

CHARGE TRANSFER LUMINESCENCE IN Ce-DOPED FLUORIDES

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New emission bands were found in Ce^{3+} doped SrF_2 and BaF_2 crystals under excitation into the charge transfer region. The bands at 4.85 eV in BaF_2 and 4.35 eV SrF_2 were found in all crystals with Ce- concentration from 0.001 to 1 mol.%, most prominent in 0.01% samples. Decay of luminescence was simple exponential in BaF_2 , decay time decreased from 1.3 ms at 65 K to 0.41 μs at 523 K. The decay curve in SrF_2 shows $t^{-0.3}$ dependence at room temperature. All experimental results were naturally explained by assumption that new emission belongs to radiative charge transfer recombination in $\text{Ce}^{2+}-\text{F}_i^0$ pairs with different distances between them.

Keywords: Charge transfer luminescence; Alkaline earth fluoride; Decay; Recombination

INTRODUCTION

Charge transfer luminescence is still relatively unknown. This transition is the reverse of the well-known charge transfer absorption. In Eu^{3+} , luminescence from the charge transfer state cannot be observed, because of fast relaxation to the $4f^5\text{D}_j$ states [1]. Charge transfer luminescence was studied recently in many oxides and sulphides doped with Yb^{3+} ions [1]. However, apart from oxides the hole, created as a result of charge transfer transitions in fluorides, becomes self-trapped in fluorides and was found on large distance from Ce^{2+} or Eu^+ ions [2]. Therefore, the back charge transfer radiative transitions can be observed in the absence of competitive transitions.

In a previous paper we focused on charge transfer absorption and on creation of defects due to charge transfer in Ce^{3+} or Eu^{2+} doped fluorides [2]. In this paper we studied the prompt back radiative transitions of defects created by charge transfer.

EXPERIMENTAL

Crystals were grown in a vacuum with additions of few % of PbF_2 as oxygen scavenger. Details of preparation were described elsewhere [2]. Excitation spectra in the range of 4–9 eV were measured with a 1 m normal incidence vacuum monochromator VMR2.

Decay curve was measured by a single photon counting technique in nano-microsecond time scale and analog-to-digital converter in millisecond time scale. The Ar filled flash lamp was used in time resolved measurements. The pulse width was 10 ns for nano-microsecond measurements and 1 μ s for millisecond measurements.

RESULTS

Emission and Excitation Spectra

New luminescence bands at shorter wavelength than the Ce^{3+} emission bands were observed in Ce^{3+} doped BaF_2 and SrF_2 crystals (Fig. 1).

The emission spectrum with known double band structure, which excited at energies below 6 eV, belongs to 5d-4f transition in Ce^{3+} ion. The 2000 cm^{-1} bands separation is due to spin orbital $^2F_{5/2}$, $^2F_{7/2}$ splitting in the Ce^{3+} ground state. Under excitation with energies above 6 eV new luminescence bands at 4.35 eV in SrF_2 and 4.77 eV in BaF_2 appear in the emission spectra. Dips at 4.2 eV in SrF_2 and 4.3 eV in BaF_2 are due to strong 4f-5d absorption by Ce^{3+} ions. Obviously the 4.77 eV band is well separated from Ce^{3+} absorption

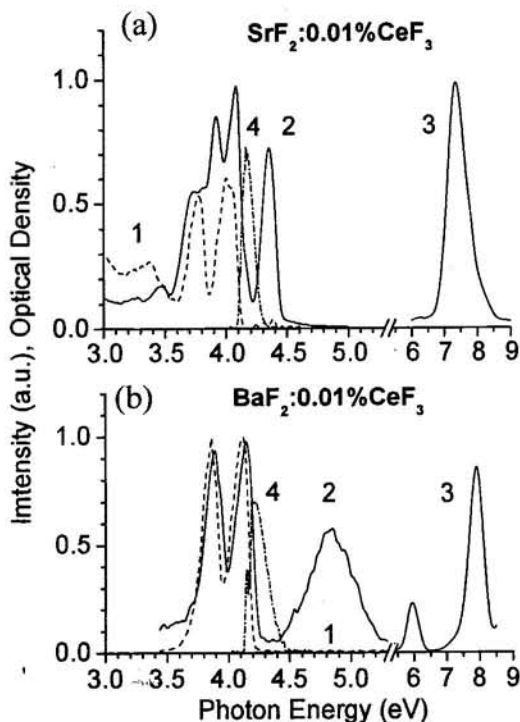


FIGURE 1 Absorption, emission and excitation spectra of $SrF_2:0.01\%CeF_3$ (a) and $BaF_2:0.01\%CeF_3$ (b) crystals. Emission and excitation spectra were normalized to equal intensity.

(a) SrF_2 emission measured at 10.5 K for excitation at 5.1 eV (1 - dashed line) and at 7.7 eV (2 - solid line). Excitation spectrum measured at 78 K for emission monitored at 4.35 eV (3 - solid line). Absorption spectrum (4 - dot-dashed line) measured at 77 K for sample with thickness 1.6 mm.

(b) BaF_2 emission measured at 78 K for excitation at 6.5 eV (1 - dashed line) and at 7.7 eV (2 - solid line). Excitation spectrum measured at 78 K for emission monitored at 4.75 eV (3 - solid line). Absorption spectrum (4 - dot-dashed line) measured at 77 K for sample with thickness 1.5 mm.

and is only slightly influenced by this absorption (see Fig. 1). Apart from this, the new emission bands in SrF_2 are influenced markedly by the Ce^{3+} absorption. Obviously, there are new bands also in the Ce^{3+} emission region in SrF_2 crystals (see Fig. 1).

All these new bands were observed also in SrF_2 and in BaF_2 crystals doping by CeF_3 in the region of 0.001–1%. However, the intensity of new bands against those of Ce^{3+} is maximal in 0.01% doped crystals.

No new bands were observed in $\text{CaF}_2:\text{Ce}^{3+}$. No similar bands were observed in undoped alkaline-earth fluoride crystals. The intensity and shape of bands do not depend markedly on temperature in the range between 10 and 300 K.

Decay of Luminescence

BaF_2

The decay curves were satisfactorily fitted by single exponential curves within all temperature ranges 60–500 K. The short component of 4.8 eV decay was observed at 78 K in microsecond time scale together with the slow decay component of millisecond lifetime.

The decay time decreased considerably with increasing temperature (Fig. 2). However the integrated intensity of the band only slightly decreased with increasing temperature (see Fig. 2). Both results provide evidence for thermal equilibrium of radiative levels. We calculate the temperature variation of decay time using a simple two-level model in the absence of quenching. The energy gap between levels is estimated as 0.06 eV.

SrF_2

Decay of $\text{SrF}_2:\text{Ce}$ charge transfer luminescence is very unusual (Fig. 3). At room temperature the luminescence intensity is constant up to a few hundreds of microseconds and then the intensity decreases with hyperbolic law $I \sim t^{-0.3}$. At 78 K the exponential component with decay time 1.8 ms is added to the decay curve (see Fig. 3). This component is close to the 1.2 ms component observed in $\text{BaF}_2:\text{Ce}$ crystal.

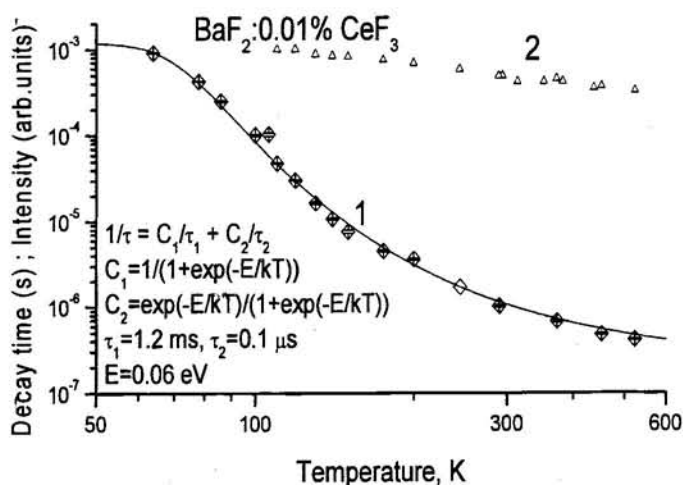


FIGURE 2 The decay time (1) and intensity (2) of 4.35 eV luminescence band of $\text{BaF}_2:0.01\%\text{CeF}_3$ vs. temperature under 7.6 eV excitation. The curve was fitted using a two level model (see text) with the parameters shown.

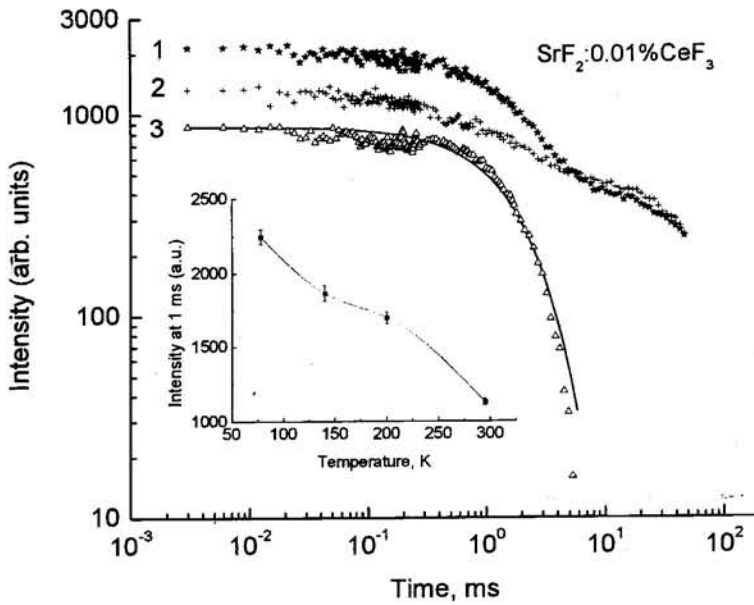


FIGURE 3 Decay of charge transfer luminescence (band at 4.35 eV) in $\text{SrF}_2:0.01\%\text{CeF}_3$ at 78 K (1) and at 295 K (2). (3) – difference curve between that of (1) and (2). The difference curve is a single exponential curve with decay time 1.8 ms. The inset shows the intensity at 1 ms as the function of temperature.

The hyperbolic decay of recombination luminescence is often observed in ionic crystals under X-ray irradiation [3] or photon band-to-band illumination [4]. Power of hyperbola (t^{-m}) is usually near 1. The ensemble of pairs can be considered as a function of distance between recombination partners – R [3]. The decay curve is a sum of many exponential curves originated from pairs with given R_i . If electron and hole centres are distributed randomly, the t^{-1} dependence should be observed [3]. However if the pair distribution is not random one should obtain t^{-m} dependence, where m is not equal to 1. For example, if the pair number with distance R between them ($N(R)$) is growth with R above then random one, one should obtain t^{-m} dependence with $m < 1$. In a short time scale the decay curve should have as limit the fastest exponent, *i.e.* the exponential decay curve, which corresponds to shortest electron-hole separation.

The exponential component appears at low temperatures in $\text{SrF}_2:\text{Ce}$. Intensity of this component grows with decreasing temperature (see inset on Fig. 3).

DISCUSSION

Nature of New Luminescence Bands

All experimental results are naturally explained if we consider the new bands as luminescence transitions between created Ce^{2+} and trapped holes. Indeed during charge transfer absorption the electrons transfer from charge-compensated interstitial fluorine states to cerium. During followed relaxation the Ce^{2+} and H centre (hole trapped by fluorine interstitial) pair are created with different distances between them [2]. The recombination energy of nearest pair effectively transfers to Ce^{3+} and we observe slow components of Ce^{3+} luminescence. We estimate the Dexter critical distances of dipole-dipole resonant transfer from charge transfer centre to Ce^{3+} as 13 Å and 17 Å in BaF_2 and SrF_2 respectively. When the distance between

recombination partners becomes sufficiently large, the luminescence photon can be emitted. At this stage we may observe the charge transfer luminescence with slow decay. Remaining defects lead to thermostimulated luminescence [2]. However the reason for exponential decay of charge transfer luminescence in BaF₂ is still unclear.

Possibility of Charge Transfer Luminescence in Re³⁺ Doped Crystals

The presence of luminescence from charge transfer state in Yb doped crystals and absence in Eu³⁺ doped crystals was explained as follows. UV radiation is efficiently absorbed by a transition to the charge transfer state of the Eu³⁺-ion. After non-radiative decay to the lower 4f levels, luminescence occurs from the ^{5D}J states (4f) of Eu³⁺. In contrast, the Yb³⁺ ion has no 4f levels at the energy of charge transfer state. Therefore the luminescence from charge transfer states is possible [1]. Using this simple energy criterion we may estimate the possibility of charge transfer luminescence in alkaline-earth fluorides doped with Re³⁺ ions. The energy of charge transfer state can be taken as 5–6 eV. The energies of fⁿ levels for Re³⁺ ion were taken from extending Dieke's diagram [5]. The best candidates are Ce, Tm, Yb, Pr, Nd, Sm, Dy are questionable candidates. Only Eu, Gd, Ho, Er should have no charge transfer luminescence at all. The low-lying 5d levels may affect this simple picture.

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