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Photoluminescence of Ce^{3+} in Some Fluoroindate Compounds

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Abstract

The luminescent properties of Ce^{3+}-doped fluoroindates with an elpasolite-type structure are reported. In these compounds the main broad emission band in the blue region under an ultraviolet excitation is ascribed to 5d→4f transitions of Ce^{3+} replaced In^{3+} isolated octahedral site. The two other weak emissions in the ultraviolet region can be assumed to originate also from Ce^{3+} ions but are located in two other types of sites. Between them, Ce^{3+} ions probably tend to go to the site of large size and high coordination numbers with higher distribution coefficient than another one which has octahedral coordination. Aggregation of Ce^{3+} in these sites providing sufficient interaction to modify the emission spectra is clearly observed in a Rb_2KInF_6 : Ce^{3+}(5%) single crystal.

1. Introduction

It has recently been proposed to use single crystal scintillators containing a large amount of ^{115}In to detect low solar neutrinos according to Raghavan's nuclear reaction [1,2]. Until now the only cerium-doped indate lattice whose luminescence was studied in the solid solution is $In_xSc_{1-x}BO_3$: Ce^{3+}. It was shown that Ce^{3+} luminescence disappears with the increase in indium content due to the oxydo-reduction arising from coexistence of In^{3+} and Ce^{3+} in the same sample [3]. Consequently we have extended this investigation to some fluoroindates and particularly to elpasolite fluoroindates which appear to be attractive ionic host crystals for rare earth elements.

Fluoroindates with the general formula A_2BInF_6 belong to a wide family of crystals whose structures derive from that of elpasolite (K_2NaAlF_6 prototype structure, Fm3m with z = 4). The structural arrangement corresponds to that of the perovskite with an additional cationic ordering between the smaller monovalent cations B and trivalent cations In in the octahedral sites. The A site has T_d symmetry with 12 coordination numbers [4]. In these lattices the $(InF_6)^{3-}$ octahedra do not share fluorine ions with each other.

The present work is devoted to the luminescent properties of Ce^{3+} in some fluoroindate compounds.

2. Materials and Methods

Starting materials with analytical grade quality were NaF, KF, RbF, InF_3 and CeF_3 supplied by Johnson-Matthey. NaF, KF and RbF were dehydrated in a vacuum at about 470 K for 6 hours and subsequently introduced into a dry box under an argon atmosphere. InF_3 and CeF_3 were purified before use under F_2 stream, in order to eliminate some traces of oxide, at 800 K and 970 K respectively. All A_2BInF_6 (A = K, Rb, B = Na, K) compounds were prepared by solid state reaction from stoichiometric mixtures. The reactions were carried out in sealed gold tubes under an argon atmosphere during 20 hours at about 850 K, 920 K and 970 K for K_3InF_6 (or written as K_2KInF_6), K_2NaInF_6 and Rb_2KInF_6 respectively. Formation of single phase was checked by X-ray diffraction using CuK_α radiation. All three compounds, without cerium dopant and 1 mole % cerium dopant, were white color and nonhygroscopic.

Single crystals of Rb_2KInF_6 doped with cerium were successfully grown [5]. However, Bridgman growth experiments on Ce^{3+}-doped K_2NaInF_6 yielded only polycrystalline samples with many inclusions because this compound exhibits an incongruent melting point. Similar behavior was also observed on K_2NaYF_6 and K_2NaScF_6 [6].

K_3InF_6 with 1% Ce was also grown by the Bridgman technique. A clear single crystalline slab was cut from the as-grown ingot and there was no region of solid solution. Under optical polarizing microscope test, the appearance of birefringence characteristic was observed. This indicates that the crystal structure of K_3InF_6 does not belong to cubic system at room temperature. Until now the crystal structure refinement of this phase has not been successful.

The luminescence measurements were performed as described earlier [5].

3. Results and discussion

3.1 K_2NaInF_6 : Ce^{3+}

For the polycrystalline of Ce^{3+}-doped K_2NaInF_6, at least two luminescent centres are observed from liquid helium temperature up to room temperature. One centre shows a blue emission band with its maximum around 410 nm at 4.2 K (Fig.1). Its maximum intensity shifts gradually to 425 nm at 300 K. The excitation spectrum of this emission peaks at 315 nm and two weaker shoulders at 300 nm and 285 nm are also observed. The blue emission is attributing to 5d→4f transitions of Ce^{3+} ion in In^{3+} isolated octahedral site [6].

Other centres with two very weak intensity emission bands strongly overlapping are observed at 4.2 K with a maximum of about 335 nm and 395 nm respectively (Fig.1). The corresponding excitation spectrum is detected in the 230-280 nm range at that temperature. This ultraviolet emission can be assumed to originate also from the Ce^{3+} ions but located in other types of sites. The weak emission spectra originating from the two sites have already been observing in other elpasolites containing Sc^{3+} and Y^{3+} [6]. On the basis of emission intensity, it may suggest that most Ce^{3+} go into the dominant In^{3+} site with only a few percent of Ce^{3+} going to other types of sites. Disordering in the host lattice assists in providing the necessary charge compensation [4, 6].

3.2 K_3InF_6 : Ce^{3+}

Ionic radius between K^+ and In^{3+} in octahedral sites is rather different (r_{K^+} = 1.38 Å, $r_{In^{3+}}$ = 0.80 Å [7]). This may induce the disordering in the host lattice cations creating an alternative In^{3+} site for Ce^{3+} ions. We have therefore investigated Ce^{3+}-activated K_3InF_6 crystals. As far as we are aware the crystal structure of this phase is not known exactly but it is definitely not cubic. We believe this host lattice has also $(InF_6)^{3-}$ isolated groups like in the elpasolite structure. Even at 4.2 K, only one luminesent centre is observed in Ce^{3+} -doped K_3InF_6. The broad emission band peaks at 420 nm under ultraviolet excitation (Fig.2). The wavelength of its maximum intensity shifts to 450 nm at 300 K. The corresponding excitation peaks at 315 nm and two weaker shoulders at 300 and 285 nm are obtained at 4.2 K. The excitation spectrum does not practically shift even at 300 K. the similarity of dominant emission and excitation spectra of Ce^{3+} in both K_2NaInF_6 and K_3InF_6 host lattices is ascribed to Ce^{3+} in In^{3+} site. Especially, only In^{3+} site in K_3InF_6 is suitable to Ce^{3+}. Disordering in the host lattice cations is seemingly negligible.

3.3 Rb_2KInF_6 : Ce^{3+}

The luminescence measurements were performed on a polished and oriented Rb_2KInF_6 : Ce^{3+} (1%) single crystal. Figure 3 shows a blue-green broad emission band peaking at 480 nm, its maximum intensity shifts to 445 nm at 4.2 K, when excited with 315 nm radiation. This emission arises from the same emitting centre observed in the two other host lattices above.

Two other emissions with lower intensities have also been detected. An ultraviolet one around 320 nm corresponding to an excitation at 245 nm (Fig.4) and a weak blue emission at 424 nm for an excitation at 270 nm (Fig.5) are observed. These two emissions can be assumed to originate also from Ce^{3+} ions in the rubidium and potassium sites respectively. Figure 6 shows the three luminescent spectra with comparative intensities originated from Ce^{3+} in three type of sites.

Similar results can be observed in Rb_2KInF_6 : Ce^{3+} (5%). However, the peak positions of excitation and emission bands of ultraviolet and blue luminescent centres are slightly different (Table 1). Figure 7 exhibits weak emission peaking at 345 nm with a band tail on the longer wavelength side corresponding to an excitation range of 245-290 nm. Some attempts to resolve the spectra of the selective excitation bands for the latter one were unsuccessful. On the basis of a comparison with a Rb_2KInF_6 : Ce^{3+} (1%) single crystal, the difficulty is probably attributed to the aggregation of Ce^{3+} in several sites except in In^{3+} isolated site.

From the behavior of a Rb_2KInF_6 single crystal with 5% doping concentration, it may suggest that the enhancement of Ce dopant induces Ce^{3+} to go to Rb^+ site with higher distribution coefficient than K^+ site. Furthermore, strong interaction between them can not be negligible.

Table 1. Experimental results of Ce^{3+} luminescence in some fluoroindate compounds at 300 K.

Host lattice	Excitation wavelength (nm)	Emission wavelength (nm)	Stokes shift value (cm^{-1})
K_2NaInF_6	260, 285, 300, 315 260	425 340, 385	8,400 9,050
K_3InF_6	285, 300, 315	450	9,500
Rb_2KInF_6 (1% of Ce^{3+})	260, 285, 300, 315 245 262, 270	480 320 424	10,700 9,100 13,4500
Rb_2KInF_6 (5% of Ce^{3+})	260, 285, 300, 315 245, 260, 280, 290	485 345	11,100 5,500

Fluoroindates with elpasolite-type structure doped with Ce^{3+} undergo the oxido-reduction problem. Depending on the excitation way, photoionization process leading to two different emitting ions Ce^{3+} (In^{3+}) or In^+ (Ce^{4+}) has already been observed in a Rb_2KInF_6 : Ce^{3+} (1%) single crystal [5]. The same results are also observed in K_2NaInF_6 and K_3InF_6 host lattices doped with Ce^{3+} are being studied and will be reported in the near future.

4. Conclusion

In some fluoroindates investigated in this report, a main emission band which can be assigned to Ce^{3+} in In^{3+} isolated site is seen. Appearance of the two emission bands with lower intensites can be also assumed to originate from Ce^{3+} ions which are located in other types of sites. For the two latter emitting centres, Ce^{3+} ions probably tend to replace the site of large size and high coordination numbers with higher distribution coefficient than another one which has octahedral coordination. The luminescent spectra modified by cerium aggregation are also reported. Our experimental results well agree with the others performed on elpasolite-type series containing Sc^{3+} and Y^{3+}

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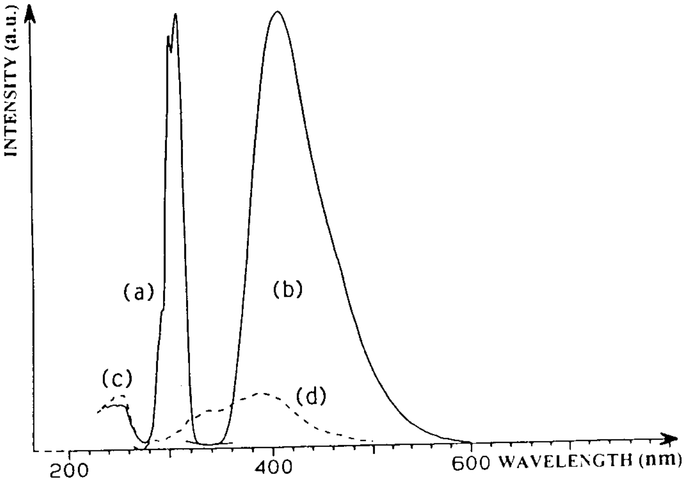

Fig.1 The excitation (a, c) and emission (b, d) spectra of blue emission (full line) and of ultraviolet emission (dashed line) performed on K_2NaInF_6 : Ce^{3+} (1%) polycrystalline at 4.2 K with comparable intensities.

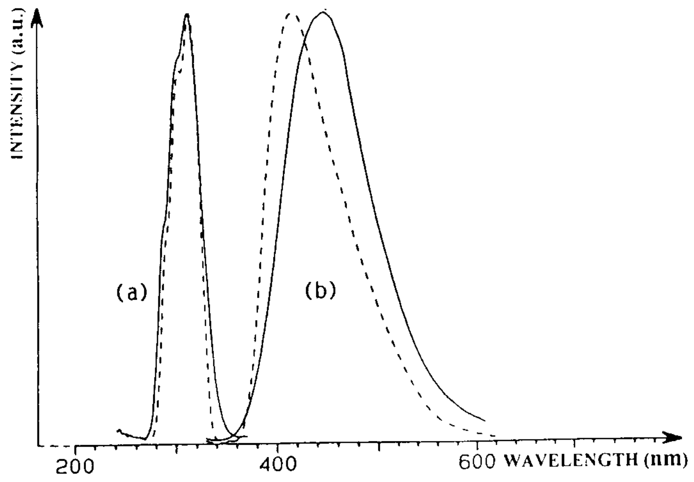

Fig.2 The excitation (a) and emission (b) spectra of K_3InF_6 : Ce^{3+} (1%) performed at 300 K (full line) and at 4.2 K (dashed line).

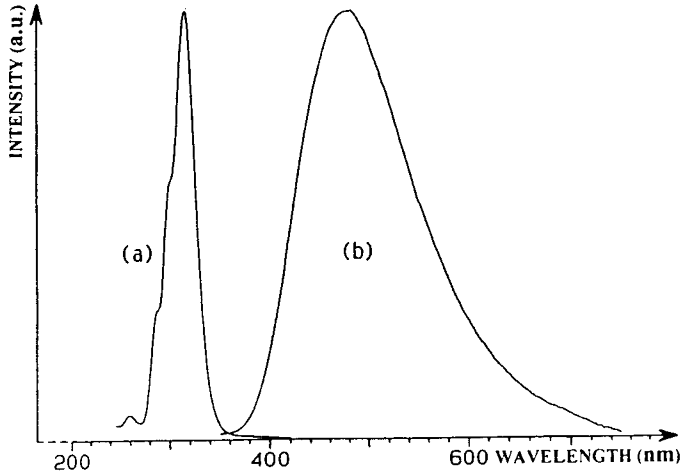

Fig.3 The excitation (a) (λ_{em} = 480 nm) and emission (b) (λ_{exc} = 315 nm) of blue-green luminescence performed on Rb_2KInF_6 : Ce^{3+} (1%) at 300 K.

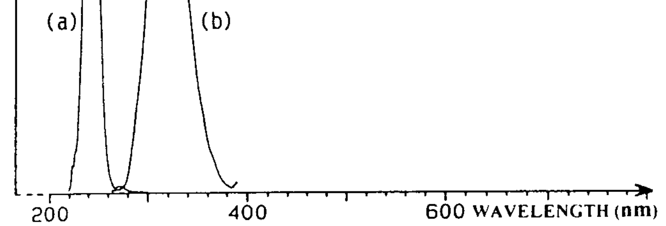

Fig.4 The excitation (a) (λ_{em} = 320 nm) and emission (b) (λ_{exc} = 245 nm) spectra of ultraviolet luminescence performed on Rb_2KInF_6 : Ce^{3+} (1%) at 300 K.

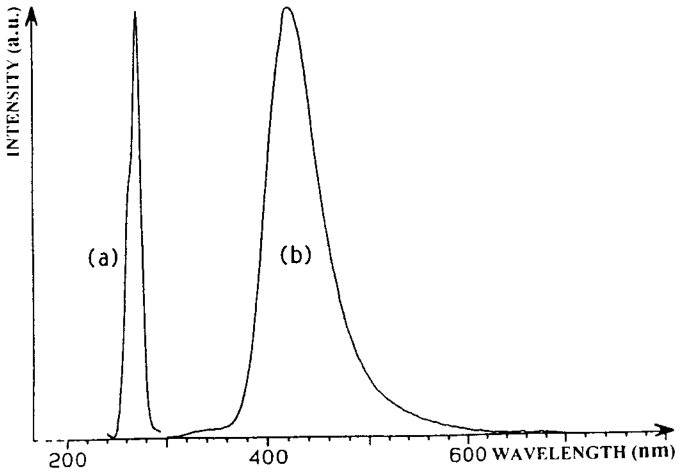

Fig.5 The excitation (a) (λ_{em} = 424 nm) and emission (b) (λ_{exc} = 270 nm) spectra of blue luminescence performed on Rb_2KInF_6 : Ce^{3+} (1%) at 300 K.

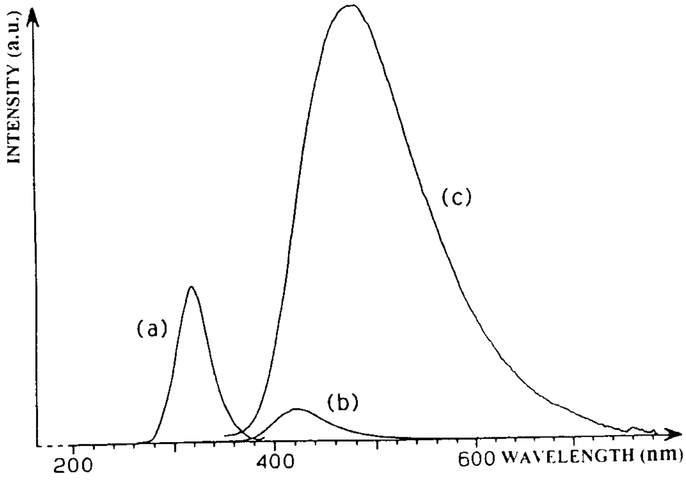

Fig.6 Emission spectra of ultraviolet (a) (λ_{exc} = 245 nm), blue (b) (λ_{exc} = 270 nm) and blue-green (c) (λ_{exc} = 315 nm) luminescence of a Rb_2KInF_6 : Ce^{3+} (1%) single crystal at 300 K (comparable intensities, corrected from the spectral response of the photomultiplier and lamp flux).

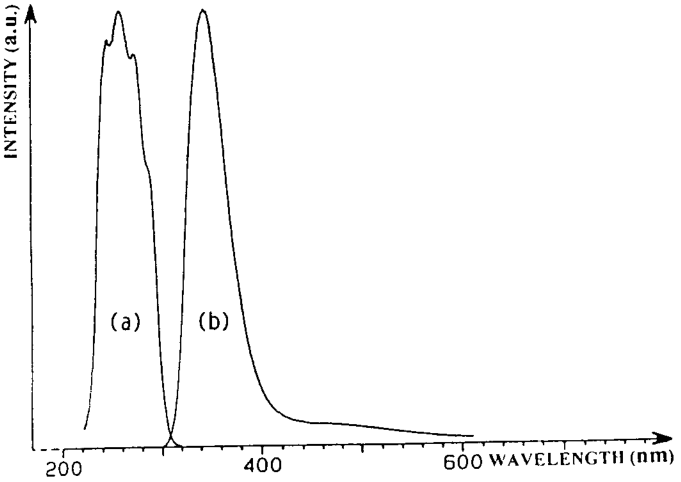

Fig.7 The excitation (a) (λ_{em} = 345 nm) and emission (b) (λ_{exc} = 260 nm) spectra of ultraviolet luminescence of a Rb_2KInF_6 : Ce^{3+} (5%) single crystal at 300 K.

6. References

[1] Raghavan, R.S. (1976), Inverse β Decay of $^{115}In \rightarrow {}^{115}Sn^*$: a New Possibility for Detecting Solar Neutrinos from the Proton-Proton Reaction, Phy.Rev. Letters, Vol.37, pp. 259-266.

[2] Gonzales-Mestres, L. (1992), New Fast Indium-Based Scintillator, Ann. de Phys. (Suppl.) Vol.6, pp. 189-192.

[3] Gaewdang, T., Chaminade, J.P., Garcia, A., Pouchard, M., Hagenmuller, P. and Jacquier, B. (1994), Luminescence of Ce^{3+} in the $In_xSc_{1-x}BO_3$ $(0 \leq x \leq 1)$ Solid Solution, J. Phys. Chem. Solids, Vol. 55, pp. 501-504.

[4] Babel, D. and Tressaud, A.(1985), Crystal Chemistry of Fluorides, In Inorganic Solid Fluorides, Academic Press, New York.

[5] Gaewdang T. (1995), Coexistence of the Ce^{3+} and In^+ Luminescent Centres in Rb_2KInF_6 : Ce^{3+} Single Crystals, Thai Journal of Physics, Vol. 1, pp. 5-12.

6] Aull, B.F. and Jenssen, H.P. (1986), Impact of Ion-Host Interaction on the 5d to 4f Spectra of Lanthanide Rare - Earth -Metal Ions II. The Ce - Doped Elpasolites, Phys. Rev., B34, pp. 6647-6655.

[7] Shannon, R.D. (1976), Ionic Radii of Elements in Solids, Acta Cryst., A32, pp.751-756.