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Charge-Transfer Bands in Crystals of Alkaline Earth Fluorides with Eu^{3+} and Yb^{3+} [1]

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Abstract—The absorption, luminescence, and excitation spectra of CaF_2, SrF_2, and BaF_2 crystals with EuF_3 or YbF_3 impurity have been investigated in the range 1–12 eV. In all cases, strong wide absorption bands (denoted as CT_1) were observed at energies below the $4f^n$–$4f^{n-1}5d$ absorption threshold of impurity ions. Weaker absorption bands (denoted as CT_2) with energies 1.5–2 eV lower than those of the CT_1 bands have been found in the spectra of CaF_2 and SrF_2 crystals with EuF_3 or YbF_3 impurities. The fine structure of the luminescence spectra of CaF_2 crystals with EuF_3 impurities has been investigated under excitation in the CT bands. Under excitation in the CT_1 band, several Eu centers were observed in the following luminescence spectra: C_{4v}, O_h, and R aggregates. Excitation in the CT_2 bands revealed luminescence of only C_{4v} defects.

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INTRODUCTION

The narrow lines in the absorption and excitation spectra in the vacuum UV region in crystals of alkaline earth fluorides with rare earth ion impurities are due to the $4f^n$–$4f^{n-1}5d$ transitions [1–3]. In addition, wide structureless bands, partially overlapping with the low-energy $4f^n$–$4f^{n-1}5d$ edge, were found in the CaF_2–Eu [1] and CaF_2–Yb [4] crystals. Later, these bands were classified as charge-transfer bands [5], which are due to transitions from the levels of the valence band, formed by the 2*p* states of surrounding fluorine ions, to the 4*f* states of rare earth impurity ions. Many oxides with the Yb^{3+} impurity exhibit charge-transfer luminescence [6]. However, luminescence of this type has not been revealed in CaF_2–Yb crystals [2, 3].

The known data on charge-transfer bands are compiled in [7]. Comparison of the energies of the $4f^n$–$4f^{n-1}5d$ bands with the estimated energies of charge-transfer bands [7] suggests that the latter should only be observed at energies below those of the $4f^n$–$4f^{n-1}5d$ bands for Eu and Yb impurities in CaF_2. For other rare earth ions, the charge-transfer bands should be overlapped by strong $4f^n$–$4f^{n-1}5d$ bands.

Eu^{3+} ions have the external electronic configuration $4f^6$ and the ground-state term $^7F_0$. Luminescence from the ^5D_j excited states of the $4f^6$ configuration gives rise to a series of narrow lines in the red spectral region. The $^5D_0$–$^7F_1$ transitions with an energy of about 2.1 eV are strongest. The presence of charge-compensating fluorine ions in the alkaline earth crystals shifts the *f*–*f* transition energies. Analysis of the luminescence and excitation spectra revealed the C_{4v}, C_{3v}, and O_h centers of symmetry in CaF_2–Eu crystals [8, 9], in which interstitial fluorine is located, respectively, in the nearest (*NN*) or next (*NNN*) positions or at a large distance from an europium ion. The shift of the $^5D_0$–$^7F_1$ line caused by the interaction of europium ions with neighboring fluorine is maximum in CaF_2 crystals due to the least distance between an europium ion and interstitial fluorine. C_{3v} centers of europium were not observed in CaF_2 crystals, C_{4v} centers were not revealed in BaF_2 crystals, and O_h cubic centers were observed in all crystals.

The purpose of this study was to analyze the charge-transfer transitions in CaF_2, SrF_2, and BaF_2 crystals with rare earth impurity ions.

EXPERIMENTAL

The crystals were grown in a graphite crucible in vacuum by the Stockbarger method. The crucible consisted of three cylindrical cavities with a diameter of 10 mm and a length of 80 mm; thus, three 10 × 50-mm crystals with different impurity concentrations could be grown simultaneously. Initially, relatively large crystals with added CdF_2 (to remove oxygen) were grown. Then, a part of an initial crystal was used to grow a crystal with impurities. The impurity concentration was varied from 0.001 to several mol %.

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The spectra in the range 4–12 eV were measured using a VMR-2 vacuum monochromator. A hydrogen discharge lamp with a fluorine magnesium window (transparent up to 10.9 eV) was used as a vacuum UV source.

The luminescence spectra were measured using an MDR2 grating monochromator at 78 K. The monochromator resolution limit was 0.4 nm, a value sufficient for recording strongly split lines in the spectra of CaF_2 crystals. Some luminescence spectra were also measured at 10 K. However, as a result of low spectral resolution, the 10-K luminescence spectra turned out to be the same. For simplicity, we will denote the transitions as 4*f*–5*d* instead of the more complete designation $4f^n$–$4f^{n-1}5d$.

RESULTS

Absorption

4*f*–5*d* absorption bands were observed in CaF_2–Eu at energies above 8.4 eV [1]. The low-energy band of the 4*f*–5*d* transitions is slightly blueshifted in the CaF_2–SrF_2–BaF_2 series. This result is in agreement with the decrease in the crystal field in this series.

All three crystals exhibit a wide band adjacent to the 4*f*–5*d* absorption edge (Fig. 1). The band width is proportional to the impurity concentration. Wide bands were observed for the first time in the spectra of CaF_2–Eu and CaF_2–Yb crystals [1]. Later, the spectral bands of CaF_2 were interpreted as charge-transfer bands [5]. The band maximum is redshifted in the CaF_2–SrF_2–BaF_2 series; this shift is consistent with the decrease in the bandgap. Such bands are denoted below as CT_1.

CaF_2–Eu and SrF_2–Eu crystals exhibit also a weak absorption band peaking in the range 6–7 eV (Fig. 1). This absorption band is absent in the spectra of BaF_2. As CT_1 bands, this band increases with the europium concentration. We denoted it as CT_2. Below, we will show that it is also a charge-transfer band. At 80 K, the charge-transfer bands are more pronounced; the band CT_1 shifts to higher energies, while the CT_2 band is not shifted (Fig. 1).

The absorption spectra of the YbF_3-containing crystals are similar to those of the crystals with the EuF_3 impurity (Fig. 2). The line due to the 4*f*–5*d* transitions is slightly blueshifted in the series from CaF_2 to BaF_2. The wide CT_1 band is redshifted in this series. A weak absorption band CT_2 is also observed, although its relative magnitude is smaller than for the crystals with the EuF_3 impurity (compare Figs. 1 and 2). The band positions only slightly shift with a decrease in temperature to 80 K.

The energies of all observed bands are listed in the table.

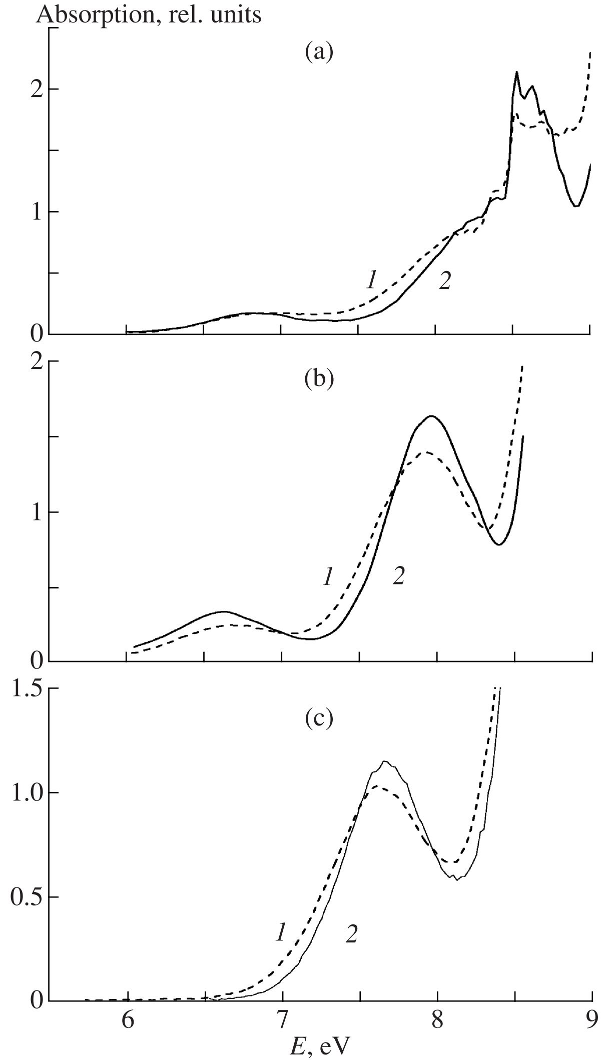

Fig. 1. Absorption spectra of (a) CaF_2, (b) SrF_2, and (c) BaF_2 crystals with 0.1 mol % EuF_3 impurity; T = (*1*) 295, (*2*) 80 K.

Luminescence, Excitation

Upon relaxation from charge-transfer states of a rare earth ion, an electron passes to the states of surrounding fluorine ions in the top of the valence band. In this case,

Energies (in eV) of broad absorption bands of alkaline earth fluoride crystals with a EuF_3 or YbF_3 impurity at 80 K (the estimated energies E_{est} of the charge-transfer bands are taken from [7])

Crystal	$E(Eu^{3+})$	$E(Yb^{3+})$	$E_{est}(Eu^{3+})$	$E_{est}(Yb^{3+})$
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

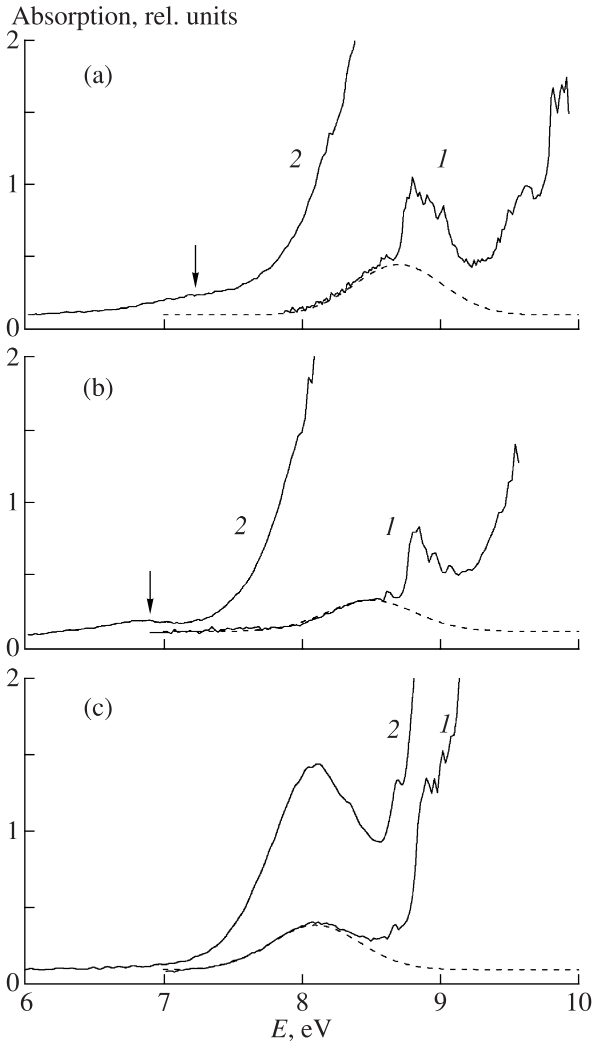

Fig. 2. Absorption spectra of (a) CaF_2, (b) SrF_2, and (c) BaF_2 crystals with an 0.1 mol % YbF_3 impurity, recorded at room temperature; the dashed line is the calculated Gaussian curve for the CT_1 band. The YbF_3 content is (a) (*1*) 0.03 and (*2*) 0.1 mol %; (b) (*1*) 0.014 and (*2*) 0.15 mol %; and (c) (*1*) 0.02 and (*2*) 0.1 mol %.

a rare earth ion is in one of the excited *f* states. Therefore, the *f*–*f* lines of rare earth ions are also observed upon excitation to the charge-transfer band [2, 3]. The absence of the 4*f*–5*d* luminescence under excitation to the broad absorption (excitation) band is one of the criteria for identifying charge-transfer bands.

The excitation spectra of Eu *f*–*f* red luminescence in the range of charge-transfer transitions consist of two bands for CaF_2 and SrF_2 crystals and one band for BaF_2 crystals. The excitation spectra are similar to the absorption ones. The excitation spectra of the CaF_2–Eu and SrF_2–Eu crystals, along with the CT_1 band, contain also a weaker CT_2 band (Fig. 3). The excitation spectra of the BaF_2–Eu crystals contain only one CT_1 band (Fig. 3).

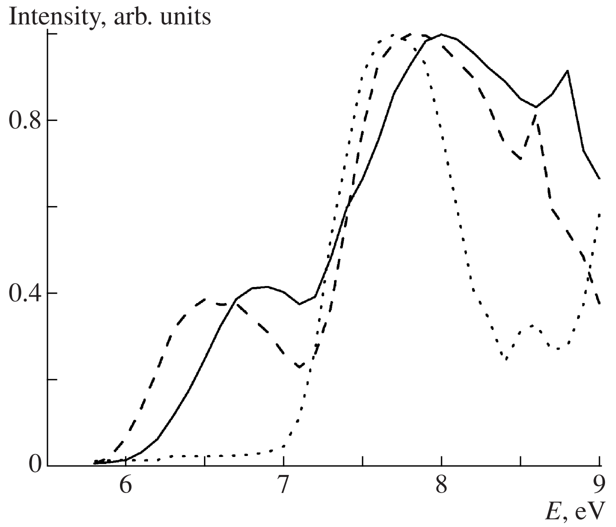

Fig. 3. Excitation spectra of (solid line) CaF_2, (dashed line) SrF_2, and (dotted line) BaF_2 crystals with 0.1 mol % EuF_3 impurity. The Eu^{3+} luminescence was recorded in a wide range 2.1 ± 0.03 eV at 78 K.

To establish the symmetry of Eu centers, emitting under excitation to charge-transfer bands, we measured the luminescence spectra with a resolution sufficient for separating individual lines. The strongest lines are due to the $^5D_0$–$^7F_1$ transition. Therefore, they were chosen to detect the center symmetry. The luminescence spectra of the CaF_2–Eu^{3+} crystals significantly differ in the case of excitation to the CT_1 and CT_2 bands (Fig. 4). The lines at 16 832 and 17 981 cm^{-1} are due to C_{4v} centers, the line at 16 937 cm^{-1} is related to O_h centers, and the line at 16 878 cm^{-1} is due to the so-called *R* aggregate centers [8]. Under excitation of CaF_2–Eu crystals to the CT_2 band, the luminescence lines of C_{4v} centers were observed, whereas excitation to the CT_1 band gave rise to the lines due to C_{4v}, O_h, and *R* centers.

The charge-transfer luminescence is efficient in crystals of oxides with the YBF_3 impurity, but it was not observed in CaF_2–Yb [3]. We also could not find charge-transfer luminescence in CaF_2–Yb, SrF_2–Yb, and BaF_2–Yb crystals under excitation to the CT_1 and CT_2 bands.

DISCUSSION

In this study, we investigated the charge-transfer transitions in Yb^{3+} and Eu^{3+} ions in SrF_2 and BaF_2 crystals and revealed another band in the spectra of CaF_2, which can be assigned to these transitions. The charge-transfer bands of SrF_2 and BaF_2 crystals are better separated from the 4*f*–5*d* absorption edge in comparison with CaF_2 (compare Figs. 1 and 2). Such a separation is due to the fact that the CT_1 charge-transfer bands shift

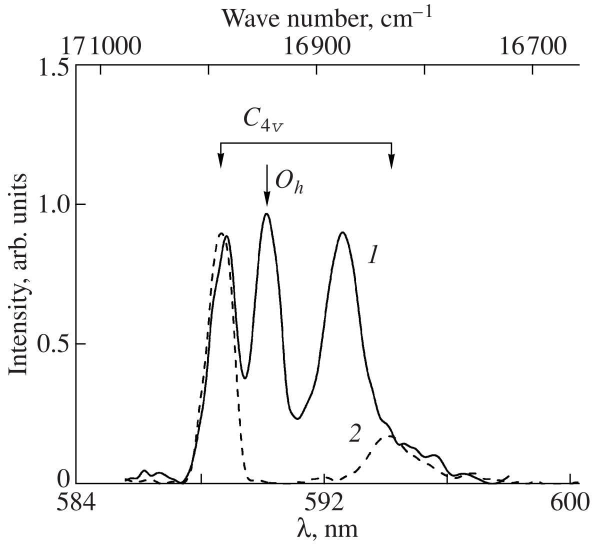

Fig. 4. Luminescence spectra of CaF_2 crystals with 0.1 mol % EuF_3 impurity in the vicinity of the $^5D_0$–$^7F_1$ transitions at 78 K. Crystals were excited by light in the range of the CT_1 and CT_2 bands, photon energies are (*1*) 7.7 and (*2*) 6.6 eV. The spectral width of the monochromator slit is 0.4 nm. The positions of the C_{4v} and O_h lines are taken from [8].

to lower energies in the CaF_2–SrF_2–BaF_2 series and, simultaneously, the 4*f*–5*d* absorption edge slightly shifts to higher energies. The experimental energies of the charge-transfer bands are in agreement with the semiempirically calculated values [7]. The calculation is based on the experimental charge-transfer energies in CaF_2–Yb and CaF_2–Eu. The calculated energies of bands in SrF_2 and BaF_2 crystals are 0.2–0.3 eV lower than our experimental energies (table).

Another CT_2 absorption band, of lower intensity, was found in CaF_2 and SrF_2 crystals with a EuF_3 or YbF_3 impurity (Figs. 1, 2). The CT_2 band is also observed in the excitation spectra of red Eu^{3+} *f*–*f* luminescence (Fig. 3). Undoubtedly, the CT_1 band in the spectra of SrF_2 and BaF_2 crystals is due (as for CaF_2 crystals) to charge-transfer transitions. The CT_2 band is likely to be a charge-transfer band. The energy of CT_2 bands is 1.5–2 eV smaller than that of CT_1 bands. One might suggest that CT_2 transitions in centers occur from interstitial charge-compensating fluorine to a rare earth ion, whereas the CT_1 transitions in centers are related to electron transfer from the surrounding lattice fluorine ions to a rare earth ion. The intensity of such transitions for the least distance in an Re^{3+}–F_i^- pair should be several times lower since there are eight lattice fluorine ions per interstitial fluorine ion. When a fluorine ion is in the next interstitial site (*NNN*), the intensity of such transitions becomes much lower. It is known that only *NNN* Re^{3+}–F_i^- pairs are observed in BaF_2 crystals; accordingly, there are no CT_2 bands in the absorption (Figs. 1, 2) or excitation (Fig. 3) spectra. If our sugges-

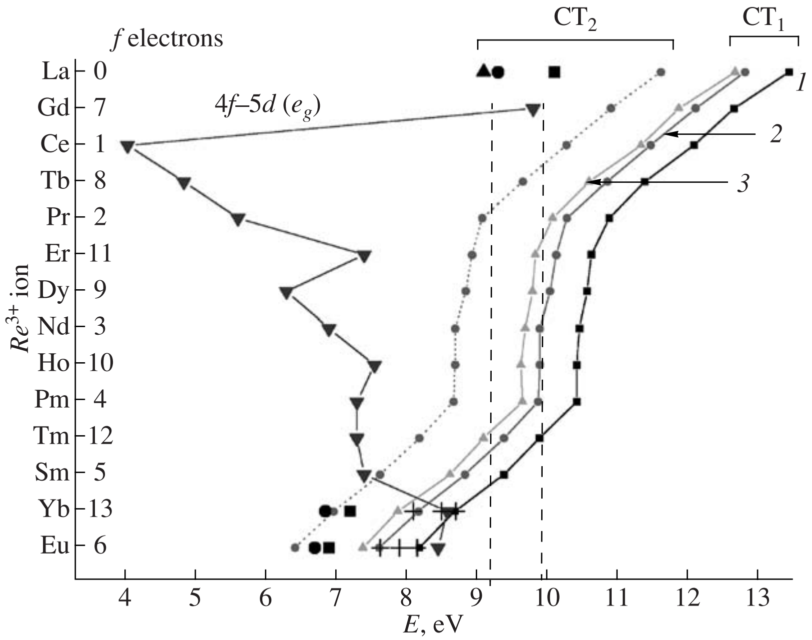

Fig. 5. Energies of the CT_1, CT_2, and 4*f*–5*d*(e_g) bands of trivalent rare earth ions in (*1*) CaF_2, (*2*) SrF_2, and (*3*) BaF_2 crystals. The estimated energies of the CT_1 bands are taken from [7] and the energies of the CT_2 bands for La^{3+} are taken from [10]. The CT_2 energies are roughly estimated as the CT_1 energies minus 1.2 eV. The vertical dashed lines are the edges of the BaF_2–CaF_2 exciton absorption.

tion is true, the luminescence spectra should differ under excitation to CT_1 or CT_2 bands.

Indeed, significant differences were found in the red luminescence spectra of Eu^{3+} under excitation to CT_1 or CT_2 bands (Fig. 4). In CaF_2 crystals, excitation to a CT_2 band causes luminescence of only C_{4v} centers, whereas, under excitation to a CT_1 band, we observed luminescence of C_{4v} and O_h centers and aggregate R centers. Thus, the experimental results allow us to confidently assign the CT_2 absorption and excitation bands to transitions in small-distance (*NN*) $Re^{3+}–F_i^-$ pairs.

Charge-transfer luminescence is known for many Yb-containing oxide crystals [6, 11]. However, the luminescence of this type was not revealed in CaF_2–Yb crystals and it is very weak in $LiYF_4$ crystals [2]. We also could not reveal charge-transfer luminescence in CaF_2–Yb, SrF_2–Yb, and BaF_2–Yb crystals under excitation to CT_1 or CT_2 bands at a temperature of 10 K. It is most likely that the soft anion sublattice of these crystals facilitates strong relaxation of excited centers and quenching of the charge-transfer luminescence.

To estimate the possibility of observing isolated charge-transfer bands, we presented in the same plot the energies of charge-transfer bands (calculated in [7]) as functions of the energies of 4*f*–5*d* transitions in rare earth (Re^{3+}) ions (Fig. 5). The energies of charge-transfer CT_1 bands are given in ascending order. The plotted data indicate that the charge-transfer band energy is lower than the energy of the first 4*f*–5*d* transitions and the charge-transfer bands are spectrally separated from the region of 4*f*–5*d* transitions for only Eu and Yb ions. For Sm and Tm ions, the CT_1 charge-transfer bands fall in the range of the 4*f*–5*d* transitions, while the charge-transfer bands for other rare earth ions lie in the range of exciton and interband absorption (Fig. 5). The CT_2 bands for a number of rare earth ions correspond to 4*f*–5*d* absorption. We failed to find CT_2 bands in the range between split 4*f*–5*d* bands from the luminescence of only C_{4v} centers based on Eu^{3+} ions. It is most likely that the 4*f*–5*d* absorption dominates over the CT_2 absorption even in the gap between the 4*f*–5*d* bands split by the crystal field.

CONCLUSIONS

The strong absorption (and excitation) bands in SrF_2 and BaF_2 crystals with a EuF_3 or YbF_3 impurity, located below the 4*f*–5*d* absorption edge, are due to the CT_1 charge-transfer transitions, in which an electron is transferred from a surrounding fluorine ion to the central rare earth ion.

The weaker absorption (and excitation) bands in CaF_2 and SrF_2 crystals with a EuF_3 or YbF_3 impurity in the range 6–7.5 eV are due to the CT_2 charge-transfer transitions of another type, in which an electron is transferred from a charge-compensating interstitial fluorine ion, located in the nearest *NN* position, to a rare earth ion.

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