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

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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\(_2\), BaF\(_2\) 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\(^0\) outer electron configuration and \(^7F_0\) ground term. Emission from lowest excited 4f\(^1\) configuration \(^5D_0\) to ground \(^7F_0\) 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\(_2\)O\(_3\)–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 \(\Phi 10 \times 50\) 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
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\textsubscript{4v} and O\textsubscript{h} of Eu\textsuperscript{3+} sites in CaF\textsubscript{2} and SrF\textsubscript{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\textsubscript{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\textsubscript{1} and CT\textsubscript{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\textsubscript{1} bands, because the intensity of 7.7 eV line is higher than that of 6–7 eV region and the absorption of CT\textsubscript{1} is several times larger than that of CT\textsubscript{2}. In another group of measurements we measured the emission spectra using 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\textsubscript{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\textsubscript{2}–Eu at energies above 8.4 eV [1]. Corresponding bands slightly shifts to higher energies in a row of CaF\textsubscript{2}–SrF\textsubscript{2}–BaF\textsubscript{2}. This observation is consistent with weakening of strength of the crystal field in this row.

Broad bands at lower energy side of 4f–4f\textsubscript{5d} 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\textsubscript{2} to BaF\textsubscript{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\textsubscript{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\textsubscript{1} bands.

Other weaker broad absorption bands were observed in CaF\textsubscript{2}–Eu and SrF\textsubscript{2}–Eu crystals, but not observed in BaF\textsubscript{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\textsubscript{2}. Later we will discuss the charge-transfer origin of these bands.

At 78 K all charge-transfer bands become more pronounced, CT\textsubscript{1} bands slightly shift to higher energies, maxima of CT\textsubscript{2} bands remains at the same positions in CaF\textsubscript{2} and SrF\textsubscript{2} (see Fig. 1).

Main features of absorption spectra of Eu-doped crystals can also be 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\textsubscript{2}–SrF\textsubscript{2}–BaF\textsubscript{2}. The broad CT\textsubscript{1} bands shift to lower energies in this row (see Fig. 2). Weaker additional absorption CT\textsubscript{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
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 CaF$_2$, SrF$_2$ crystals and one band in BaF$_2$ crystal (Fig. 3). The excitation spectra are similar to absorption spectra. The excitation spectra of CaF$_2$–Eu and SrF$_2$–Eu besides the main charge-transfer CT$_1$ bands contain also weaker CT$_2$ bands in 6–7 eV region. The excitation spectrum of BaF$_2$–Eu contains only main CT$_1$ charge-transfer bands (see Fig. 3). Therefore, we may conclude that CT$_2$ broad absorption and excitation bands at 6.9 eV in CaF$_2$–Eu and 6.7 eV in SrF$_2$–Eu belong to europium impurity.

To answer the question as to which type of sites (O$_{h}$, C$_{4v}$, or aggregates) were observed (Fig. 3), we may conclude that CT$_2$ broad absorption and excitation bands at 6.9 eV in CaF$_2$–Eu and 6.7 eV in SrF$_2$–Eu belong to europium impurity.

The differences in emission spectra of SrF$_2$–Eu excited into CT$_1$ and CT$_2$ bands are well pronounced too (Fig. 5). According to known paper [8] the relative intensity of $^5$D$_{0}$–F$_{1}$ 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 Eu$^{3+}$. The relative intensity of O$_{h}$ line in crystals with larger europium concentration was very small. Under excitation into CT$_2$ 6.7 eV band the emission lines of C$_{4v}$ sites only were observed, while under excitation into CT$_1$ 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 CT$_1$ or CT$_2$ bands.

4. Discussion

We extend the investigation of Yb$^{3+}$, Eu$^{3+}$ charge transfer transitions to other fluorite crystals — to SrF$_2$ and BaF$_2$ crystals. The charge-transfer bands in these crystals become more separate from strong absorption 4f–4f5d bands than those in CaF$_2$ (see Figs. 1 and 2). This low-energy shift is obviously due to reduction of bang gap in a row of CaF$_2$–SrF$_2$–BaF$_2$. 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 CaF$_2$, while the estimated energies in BaF$_2$ and SrF$_2$ are less than experimental energies by 0.2–0.3 eV (see Table 1).

Another broad CT$_2$ band due to Eu or Yb impurity was observed at energies 6.7–7.2 eV in CaF$_2$ and SrF$_2$ crystals (see Table 1). The excitation spectra of red Eu$^{3+}$ luminescence also show these bands in CaF$_2$ and SrF$_2$ and absence the band in BaF$_2$ crystals (Fig. 4). Moreover the Eu emission of CaF$_2$ and SrF$_2$ 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

### Table 1

<table>
<thead>
<tr>
<th>Crystal</th>
<th>E(Eu$^{3+}$)</th>
<th>E(Yb$^{3+}$)</th>
<th>E(Eu$^{3+}$)$_{est}$</th>
<th>E(Yb$^{3+}$)$_{est}$</th>
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<td>8.7</td>
<td>8.2</td>
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<tr>
<td>SrF$_2$</td>
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<td>8.50</td>
<td>7.6</td>
<td>8.2</td>
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<tr>
<td>BaF$_2$</td>
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<td>8.14</td>
<td>7.4</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Estimated energies E(Re$^{3+}$)$_{est}$ of charge transfer bands were calculated using model of Dorenbos [11].

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**Fig. 3.** Excitation spectra of CaF$_2$ crystal doped by 0.1 mol.% EuF$_3$. Emission of Eu ions was monitored at 2.1 eV ± 0.1 eV at 78 K.

**Fig. 4.** Emission spectra of CaF$_2$ crystal doped by 0.1 mol.% EuF$_3$ in the region of $^5$D$_{0}$–F$_{1}$ transitions at 78 K with vacuum ultraviolet excitation. Crystal was excited by unfiltered light from DDS30 lamp which was directly connected with MgF$_2$ window of cryostat (curve 1) (excitation mainly into CT$_1$ band), and separated from window by 5 mm air space (curve 2) (excitation into CT$_2$ band).

**Fig. 5.** Emission spectra of SrF$_2$ crystal doped by 0.01 mol.% EuF$_3$ in the region of $^5$D$_{0}$–F$_{1}$ transitions at 78 K with vacuum ultraviolet excitation into 7.8 or 6.7 eV absorption bands. Crystal was excited by unfiltered light from DSS30 lamp which was directly connected with MgF$_2$ 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].
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$_{6v}$ 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 LiF$_2$–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 (e$^*_2$) 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.

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


Fig. 6. Energies of CT$_1$, CT$_2$ bands and 4f–5d ($e^*_2$) 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.