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Charge-transfer bands in alkaline-earth fluoride crystals doped by Eu^{3+} or Yb^{3+} ions

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ABSTRACT

Absorption, emission and excitation spectra of CaF_2 , SrF_2 , BaF_2 crystals doped by YbF_3 or EuF_3 impurities were studied in 1–12 eV spectral region. The intensive absorption broad bands (denoted as CT_1) were observed in all cases just below the 4f–5d absorption region. Less intensive absorption bands, denoted as CT_2 , having energies 1.2–1.5 eV lower than those of CT_1 , were observed in CaF_2 , SrF_2 crystals doped by EuF_3 or YbF_3 impurities.

High resolution emission spectra of Eu-doped CaF_2 and SrF_2 crystals excited into CT_1 and CT_2 bands were measured. Under excitation into CT_1 bands, all present Eu sites (C_{4v} , O_h and some aggregates) were observed in emission spectra. While under excitation into CT_2 bands, only the emission of C_{4v} sites was observed.

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1. Introduction

Narrow lines in absorption and excitation spectra in vacuum ultraviolet region of rare-earth doped fluoride crystals are due to 4f–5d transitions in rare-earth ions [1–3]. Beside these lines, the broad unstructured tail at lower energies was observed in CaF_2 – Eu^{3+} [1] and CaF_2 – Yb^{3+} [4] crystals. Later these broad bands were classified as charge-transfer bands [5] when transitions occur from top of valence band to 4f states of trivalent rare-earth ions. In many oxide crystals doped by Yb^{3+} the charge-transfer luminescence was observed [6]. However no charge-transfer luminescence was observed in CaF_2 – Yb [2,3].

Trivalent europium ion has $4f^6$ outer electron configuration and 7F_0 ground term. Emission from lowest excited $4f^6$ configuration 5D_j to ground 7F_j results in a number of sharp lines in red region of spectrum. The presence of charge compensated fluorine perturbed all transitions. One could unambiguously distinguish sites with C_{4v} , C_{3v} and O_h symmetry [7,8], in which the fluorine interstitial is in the nearest-neighbor (NN) position, next nearest-neighbor (NNN) position or is absent, respectively. The perturbation in CaF_2 crystal is maximal because of the small interionic distance. It is known that europium C_{3v} sites were not observed in CaF_2 crystals, C_{4v} sites

were not observed in BaF_2 crystals, cubic Eu^{3+} ions (O_h sites) were observed in all crystals [7].

The interest to investigation of charge-transfer transitions was reinforced by prospective using of Yb doped crystals as fast scintillators. The important considered application is solar neutrino real-time spectroscopy [9]. Recently, the Al_2O_3 –Yb crystal, showing an intensive charge-transfer luminescence with light yield no less than the yield of fast component of BaF_2 , was proposed as fast scintillator material [10].

The goal of this paper is to investigate charge-transfer transitions in Re^{3+} doped CaF_2 , SrF_2 and BaF_2 crystals.

2. Experimental

Crystals were grown in vacuum in graphite crucible by Stockbarger method. Graphite crucible contains three cylindrical cavities with 10 mm diameter and 80 mm long, so three crystals $\varnothing 10 \times 50$ mm with different impurity concentrations were grown at ones. As the first step large oxygen-free crystal was grown with addition of CdF_2 an oxygen scavenger in a simple large volume crucible. Parts of this crystal were then used to grow impurity doped crystals. Concentration of impurities varied from 0.01 to 1 molar percent.

The excitation spectra in 4–12 eV region were measured with grating vacuum monochromator VMR2. The hydrogen VMF25 lamp with MgF_2 window or deuterium LDD lamp with fused silica

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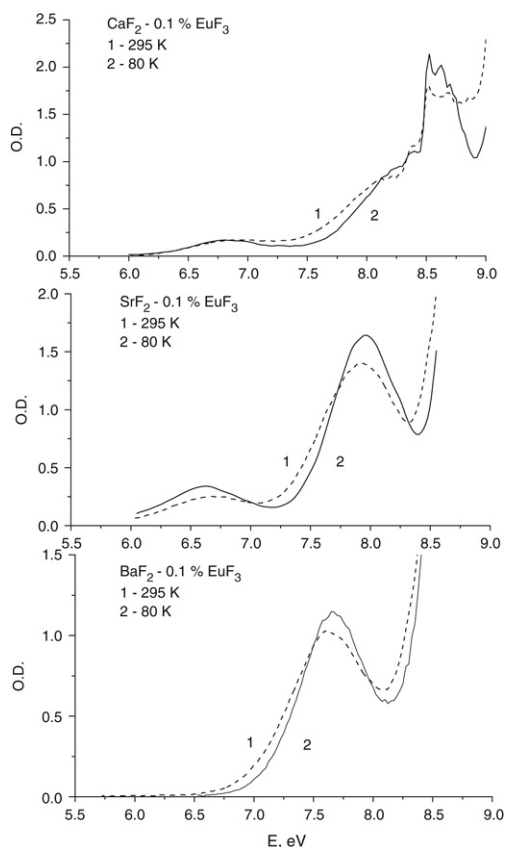


Fig. 1. Absorption spectra of CaF_2 , SrF_2 and BaF_2 crystal doped by EuF_3 .

window were used as vacuum ultraviolet sources. Emission spectra were measured with grating monochromator MDR2.

High resolution europium fluorescence spectra were recorded using grating monochromator MDR2 or double grating spectrometer SDL1. The practical resolution of monochromator and spectrometer was 0.2 nm which was enough to resolve individual lines of C_{4v} and O_h of Eu^{3+} sites in CaF_2 and SrF_2 crystals. Normally the excitation over vacuum monochromator was used. However in the case of measuring high resolution spectra the excitation intensity was not enough. Therefore we used the excitation by unfiltered deuterium lamp with quartz window closely attached to MgF_2 window of cryostat. The main goal of measurements of high resolution spectra was to find the difference between emission spectra measured with excitation into CT_1 and CT_2 bands, having absorption maxima near 8 and 7 eV respectively (see later). Deuterium discharge lamp has most intensive line at 7.7 eV and less intensive continuum below 7 eV. So we could measure emission spectra under excitation mostly into CT_1 bands, because the intensity of 7.7 eV line is higher than that of 6–7 eV region and the absorption of CT_1 is several times larger than that of CT_2 . In another group of measurements we measured the emission spectra using emission of deuterium lamp over 5–6 mm of air. The air absorbed the lamp emission above 6.5 eV. In this case we measured spectra with excitation only into CT_2 bands. The emission spectra were qualitatively similar to those measured with lower resolution using excitation over vacuum monochromator.

3. Results

3.1. Absorption

The bands of 4f–5d transitions were observed in CaF_2 –Eu at energies above 8.4 eV [1]. Corresponding bands slightly shifts to

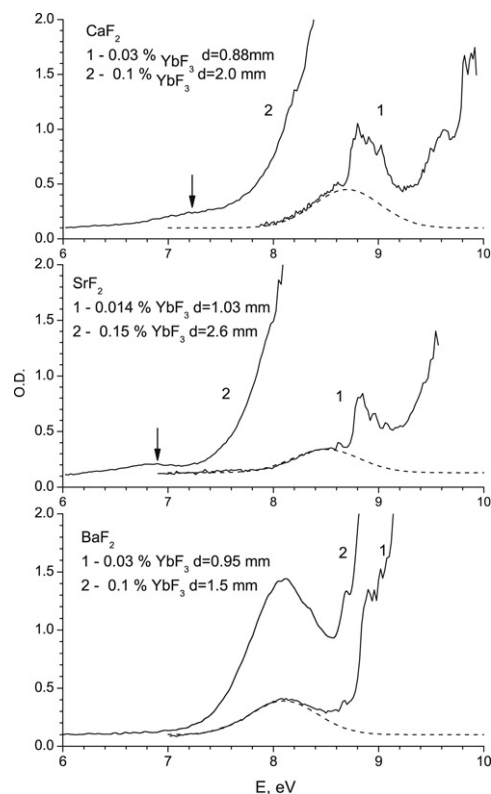


Fig. 2. Absorption spectra of CaF_2 , SrF_2 and BaF_2 crystal doped by YbF_3 at room temperature. Dashed curves show the fitted CT_1 absorption bands.

higher energies in a row of CaF_2 – SrF_2 – BaF_2 . This observation is consistent with weakening of strength of the crystal field in this row.

Broad bands at lower energy side of 4f–4f5d spectra were observed in all three fluorides in 7–8.2 eV region (Fig. 1). The maximum of bands shifts to lower energies in a row from CaF_2 to BaF_2 , which is consistent with reducing of the band gap of crystals in this row. For the first time broad unstructured bands were observed in CaF_2 doped by Yb or Eu by Schlesinger [1]. Later bands were assigned to charge-transfer bands by Blasse [5]. We will note these bands as CT_1 bands.

Other weaker broad absorption bands were observed in CaF_2 –Eu and SrF_2 –Eu crystals, but not observed in BaF_2 –Eu crystals (see Fig. 1). These bands increase with increasing of Eu concentration in similar way as other Eu bands. We denoted these bands as CT_2 . Later we will discuss the charge-transfer origin of these bands.

At 78 K all charge-transfer bands become more pronounced, CT_1 bands slightly shift to higher energies, maxima of CT_2 bands remains at the same positions in CaF_2 and SrF_2 (see Fig. 1).

Main features of absorption spectra of Eu-doped crystals can be also found in spectra of Yb-doped crystals (Fig. 2). The lines of 4f–5d Yb transitions slightly shift to higher energies in a row of CaF_2 – SrF_2 – BaF_2 . The broad CT_1 bands shift to lower energies in this row (see Fig. 2). Weaker additional absorption CT_2 bands near 7 eV were also observed, while their intensity is lower than those in Eu-doped crystals (compare Figs. 1 and 2). The position of absorption bands very slightly change when temperature decreases to 78 K.

Maxima of all observed bands are collected in Table 1.

3.2. Emission, excitation

During de-excitation from charge-transfer state the electron transfer from rare-earth ion to top levels of valence band, leaving

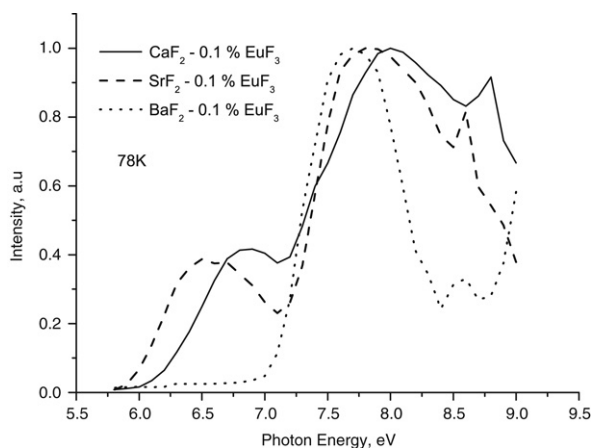


Fig. 3. Excitation spectra of CaF₂ crystal doped by 0.1 mol.% EuF₃. Emission of Eu ions was monitored at 2.1 eV ± 0.1 eV at 78 K.

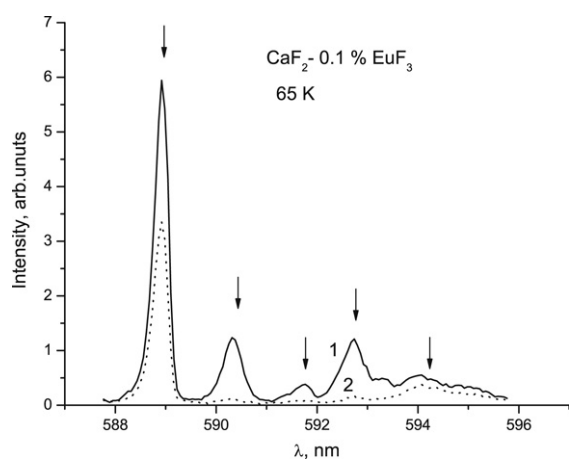


Fig. 4. Emission spectra of CaF₂ crystal doped by 0.1 mol.% EuF₃ in the region of ⁵D₀–⁷F₁ transitions at 78 K with vacuum ultraviolet excitation. Crystal was excited by unfiltered light from DDS30 lamp which was directly connected with MgF₂ window of cryostat (curve 1) (excitation mainly into CT₁ band), and separated from window by 5 mm air space (curve 2) (excitation into CT₂ band).

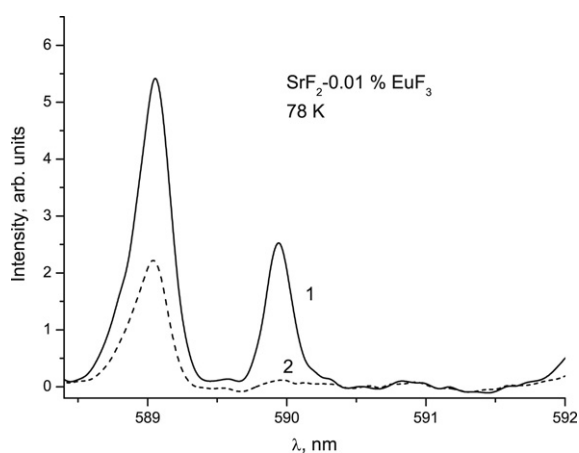


Fig. 5. Emission spectra of SrF₂ crystal doped by 0.01 mol.% EuF₃ in the region of ⁵D₀–⁷F₁ transitions at 78 K with vacuum ultraviolet excitation into 7.8 or 6.7 eV absorption bands. Crystal was excited by unfiltered light from DDS30 lamp which was directly connected with MgF₂ window of cryostat (curve 1), and separated from window by 5 mm air space (curve 2). Position of C_{4v}, O_h lines were taken from paper [7,8].

rare-earth ion in one of f-levels. Therefore the f–f lines are also observed after excitation into charge transfer bands similar to

Table 1

Energies in eV of broad absorption bands of alkaline-earth fluoride crystals doped by EuF₃ or YbF₃ at 80 K

Crystal	E(Eu ³⁺)	E(Yb ³⁺)	E(Eu ³⁺) _{est}	E(Yb ³⁺) _{est}
CaF ₂	8.35	8.7	8.2	8.7
	6.85	7.2		
SrF ₂	7.95	8.50	7.6	8.2
	6.65	6.9		
BaF ₂	7.70	8.14	7.4	7.9

Estimated energies E(Re³⁺)_{est} of charge transfer bands were calculated using model of Dorenbos [11].

direct excitation into f–f or f–d bands [2,3]. The excitation spectra of Eu f–f luminescence at 2.1 eV show two bands in CaF₂, SrF₂ crystals and one band in BaF₂ crystal (Fig. 3). The excitation spectra are similar to absorption spectra. The excitation spectra of CaF₂–Eu and SrF₂–Eu besides the main charge-transfer CT₁ bands contain also weaker CT₂ bands in 6–7 eV region. The excitation spectrum of BaF₂–Eu contains only main CT₁ charge-transfer bands (see Fig. 3). Therefore, we may conclude that CT₂ broad absorption and excitation bands at 6.9 eV in CaF₂–Eu and 6.7 eV in SrF₂–Eu belong to europium impurity.

To answer the question as to which type of sites (O_h, C_{4v}...) are excited in CT₁ or CT₂ bands we measured the high resolution emission spectra. Under excitation of CaF₂–Eu crystal into low energy CT₂ band the line at 588.93 nm and broad line at 594.1 nm were observed (Fig. 4), which are due to ⁵D₀–⁷F₁ transitions of C_{4v} sites [7,12]. In addition, under excitation into main charge-transfer CT₁ band besides the lines of C_{4v} sites, the lines at 590.31, 591.72, 592.73, 593.4 nm were observed as well (see Fig. 4); these four lines belong to R, Q aggregates and possibly to O_h sites [12].

The differences in emission spectra of SrF₂–Eu excited into CT₁ and CT₂ bands are well pronounced too (Fig. 5). According to known paper [8] the relative intensity of ⁵D₀–⁷F₁ line of O_h sites to that of C_{4v} is growth with decreasing of Eu concentration. According to this we observe relatively large O_h line only in crystal doped by 0.01 mol.% of Eu³⁺. The relative intensity of O_h line in crystals with larger europium concentration was very small. Under excitation into CT₂ 6.7 eV band the emission lines of C_{4v} sites only were observed, while under excitation into CT₁ 7.8 eV absorption band emission line of C_{4v} and O_h sites were observed (see Fig. 5).

No charge-transfer luminescence was observed in the crystals studied at 78 K and 10 K under excitation into charge-transfer CT₁ or CT₂ bands.

4. Discussion

We extend the investigation of Yb³⁺, Eu³⁺ charge transfer transitions to other fluorite crystals – to SrF₂ and BaF₂ crystals. The charge-transfer bands in these crystals become more separate from strong absorption 4f–4f5d bands than those in CaF₂ (see Figs. 1 and 2). This low-energy shift is obviously due to reduction of band gap in a row of CaF₂–SrF₂–BaF₂. The charge-transfer energies, calculated using empirical model of P. Dorenbos [11], agree with our experimental energies. The model takes into account experimental charge-transfer energies in CaF₂, while the estimated energies in BaF₂ and SrF₂ are less than experimental energies by 0.2–0.3 eV (see Table 1).

Another broad CT₂ band due to Eu or Yb impurity was observed at energies 6.7–7.2 eV in CaF₂ and SrF₂ crystals (see Table 1). The excitation spectra of red Eu³⁺ luminescence also show these bands in CaF₂ and SrF₂ and absence the band in BaF₂ crystals (Fig. 4). Moreover the Eu emission of CaF₂ and SrF₂ crystals under 6.6 eV excitation show only C_{4v} emission lines, while under excitation into main charge-transfer bands the lines of all present Eu sites (C_{4v}, O_h and aggregates) were observed. All these results allow us

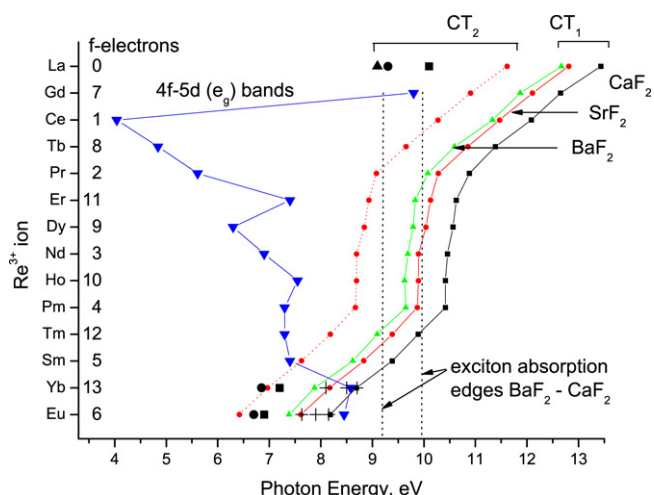


Fig. 6. Energies of CT_1 , CT_2 bands and 4f–5d (e_g) bands of rare earth ions in BaF_2 , SrF_2 , CaF_2 hosts. The estimated energies of CT_1 bands were taken from paper of Dorenbos [11]. Energies of La^{3+} CT_2 bands were taken from previous paper [13]. The CT_2 energies are roughly estimated as CT_1 energies minus 1.2 eV.

to conclude that the low-energy charge-transfer band is due to transitions from NN charge compensated interstitial fluorine to Eu or Yb ion. According to this the low energy CT_1 bands were not observed in BaF_2 –Eu crystals at room temperature, where C_{4v} Eu sites are absent.

Charge-transfer luminescence is known for many oxides doped by Yb ions [6]. However no such luminescence was found in CaF_2 –Yb and only very weak charge-transfer luminescence was found in $LiYF_4$ –Yb [2]. We could not find any measurable luminescence of CaF_2 –Yb, SrF_2 –Yb or BaF_2 –Yb crystals at 10 K under excitation into any of charge-transfer bands. It seems that the lattice relaxation in excited charge transfer state is very large, so the electron nonradiatively transfers to the ground state.

Known data on charge transfer absorption band were collected in the paper of Dorenbos [11]. Comparison of position of low energies 4f–5d bands and proposed charge transfer bands [11] allows one to conclude that only in Eu and Yb doped CaF_2 crystals the charge transfer bands could be observed below the 4f–5d absorption. For other rare-earth ion the charge-transfer bands should be covered by strong 4f–5d absorption bands. To estimate the position of charge-transfer bands against those of 4f–5d transitions we plot the energies of CT bands and those of 4f–5d bands for all rare earth ions introduced to CaF_2 , SrF_2 or BaF_2 crystals (Fig. 6). Data were sorted by ascending of CT_1 energies. According to this plot the charge-transfer bands have the energies lower than those of 4f–5d bands only for Eu and Yb ions. For Sm and Tm ions CT_1 energies are within 4f–5d bands but still less the exciton absorption edges. For all other ions CT_1 bands are covered by exciton absorption and could not be observed. However

CT_2 bands could be observed also for a number of ions between separated 4f–5d bands (see Fig. 6). We unsuccessfully tried to find CT_2 excitation bands in the region between splitted 5d bands in crystals doped by Sm or Tm. Obviously the 4f–5d absorption prevents the observation of CT_2 bands.

5. Conclusion

Investigation of absorption and excitation spectra of Eu^{3+} , Yb^{3+} doped alkaline-earth fluoride crystals in vacuum ultraviolet region as well as high resolution emission spectra of Eu^{3+} doped crystals lead us to following conclusions:

CT_1 absorption bands, which were observed in the 7–9 eV region just below the 4f–5d absorption edge of Eu^{3+} or Yb^{3+} in SrF_2 and BaF_2 , belong to charge-transfer transitions, when electron transfers from surrounding fluorines to central rare-earth ion.

CT_2 absorption bands, observed in the 6–8 eV region in CaF_2 , SrF_2 doped by Eu^{3+} or Yb^{3+} ions, belong to charge transfer transitions of another type, where electron transfers from nearest neighboring charge compensation fluorine to rare-earth ion.

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References

- [1] T. Szczurek, M. Schlesinger, Rare earths spectroscopy, in: B. Jezowska-Trzebiatowska, J. Legendziewicz, W. Streck (Eds.), Proc. Int. Symp. on Rare Earths Spectroscopy (Wroclaw, Poland, Sept. 1984), World Scientific, Singapore, 1985, p. 309.
- [2] van L. Pieterse, M.F. Reid, R.T. Wegh, S. Soverna, A. Meijerink, Phys. Rev. B 65 (2002) 045113.
- [3] van L. Pieterse, M.F. Reid, G.W. Burdick, A. Meijerink, Phys. Rev. B 65 (2002) 045114.
- [4] M. Schlesinger, T. Szczurek, M.K. Wade, G.W.F. Drake, Phys. Rev. B 18 (1978) 6388.
- [5] G. Blasse, J. Phys. Chem. Solids 50 (1989) 99.
- [6] van L. Pieterse, M. Heeroma, E. de Heer, A. Meijerink, J. Lumin. 91 (2000) 177.
- [7] J.R. Wells, R.J. Reeves, Phys. Rev. B 64 (2001) 035102.
- [8] J.P. Jouart, C. Bissieux, G. Mary, M. Egee, J. Phys. C: Solid State Phys. 18 (1985) 1539.
- [9] N. Guerassimova, C. Dujardin, N. Garnier, C. Pedrini, A.G. Petrosyan, I.A. Kamenskikh, V.V. Mikhailin, I.N. Shpinkov, D.A. Spassky, K.L. Ovanesyan, G.O. Shirinyan, R. Chipaux, M. Cribier, J. Mallet, J.P. Meyer, Nucl. Instrum. Meth. Phys. Res. A 486 (2002) 278.
- [10] J.B. Shim, A. Yoshikawa, M. Nikl, J. Pejchal, A. Vedda, T. Fukuda, Radiat. Meas. 38 (2004) 493.
- [11] P. Dorenbos, J. Phys. C: Solid State Phys. 13 (2003) 8417.
- [12] R.J. Hamers, J.R. Wietfeldt, J.C. Wright, J. Chem. Phys. 77 (1982) 683.
- [13] E. Radzhabov, M. Kirm, A. Nepomnyashchikh, Phys. Status Solidi A 204 (2007) 670.