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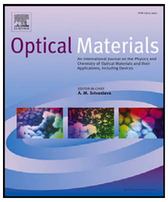

Research article

Fine structure of 4f–5d absorption spectra of MeF_2-Yb^{3+} in the vacuum ultraviolet region under synchrotron excitation

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ABSTRACT

Narrow dips were found in the excitation spectra of crystals of alkaline earth fluorides doped with ErF_3 or/and YbF_3. The positions of the dips are in good agreement with the positions of the narrow absorption lines Er^{3+}, Yb^{3+} measured earlier. The absorption lines of the crystals were calculated from the excitation spectra. The observed dips in the excitation spectra are due to the absorption lines of 4f–5d transitions in lanthanide ions.

1. Introduction

The absorption (excitation) spectra of 4f–5d interconfiguration transitions of trivalent lanthanide ions at low temperatures exhibit a fine structure that is more pronounced in low-energy bands [1–3]. At room temperature, the structure of the bands disappeared, leaving wide absorption bands. However, the vacuum ultraviolet (VUV) absorption spectrum of Yb^{3+} ions in CaF_2 demonstrated marked differences from the consistent pattern of the other rare-earth ions at low temperatures [2]. The development of modern, bright VUV synchrotron sources allowed to measure VUV excitation spectra of lanthanide ions more precisely [4]. Nevertheless, the spectral resolution of excitation spectra in the VUV region remained relatively low. The appearance of modern undulator luminescence endstation FINESTLUMI of FinEstBeAMS beamline at MAX IV synchrotron makes it possible to obtain excitation spectra with a previously unattainable high resolution [5–7].

In this work, we studied the 4f–5d excitation, absorption overexcitation, emission spectra of Yb^{3+}, Er^{3+}, ions in alkaline-earth fluoride crystals with a high resolution.

2. Experimental

Crystals were grown in a vacuum in a graphite crucible by the Stockbarger method in the Institute of Geochemistry SB RAS [8]. The graphite crucible contained six cylindrical cavities with a diameter of 10 mm and a length of 80 mm, which made it possible simultaneously to grow six samples with sizes 10 × 50 mm with different amounts of impurities. A few percentages of CdF_2 was added into raw materials for purification from oxygen during growth.

Spectra were measured at 7 K at the photoluminescence endstation FINESTLUMI of the FinEstBeAMS undulator beamline at 1.5 GeV storage ring of MAX-IV synchrotron facility (Lund, Sweden) [5,7,9]. An important advantage of the photoluminescence endstation FINESTLUMI is the high brightness as well as the grazing incidence monochromatization of the VUV radiation making it possible to carry out measurements with high spectral resolution (or very narrow spectral width). The highest resolution was about 1.2 meV at 21 eV [6] (which corresponds to a spectral slit width of 0.003 nm). In previous measurements of the excitation spectra of lanthanide ions in fluoride crystals on the DESY synchrotron in Hamburg, Germany, the spectral resolution usually was about 0.3 nm [4], with the ultimate resolution of 0.1 nm [10].

3. Results

A unique feature of Yb^{3+} ions in CaF_2 crystals is the partial conservation of the fine structure of the 4f–5d absorption spectrum at room temperature [1]. We observed narrow absorption lines at room temperature also in SrF_2 and less evident in BaF_2 crystals (Fig. 1). The absorption lines narrow with decreasing temperature.

Our measurements revealed unusual narrow dips in the excitation spectra of crystals of alkaline earth fluorides doped with Ln^{3+} lanthanides. We assumed that in crystals with a double activation, these dips may be due to narrow absorption lines of ‘inactive’ lanthanide. In the case of the spectra of MeF_2-Er-Yb, this is confirmed by comparing the positions of the dips with the known absorption spectra of MeF_2-Yb.

Yb^{3+} ions are characterized by a 4f–4f absorption band at about 950 nm and a corresponding emission band at about 980 nm. Since

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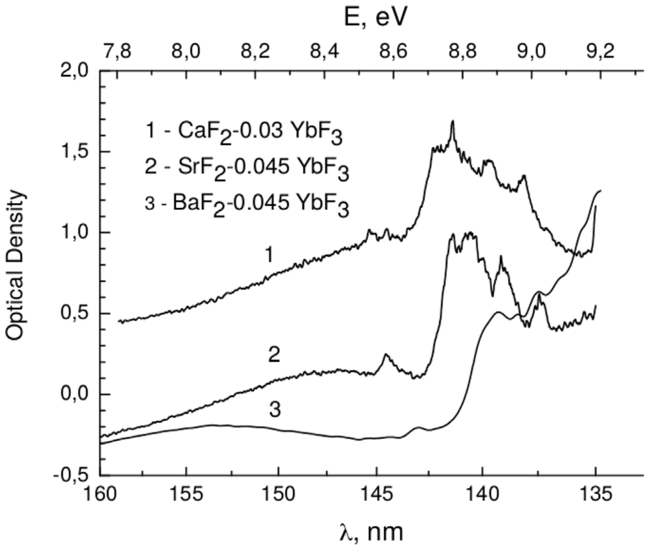

Fig. 1. Absorption of MeF_2-YbF_3 at room temperature.

we measured the excitation spectra of Er^{3+} ions emitting in the visible region, the absorption of Yb^{3+} appears in the excitation curve as dips. Drawing a smooth baseline on the erbium excitation spectrum in MeF_2-Er^{3+}-Yb^{3+} crystals, narrow absorption lines belonging to Yb^{3+} can be distinguished.

3.1. *Me*F_2-*Yb*F_3 *absorption*

Broad absorption bands of MeF_2-YbF_3 in the 140–170 nm region belong to charge transfer transitions [11], at the short-wavelength edge of which the 4f–5d bands of Yb^{3+} ions are observed (see Fig. 1) [2]. Charge transfer and 4f–5d transition bands are shifted to shorter wavelengths in the CaF_2-SrF_2-BaF_2 series. The shift is due to a decrease in the splitting of the 5d levels by the crystal field in this series. The exciton absorption edge shifts strongly in the CaF_2-SrF_2-BaF_2 series and is superimposed with the 4f–5d absorption in BaF_2 (see Fig. 1).

3.2. *Me*F_2-*Yb,Er excitation*

In alkaline-earth fluoride crystals with a double activation of Yb^{3+}-Er^{3+} ions, broad excitation bands of 4f–5d transitions of Er^{3+} ions emitting in the green and red spectral regions were observed in the VUV region of 8–11 eV. Several narrow spectral dips were observed in the spectrum (Fig. 2).

Two groups of narrow lines are observed in the absorption spectrum of MeF_2–0.1% ErF_3–0.1% YbF_3. The half-width of some lines is about 4 meV. The energy range 8.5–9.3 eV refers to the first absorption band of Yb^{3+} 4f–5d(e_g), and transitions above 9.5 eV belong to the second band of 4f–5d(t_{2g}).

Observed spectral dips can be compared with lines of 4f–5d transitions in Yb^{3+} ions in CaF_2. The observed spectral dips in the excitation spectrum can be converted to the absorption lines of Yb^{3+} ions in the usual manner $D = log(I/I_o)$. Here $I_o(\lambda)$ is smooth baseline of Er-excitation spectrum (see Fig. 2).

The absorption spectrum of the 4f–5d transitions calculated from the excitation spectrum (Fig. 3) coincides well with the absorption spectrum of CaF_2-Yb measured in the articles [1,3]. The absorption lines measured by us are significantly narrower and, accordingly, more intense, which is due to the sufficiently higher spectral resolution.

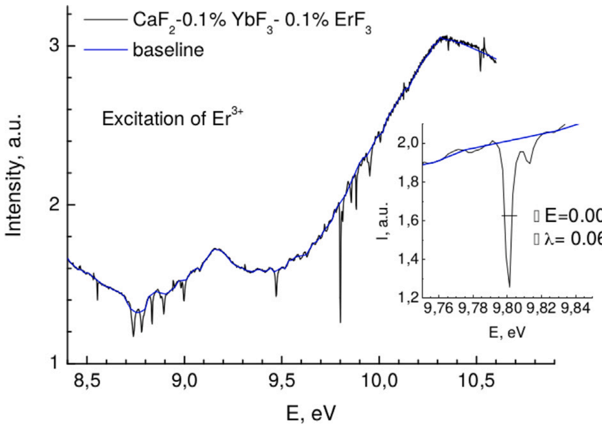

Fig. 2. Part of excitation spectra of CaF_2–0.1ErF_3–0.1YbF_3 at 7K showing narrow spectral dips on Er^{3+} excitation curve. The smooth red line is the baseline used for estimation of absorption spectrum.

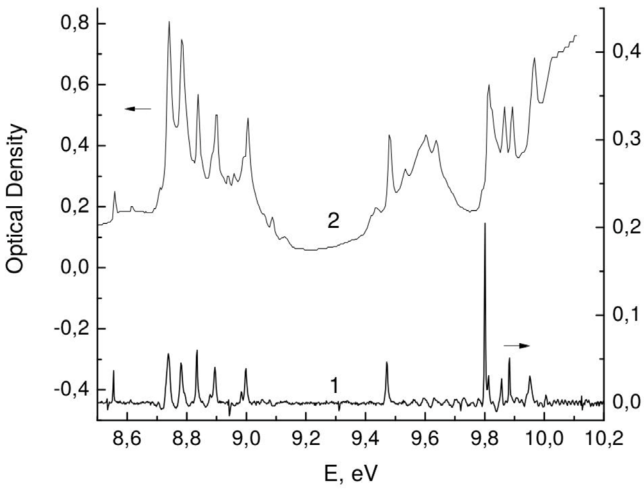

Fig. 3. Absorption lines of CaF_2–0.1YbF_3–0.1ErF_3 calculated from excitation spectrum Fig. 2 (1) compared with the absorption spectrum of CaF_2–0.005 YbF_3.
Source: Adapted from paper [1].

3.3. *Ca*F_2-*Yb*$^{2+}$-*Yb*$^{3+}$

Besides the normal 5d–4f luminescence in most materials, the Eu^{2+}, Yb^{2+} in certain crystals show “anomalous” broadband luminescence with large Stokes shift [12–15]. For such crystals, the excited 5d level falls into the conduction band. Luminescence occurred after transitions from conduction band states, having less energy than the 5d level, to 4f level of lanthanide impurity ion [12,16].

In the CaF_2-YbF_3 crystals under synchrotron radiation illumination in the region of interband transitions (> 14 eV), some of the Yb^{3+} ions were converted into Yb^{2+}. Since the yellow luminescence of Yb^{2+} ions was excited in the 4–12 eV region, this made it possible to measure in narrow absorption lines of Yb^{3+} ions in the Yb^{2+} excitation spectrum.

In our grown CaF_2-YbF_3 crystals, no absorption or emission bands caused by Yb^{2+} were observed, Yb^{2+} ions absorption appeared after X-ray irradiation at room temperature. During measurements at the synchrotron under illumination with intense fluxes of VUV radiation in the interband absorption region (more than 14 eV), a broad luminescence band at about 2.25 eV appeared in the spectrum due to the anomalous luminescence of Yb^{2+} ions. The excitation spectrum of this Yb^{2+} luminescence band correlated well with both the absorption spectrum of Yb^{2+} [17] and with the excitation spectrum of CaF_2-Yb^{2+} [18].

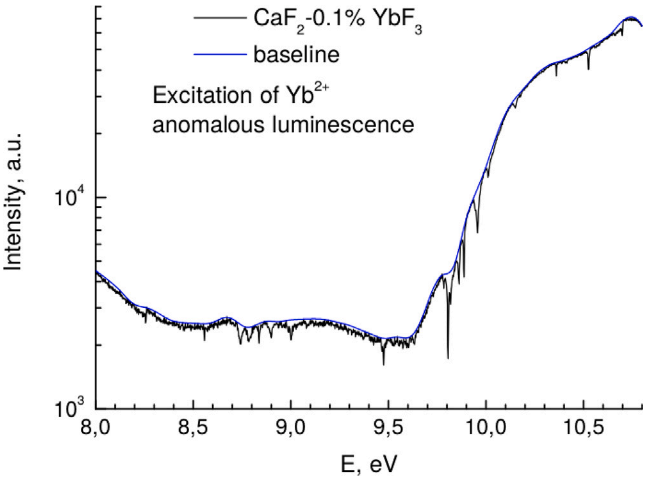

Fig. 4. Part of excitation spectra of CaF_2–0.1YbF_3 at 7K showing narrow spectral dips on excitation curve of Yb^{2+} anomalous luminescence.

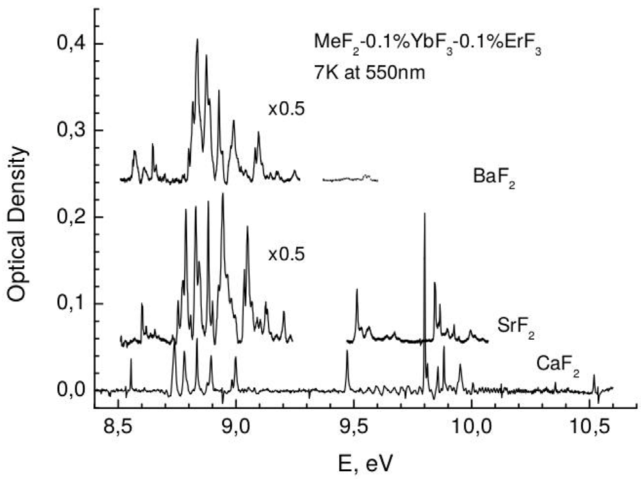

Fig. 5. Absorption spectra of Yb^{3+} lines in MeF_2–0.1YbF_3–0.1ErF_3 at 7K. The SrF_2, BaF_2 spectra are shifted up and reduced for ease of perception.

The excitation spectrum was observed in the range 3.5–11 eV, which made it possible for us to see the absorption lines of Yb^{3+} from the excitation spectrum of Yb^{2+} (Fig. 4).

The excitation spectrum of Yb^{2+} anomalous luminescence (see Fig. 4) in the range of 8–11 eV repeats all narrow dips like the excitation spectrum of CaF_2-Yb-Er (see Fig. 2). Obviously, in both cases, the narrow dips are due to the absorption lines of Yb^{3+} ions.

3.4. MeF_2*-Er*$^{3+}$

The emission spectra of MeF_2-Er^{3+} crystals contain the most intense bands of Er^{3+} at 550 ($^4S_{3/2}$–$^4I_{15/2}$), 660 ($^4F_{9/2}$–$^4I_{15/2}$), 980 ($^4I_{11/2}$–$^4I_{15/2}$), and 1550 nm ($^4I_{13/2}$–$^4I_{15/2}$) with a developed structure due to interaction with the crystal field [19].

The dips in the excitation spectra were found in MeF_2–0.1 ErF_3 crystals also (see Fig. 6). Spectral dips were largest in CaF_2 crystals and smallest in BaF_2 crystals. The lines shift towards high energies on going from CaF_2 to BaF_2, similar to the shift for Yb^{3+} lines (see Fig. 6).

In this case, we observe absorption lines of the 4f–5d transitions of Er^{3+}, which do not lead to emission in the 550 nm region. It is known that 5d–4f luminescence and 4f–4f luminescence of trivalent lanthanides in alkaline earth fluorides are characterized by different excitation spectra in vacuum ultraviolet radiation [20].

4. Discussion

In this article, we first drew attention to the obvious narrow dips in the excitation spectra in crystals with double activation. Measurements of dips in 4f–5d excitation spectra of lanthanide ions in vacuum ultraviolet have become possible due to the high spectral resolution of the MAX-IV synchrotron.

The necessary condition for observing narrow dips is a broadband excitation spectrum of one activator and narrow absorption lines of another activator within the excitation range. Comparison of the dips in the excitation spectrum of CaF_2-Yb-Er (see Figs. 2, 4) and the absorption lines of CaF_2-Yb [1] makes it possible to unambiguously interpret the dips as due to absorption lines of trivalent ytterbium in all MeF_2 crystals (see Fig. 5).

It can be noted that the optical density of CaF_2-Yb lines measured in [3] is several times higher than that calculated by us from the excitation spectrum. Obviously, our proposed estimate of the optical absorption is not entirely correct. However, it allows us to compare the relative absorption in several related crystals with the same impurity level.

The line at 9.801 eV in CaF_2–0.1ErF_3–0.1YbF_3 has the smallest half-width among those measured by us, equal to about 4 meV. This value is close to the spectral resolution of the setup.

The shift of the spectrum towards high energies in the row of CaF_2–SrF_2–BaF_2 is due to a decrease in the crystal field strength and, accordingly, a decrease in the 5d (t_{2g}-e_g) splitting in this series.

The energies of the 4f–5d absorption lines increase in the series from CaF_2 to BaF_2 by about 0.1 eV (Fig. 5), the same value as for the wide 4f–5d bands (see Fig. 1). The relative intensities of the lines in the range of 8.5–9.3 eV increase on going from CaF_2 to SrF_2, BaF_2 (see Fig. 5) although the wide bands 4f–5d hardly change in value (see Fig. 1).

The appearance of narrow absorption bands was associated with strong screening of 5d states by the $5p^6$, $6s^2$ states [3]. If this is the case, then the increase in the intensity of narrow absorption lines in the series CaF_2 to SrF_2, BaF_2 is due to an increase in the screening of 5d states by the $5p^6$, $6s^2$ states. In our opinion, this is unlikely since the radius of the cation site increases with the Ca-Sr-Ba transition, which also means that the electron shells of Yb^{3+} should be the most compressed, and absorption lines should be more intense in CaF_2. Calculations are required to clarify this.

Interpretation of the nature of the dips in the excitation spectra of MeF_2-Er is more complicated than in crystals with double activation. The dips in the excitation spectra of CaF_2-Er almost completely coincide with the lines in the CaF_2-Er absorption spectra measured by [3] (see vertical bars on Fig. 6). CaF_2-Er^{3+} zero-phonon lines, measured for 5d–4f emission at 167 nm, are located at slightly higher energies [21]. This means that the excitation of Er^{3+} ions in narrow 4f–5d absorption lines is less efficiently converted into a green f-f emission then in wide bands. The mechanism of this phenomenon requires further research.

5. Conclusion

Due to the high spectral resolution of vacuum ultraviolet radiation at the Lund synchrotron, we have discovered narrow spectral dips caused by $4f^n$–$4f^{n-1}5d$ absorption of Yb^{3+}, Er^{3+} ions in the excitation spectra of f-f luminescence or anomalous luminescence in alkaline earth fluoride crystals. The dips are due to the extremely narrow $4f^n$–$4f^{n-1}5d$ absorption lines of trivalent lanthanides Yb^{3+}, Er^{3+}.

The small width of the absorption lines of the 4f–5d transitions of Yb^{3+}, Er^{3+} in all alkaline-earth fluorides confirms the assumption [1]

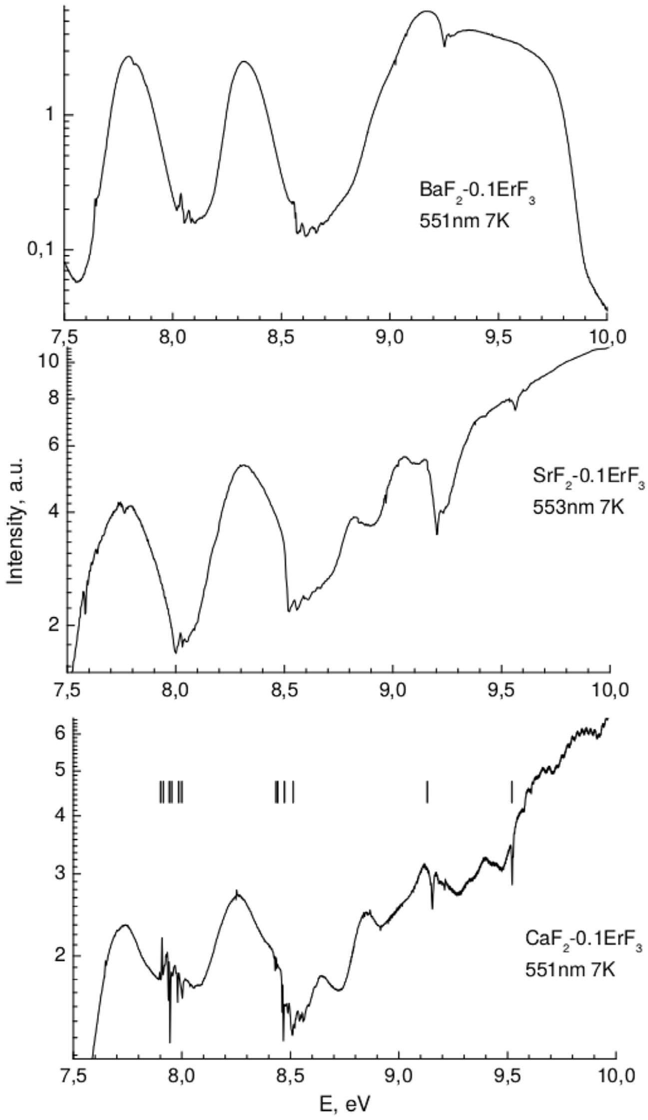

Fig. 6. Excitation spectra of Er^{3+} lines in MeF_2–$0.1ErF_3$ at 7K. Luminescence intensity is presented on a logarithmic scale to identify lines of small magnitude. Vertical bars on the CaF_2-Er plot show the positions of the absorption lines measured in [3].

about the strong screening of 5d states by the states of $5p^6$, $6s^2$ shells.

CRediT authorship contribution statement

E. Radzhabov: Conceptualization, Methodology, Writing – original draft. **R. Shendrik:** Data curation, Writing – original draft. **V. Pankratov:** Data curation, Writing – original draft. **K. Chernenko:** Data curation.

Data availability

No data was used for the research described in the article.

Acknowledgments

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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