of caesium, rubidium and potassium are reported. The optical absorption spectra showed a band in the 5.2 to 5.3 eV region in each of the three phosphors. Additional weak shoulders in the lower energy region were also observed. These absorption bands are attributed to the $4f^7 \rightarrow 4f^6 5d$ transitions of europium which has entered the lattices predominantly in its divalent state. Fluorescence measurements also showed the host-dependent emission of Eu^{2+} in the 2.73 to 3.14 eV region with corresponding excitation spectra peaking in the 3.68 to 3.86 eV region. All these emission and excitation bands are assigned to Eu^{2+} ions due to transitions between the levels of $4f^7$ configuration and the excited mixed configuration of $4f^6 5d$. The presence of trivalent europium could not be detected by luminescence studies in any of the three sulphate lattices.

1. Introduction

It is well known that most of the rare-earths (RE) prefer the trivalent state when they are doped into ionic solids. However, there are a few exceptions which can exist in both trivalent and divalent states (e.g. samarium, europium, ytterbium). In some cases it has been found that exposure of a sample containing the trivalent rare earth to high-energy radiations produces small amounts of its divalent state in the crystal [1, 2]. The characteristic absorption spectra of trivalent RE ions would consist of weak sharp lines. The 4f orbits of RE ions are so deeply buried within the electronic shell that the energy levels of $4f^n$ configuration are only slightly perturbed when the ions are placed in a crystal. This characteristic has been of great help in identifying the various $f \rightarrow f$ transitions of many RE^{3+} ions. Generally, the absorption and emission bands of Eu^{3+} have shown strong host-dependence suggesting a crystal-field effect for the excited state involved in the transitions. Two sets of absorption bands were reported for Eu^{2+} in alkaline earth fluorides [3]. The Eu^{3+} absorption (found in different hosts in the ultraviolet region) was attributed to transitions to the charge transfer (CT) state of a Eu^{3+}–anion complex. Such broad absorption bands were observed in oxides, oxysulphides and oxyhalides [4–6]. An interesting feature of these charge transfer absorptions is that they were found to excite strongly the $^5D \rightarrow {}^7F$ emissions of Eu^{3+}, though little is known about the paths by which excitation into the CT state feed the ^5D levels [7]. It is quite interesting to note that there is at least one report of observation of europium luminescence of both its trivalent and divalent ionic states in the same host simultaneously. This was observed in $CaSO_4$: Eu in which the Eu^{3+} fluorescence was reported to consist of sharp bands near red [8]. With a view to pursue such characteristics of this particular RE, its optical properties were studied in three alkali sulphate lattices. In an earlier work on europium-doped K_2SO_4, it was reported that the observed absorption and emission bands are due to transitions between the $4f^7$ and $4f^6 5d$ levels of Eu^{2+} ions [9]. Here the results of such studies on two other alkali sulphates (Cs_2SO_4 and Rb_2SO_4) doped with europium are compared with those on K_2SO_4:Eu.

2. Experimental procedure

The starting materials used were suprapure quality sulphates of caesium and rubidium. Crystals were grown from aqueous solutions by slow evaporation. Europium oxide was treated with concentrated sulphuric acid to obtain europium sulphate. An aqueous solution of this was added to the aqueous solutions of the two host sulphates in different concentrations. All samples were quenched from 250 °C before each measurement. Optical absorption spectra were recorded using a Hitachi U3400 spectrophotometer. An Aminco–Bowman spectrophotofluorometer was used to carry out the fluorescence measurements.

3. Results

3.1. Optical absorption

Undoped samples of the three sulphates showed no absorption band throughout the visible and ultraviolet regions down to 200 nm. The europium-doped samples each showed a band in the ultraviolet region with weak shoulders on the lower energy side. The prominent peak occurred around 5.2 eV in Cs_2SO_4:Eu and 5.3 eV in Rb_2SO_4:Eu and K_2SO_4:Eu. A shoulder around 3.85 eV is particularly

---

* Author to whom all correspondence should be addressed.

0022-2461/90 $03.00 + .12 © *1990 Chapman and Hall Ltd.*

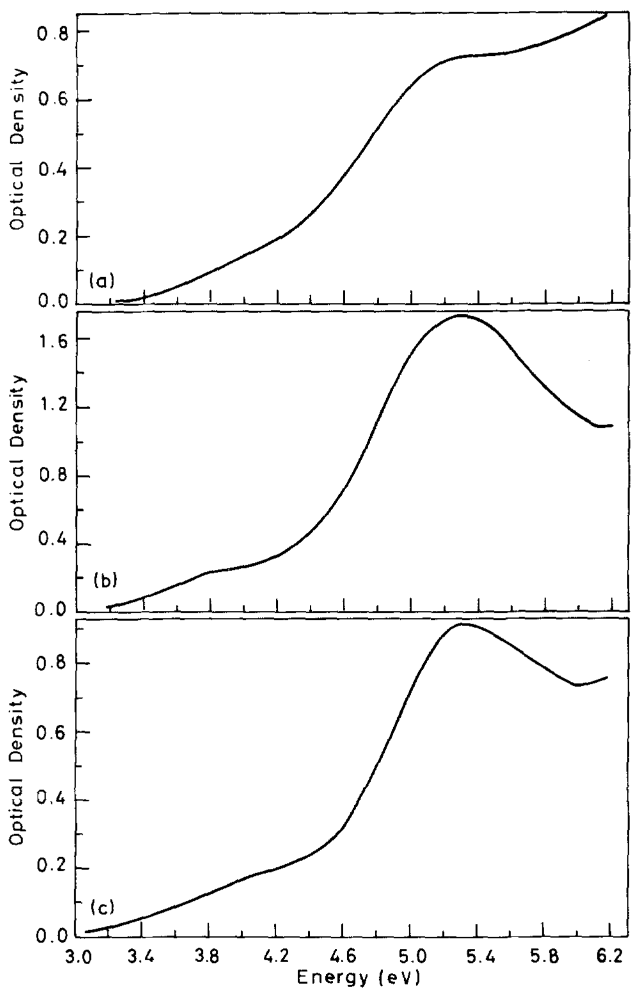

Figure 1 Optical absorption spectra of europium-doped (a) caesium sulphate, (b) rubidium sulphate, (c) potassium sulphate.

noticeable in Rb_2SO_4:Eu. Fig. 1 shows the optical absorption spectra of the three europium-doped samples.

3.2. Fluorescence

Exciting the samples with photons around 5.3 eV (the main absorption band seen) did not yield any measurable fluorescence. However, excitation at wavelengths where weak shoulders were observed in the absorption spectra yielded a single emission band in each case. This emission band peaked around 2.73 eV in Cs_2SO_4:Eu, 3.14 eV in Rb_2SO_2:Eu and 3.05 eV in K_2SO_4:Eu. The corresponding excitation spectra were found to follow a similar pattern in the three cases. These consisted of a band peaking around 3.68 eV in Cs_2SO_4:Eu and 3.86 eV in the other two phosphors, with a shoulder showing up around 4.3 eV. This shoulder is more prominent in the case of Cs_2SO_4:Eu. Fig. 2 shows the excitation and emission spectra of the three europium-doped alkali sulphates.

4. Discussion

As mentioned earlier, europium can enter a host lattice in its divalent as well as trivalent state. Hence, the first task is to ascertain which valence state is predominantly present in these phosphors. This can be done fairly accurately with the help of optical absorption and fluorescence results because reports of such studies on both Eu^{3+} and Eu^{2+} are available in literature.

Eu^{3+} has a $4f^6\,5s^2\,5p^6$ electronic configuration with ^7F ground state. The absorptions and emissions of this ion have been found to be due to transitions between levels associated with the 4f electrons. These electrons are well shielded from the crystal field by the filled 5s and 5p orbits. Hence the energy levels corresponding to these electrons are little affected by the crystal field. The first group of excited levels in this configuration corresponds to the ^5D-state. The lowest of these ($^5D_0$) is separated from the lowest of the ground state levels ($^7F_0$) by about 2.13 eV while the highest one ($^5D_4$) is above $^7F_0$ by about 3.42 eV.

Kingsley and Prener [10] have reported both absorption and emission bands due to transitions between the ^7F ground and the ^5D excited levels of Eu^{3+} in CdF_2. Because the oscillator strengths for these transitions are very small, they had to use thick samples (~15 mm) containing up to 10 mol % Eu for the measurements. The absorption lines observed at room temperature were found to be between 2.09 and 2.36 eV. The corresponding emissions occurred between 1.52 and 2.14 eV.

A broad ultraviolet absorption has also been reported for Eu^{3+} in many crystals, especially in oxygen-dominated lattices [4–6], which was ascribed to the charge transfer states (CTS) of the Eu^{3+}-anion complex, i.e. an electron from the highest filled oxygen orbital being promoted to the 4f shell of Eu^{3+} ion.

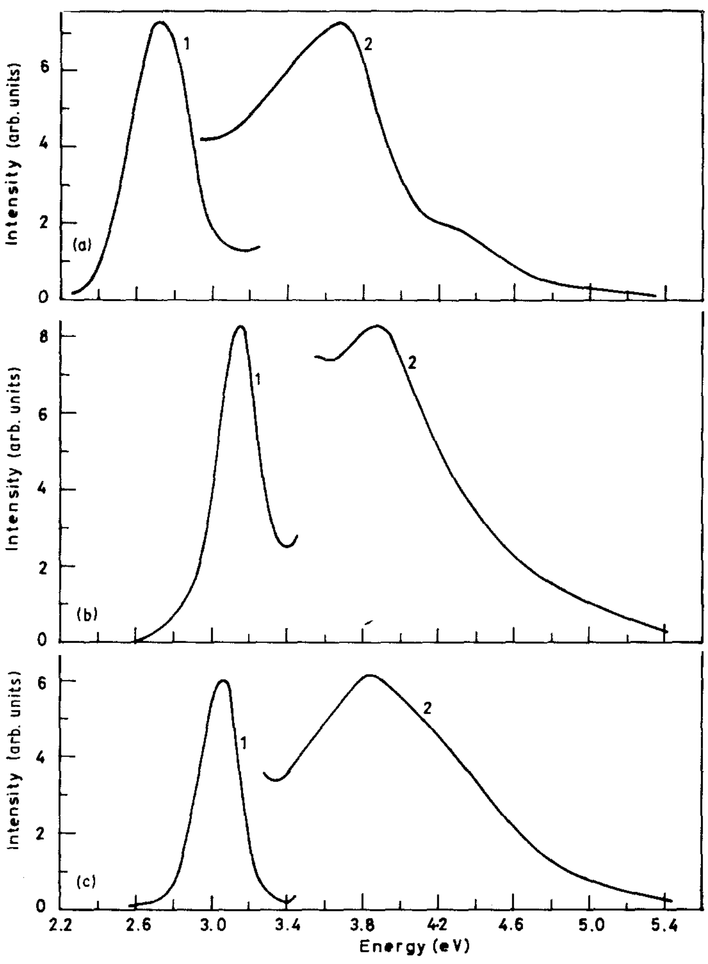

Figure 2 Fluorescence of europium-doped (a) caesium sulphate, (1) emission for 3.68 eV excitation, (2) excitation for 2.73 eV emission; (b) rubidium sulphate, (1) emission for 3.86 eV excitation, (2) excitation for 3.14 eV emission; (c) potassium sulphate, (1) emission for 3.86 eV excitation, (2) excitation for 3.05 eV emission.

This CTS ultraviolet band appeared in the 3.78 to 5.33 eV region in different oxides [11]. However, more interesting is the observation that this CTS band has been found strongly to excite the ^5D to ^7F line emissions of Eu^{3+}.

Thus the fluorescence results must also be looked into before the observed ultraviolet absorption is assigned as the CTS band of Eu^{3+}. The $^5D \rightarrow {}^7F$ emission lines are reported in many hosts. In CdF_2, these were observed around 2.1 eV under selective dye-laser excitation [12]. Sekita [13] reported these emissions between 1.76 and 2.14 eV in $Bi_2Ge_3O_9$: Eu^{3+}. The corresponding excitations were observed between 2.31 and 3.47 eV. There is an earlier report of Eu^{3+} emission in a sulphate lattice. Three emissions at 1.77, 1.99 and 2.08 eV were reported in the $CaSO_4$:Eu phosphor [8].

The fluorescent emission and excitation bands observed in the present studies (Fig. 2) are distinctly different from those above. The Eu^{3+} emissions near the red region could not be excited by the 5.2 to 5.3 eV photons (corresponding to the optical absorption band). Thus although the position of the optical absorption band may suggest it to be the CTS band of Eu^{3+}, the fluorescence results do not support the idea. It should be remembered that these line emissions could not be observed by exciting the samples in the 2.3 to 3.5 eV region where Eu^{3+} ions could be usually excited.

Obviously attention should now be turned to the divalent state of this dopant. Eu^{2+} has a $4f^7$ valence electronic configuration with $^8S_{7/2}$ ground state. The lowest excited state within the $4f^7$ configuration is the ^6P_J manifold. Transitions to these levels, although in the ultraviolet region, will lead to line spectra. The next excited levels correspond to the $4f^6\,5d$ configuration. The positions of these levels are generally above ^6P_J, but because the 5d orbit is exposed to the crystal field, the split components of this configuration can lie below ^6P_J. The $4f^7 \rightarrow 4f^6\,5d$ transitions are allowed ones. The broad ultraviolet absorptions and emissions near the violet region found for Eu^{2+} have generally been assigned to transitions between these levels.

Eu^{2+} absorption bands have been reported in different hosts. An intense broad band at 3.79 eV and a weak one around 3.5 eV were reported at room temperature for $SrCl_2$ containing 0.1 mol % $EuCl_2$ [14]. In alkaline earth fluorides, two sets of absorption bands were observed around 5.5 and 3.88 eV [3]. The absorption showed a weak band in $BaFX$:Eu^{2+} (X = Cl, Br) around 4.59 eV [15]. All these observed bands have been attributed to the 4f → 5d transitions of Eu^{2+} ions. In KCl:Eu, the main absorption band for Eu^{2+} was reported around 5.17 eV [16]. A two-band absorption was observed in RbBr for Eu^{2+} in the 3 to 4 and 4.4 to 5.4 eV regions [17].

Studies on the $4f^{n-1}\,5d$ configurations of RE ions have established that the behaviour of the f-electron cloud has only a weak dependence on the d-electron and the crystalline environment. In other words, after absorption of radiation, the $4f^{n-1}$ electrons would be practically as unaffected as the $4f^n$ electrons were.

However, the cloud of 5d electrons is external in the excited configuration of $4f^{n-1}5d$. This obviously would be influenced by the crystalline surroundings [18]. Thus the band positions under f → d transitions are expected to vary from host to host. Unfortunately, detailed information about the various levels of the $4f^6 5d$ mixed configuration of Eu^{2+} is not available as earlier work has been mainly on the lowest level of this configuration.

The observed absorption band in the 5.2 to 5.3 eV region along with the weaker absorptions at lower energies in the three europium-doped sulphates are thus attributable to the Eu^{2+} ions present in the lattices under transitions from the ground state ($4f^7$) to various levels in the excited configuration of $4f^6 5d$.

The results of fluorescence measurements also suggest that the dopant has entered the sulphate lattices predominantly in its divalent state. The absence of sharp line emissions near the red region rules out the presence of Eu^{3+} in optically detectable concentrations. Thus the emissions observed in the 2.73 to 3.14 eV region and corresponding excitation spectra in the 3.68 to 3.86 eV region must be associated with Eu^{2+} ions.

The first excited levels within the $4f^7$ configuration of Eu^{2+} correspond to the ^6P_J state. The $^6P \rightarrow {}^8S$ line emissions, if any, will be in the ultraviolet region. However, the energy of this emission must remain essentially the same in different hosts as the 4f levels are not affected by crystal fields. In the present studies, the case is obviously different with the emissions occurring at three different energies: 2.73, 3.05 and 3.14 eV. This indicates that the observed emissions are associated with some other energy level which shows a strong host dependence.

The f → f line emission of Eu^{2+} was detected in the X-ray fluorescence of europium-activated mixed halides (fluorine and chlorine) or barium and strontium at 3.42 eV and was assigned to the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition [19]. A study on europium-doped sulphates revealed this emission line to be absent in them except for the $BaMg(SO_4)_2$:Eu phosphor [20]. Thus although the emission bands observed in the present case are associated with Eu^{2+}, they might not be due to the f → f transitions of this ion. The next excited levels of Eu^{2+} correspond to the mixed configuration of $4f^6 5d$. Eu^{2+} emissions observed in different hosts were found to be different and were generally assigned to transitions from this level to the $^8S_{7/2}$ ground state. In such a case, because the 5d level is exposed to crystal field, this type of behaviour for the emission can be fully justified. In $BaSO_4$:Eu, this emission was reported to be near 3.3 eV [9]. In the KCl lattice, the same emission was observed around 2.95 eV [16]. There are many reports of this emission in alkaline earth halides [21, 22]. In these hosts, this emission was found to show up around 2.95, 3.03 and 3.1 eV in various cases.

The above results are in agreement with the fluorescence emissions observed in the present cases which can be attributed to the $4f^6 5d \rightarrow 4f^7$ transition of Eu^{2+} ions. The differences in emission energies (2.73 eV in Cs_2SO_4:Eu, 3.05 eV in K_2SO_4:Eu and 3.14 eV in Rb_2SO_4:Eu) are only to be expected, as the transitions responsible for these emissions take place from the 5d level, which has a splitting due to crystal field. The exact positions of the $4f^6 5d$ levels will strongly depend on the surroundings of the Eu^{2+} ions.

The excitation spectra of these emissions show that the strongly absorbing level is not the fluorescing level. Moreover, there seems to be more than one level to which excitations are possible to bring about this emission. The peak positions in the excitation spectra (3.68 to 3.86 eV) actually show up as weak shoulders in the optical absorption spectra (Figs 1 and 2). This is especially noticeable in Rb_2SO_4:Eu. Another excited level to induce this emission seems to be near 4.3 eV as suggested by the excitation spectra.

5. Conclusions

From the optical absorption and fluorescence studies made on europium-doped samples, it can be concluded that:

1. europium enters these alkali sulphate lattices predominantly in its divalent state;
2. the ultraviolet absorption bands observed are due to the $4f^7 \rightarrow 4f^6 5d$ transitions of Eu^{2+} ions;
3. the observed emissions and excitations are also associated with Eu^{2+} under the above transitions.

References

1. W. HAYES and J. W. TWIDELL, *J. Chem. Phys.* **35** (1961) 1521.
2. D. S. McCLURE and Z. KISS, *ibid.* **39** (1963) 3251.
3. A. A. KAPLYANSKII and P. P. FEOFILOV, *Opt. Spect.* **13** (1962) 129.
4. G. BLASSE, *J. Chem. Phys.* **45** (1966) 2356.
5. J. W. HAYNES and J. J. BROWN, *J. Elec. Chem. Soc.* **115** (1968) 1060.
6. G. BLASSE and A. BRIL, *J. Chem. Phys.* **46** (1967) 2579.
7. C. W. STRUCK and W. H. FONGER, *J. Lumin.* **1–2** (1970) 456.
8. V. N. BAPAT, *J. Phys. C* **10** (1977) L465.
9. V. S. KISHAN KUMAR, S. B. S. SASTRY and B. S. V. S. R. ACHARYULU, *Phys. Status Solidi (b)* **155** (1989) 679.
10. J. D. KINGSLEY and J. S. PRENER, *Phys. Rev.* **126** (1962) 458.
11. H. E. HOEFDRAAD, *J. Solid State Chem.* **15** (1975) 175.
12. J. P. JOUART, C. BISSIEUX, M. EGEE, G. MARY and M. de MURICA, *J. Phys. C* **14** (1981) 4923.
13. M. SEKITA, *J. Lumin.* **22** (1981) 335.
14. S. FREED and S. KATCOFF, *Physica* **14** (1948) 17.
15. K. TAKAHASHI, K. KOHDA and J. MIYAHARA, *J. Lumin.* **31–32** (1984) 266.
16. V. V. BRYUKVIN and E. E. PENZINA, *Opt. Spect.* **52** (1982) 646.
17. S. B. S. SASTRY and S. SAPRU, *J. Lumin.* **23** (1982) 281.
18. M. V. EREMIN, *Opt. Spect.* **26** (1968) 317.
19. A. M. GURVICH, V. B. GUTAN, M. A. LLINA, V. P. KAVTOROVA, R. V. KATOMINA, M. G. MYAGIKOVA and T. I. SAVIKHINA, *ibid.* **52** (1982) 175.
20. F. M. TAYN, W. LEHMANN, D. M. FELDMAN and J. MURPHY, *J. Electro. chem. Soc.* **121** (1974) 1475.
21. K. S. V. NAMBI, V. N. BAPAT and S. M. D. RAO, *J. Phys. C* **12** (1979) L745.
22. F. D. S. BUTEMENT, *Trans. Faraday Soc.* **44** (1948) 617.

Received 27 March
and accepted 24 April 1990