



# Study of Nd<sup>2+</sup> absorption in x-irradiated CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub> crystals



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## HIGHLIGHTS

- We found absorption attributed to Nd<sup>2+</sup> in CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub>.
- The charge reduction of the neodymium by irradiation is not temperature-stable.
- The band at 6 eV CaF<sub>2</sub>, SrF<sub>2</sub> and BaF<sub>2</sub> doped with Nd could be attributed to F<sub>3</sub><sup>-</sup> centers.

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## ABSTRACT

The absorption spectra of x-irradiated alkaline-earth fluoride (CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub>) crystals doped with Nd<sup>3+</sup> ions have been investigated. X-irradiation results in creating the absorption bands of inter-configuration 4f<sup>n</sup>–4f<sup>n-1</sup>–5 d<sup>1</sup> transitions of Nd<sup>2+</sup>. The charge reduction of the neodymium by irradiation is not temperature-stable and the ions reoxidation (Nd<sup>2+</sup> → Nd<sup>3+</sup>) occurs under heating to 570 K in CaF<sub>2</sub>, 520 K in SrF<sub>2</sub> and 470 K in BaF<sub>2</sub>.

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## 1. Introduction

Most of the rare earths in the solid state are trivalent, except for some compounds involving Eu, Sm, Tm and Yb, which can become divalent (Meyer, 2012; Cotton, 2006; Meyer and Meyer, 1992). Crystals of alkaline earth fluorides (CaF<sub>2</sub>, SrF<sub>2</sub>) proved to be a very special host for studying rare-earth ions, as it was found that ionizing, additive or electrochemical coloration could convert those trivalent rare-earth ions located at essentially cubic sites into the divalent state (McClure and Kiss, 1963; Shendrik et al., 2016, 2014). Light lanthanides Ce<sup>3+</sup>, Pr<sup>3+</sup>, and Nd<sup>3+</sup> ions are the impurities having potential for scintillation applications due to short luminescence decay time (Radzhabov et al., 2012). However, the divalent rare earth ions take place in energy transfer in SrF<sub>2</sub> and CaF<sub>2</sub> scintillation crystals, which is a profound drawback of these scintillators due to the presence of intense slow components in the

luminescence decay (Shendrik and Radzhabov, 2012; Shendrik et al., 2013).

Crystals of alkaline earth fluorides doped with divalent neodymium can be used as Q-switches and passive mode-locking in lasers of the near IR wavelength range (1.3–1.6 μm) (Tokarev et al., 1991; Nepomnyachikh et al., 1991; Basiev et al., 1991). With this in mind, the optical study of Nd<sup>2+</sup> ions in such crystals focuses on broad band in the near-IR range. This absorption band covers the spectral region about 5 × 10<sup>3</sup> cm<sup>-1</sup> and the band maximum shifts to the short-wave range in homological row CaF<sub>2</sub>–SrF<sub>2</sub>–BaF<sub>2</sub> (Basiev et al., 1991). More comprehensive optical investigation of Nd<sup>2+</sup> has not been conducted so far.

This study is basically centered on the Nd<sup>2+</sup> absorption in x-irradiated crystals of alkaline earth fluorides (CaF<sub>2</sub>, SrF<sub>2</sub>, BaF<sub>2</sub>) doped with NdF<sub>3</sub> within temperature range 80–600 K.

## 2. Experimental methodology

The CaF<sub>2</sub>, SrF<sub>2</sub> and BaF<sub>2</sub> crystals doped with NdF<sub>3</sub> (from 0.1 to few mol. percent) have been grown from the melt by the

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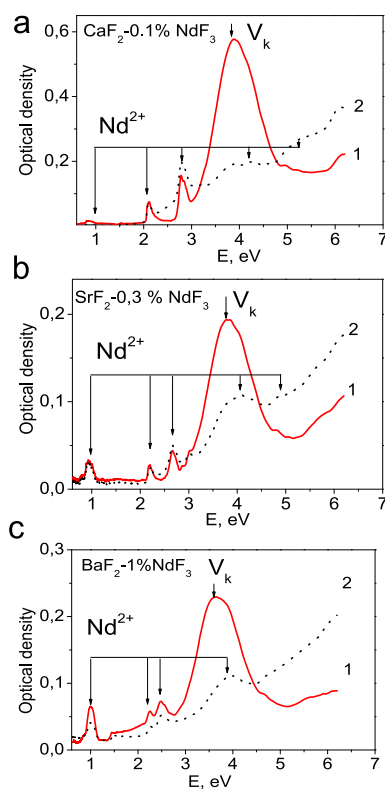
E-mail address: [sizova@igc.irk.ru](mailto:sizova@igc.irk.ru) (T. Sizova).

Stockbarger method in graphite crucibles in vacuum. At the first stage, pure crystals were grown with addition of some amount of  $\text{CdF}_2$  to the raw material in order to remove oxygen. Then crystals with an impurity of rare earth fluorides ( $\text{MeF}_3$ ) were grown from the crystalline raw material. The absence of oxygen in the final crystals was controlled by the absence of oxygen luminescence (Radzhabov and Figura, 1994) under sample illumination by DDS-30 UV deuterium discharge lamp. The crystals  $\text{CaF}_2\text{-Nd}$ ,  $\text{SrF}_2\text{-Nd}$ ,  $\text{BaF}_2\text{-Nd}$  were irradiated at 80 K or 300 K by X-rays from Pd tube operating at 35 kV and 20 mA for not more than 1 h. The thermal decay of the radiation defects in temperature range 80–600 K was studied. The optical absorption spectra were measured at 80 and 300 K with a Perkin–Elmer Lambda 950 UV/VIS/NIR spectrophotometer at the Isotope-geochemical research center for Collective Use, Siberian Branch, Russian Academy of Sciences.

### 3. Results

The X-irradiation at 80 K of  $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$  doped with  $\text{Nd}^{3+}$  results in creation of strong absorption band in the ultraviolet and of bands in the visible and infrared regions (Fig. 1). The absorption bands at 3.9 eV belong to absorption of  $V_k$  centers (self-trapped hole) formed during irradiation process (Merz and Pershan, 1967). The absorption bands at 0.8 eV (peak 1), 2.1 eV (peak 2), 2.8 eV (peak 3) in the spectra of  $\text{CaF}_2$  are caused by inter-configuration  $4f^n - 4f^{n-1} - 5d^1$  transitions of  $\text{Nd}^{2+}$  (McClure and Kiss, 1963; Arkhangel'skaya et al., 1967). The energies of the absorption bands of the x-irradiated  $\text{SrF}_2$  and  $\text{BaF}_2$  doped with Nd (see Table 1) are close to those of  $\text{Nd}^{2+}$  in irradiated  $\text{CaF}_2$  doped with  $\text{Nd}^{3+}$ .

The heating of the x-irradiated crystals to 120 K leads both to annealing of  $-V_k$  centers and the appearance of two absorption bands in the ultraviolet (peaks 4 and 5) which were hidden under



**Fig. 1.** Optical absorption of  $\text{CaF}_2$  (a),  $\text{SrF}_2$  (b),  $\text{BaF}_2$  (c) doped with  $\text{NdF}_3$  after x-irradiation at 80 K (curve 1) and after heating x-irradiated crystals to 120 K (curve 2). Absorption spectra were measured at 80 K.

**Table 1**

Experimental energies in eV of absorption bands in  $\text{Nd}^{2+}$  in x-irradiated  $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$  doped with  $\text{Nd}^{3+}$ .

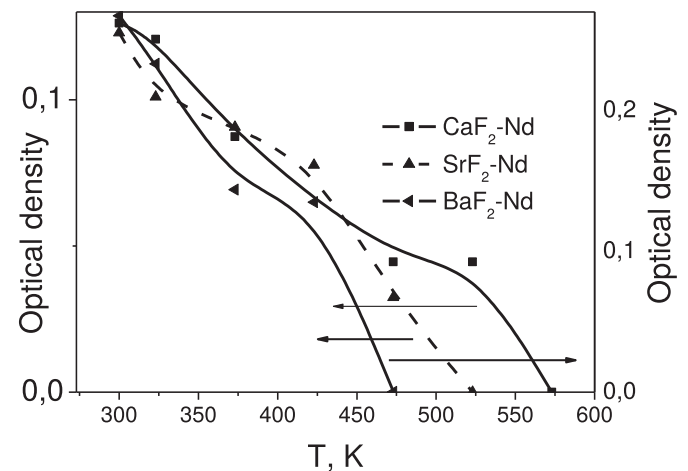
Crystal	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
$\text{CaF}_2$	0.8	2.1	2.8	4.2	5.2
$\text{SrF}_2$	0.9	2.2	2.8	4	5
$\text{BaF}_2$	1.2	2.2	2.5	3.9	–

the absorption of  $V_k$  centers (see Table 1). These bands are due to absorption of  $\text{Nd}^{2+}$  and were observed first in additively colored  $\text{CaF}_2$  crystals (Arkhangel'skaya et al., 1967).

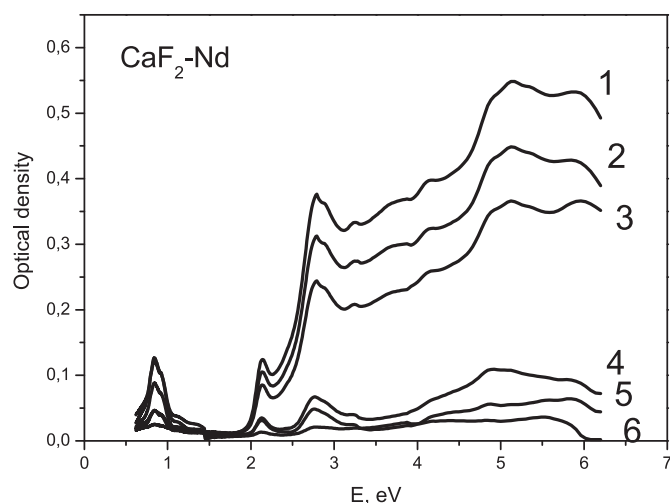
In previous works the absorption spectra of  $\text{Nd}^{2+}$  have been observed in  $\text{SrF}_2$  crystals in the range 340–1400 nm (Kaminskii and Li, 1968); but in ultraviolet region a wide structureless band was formed. In our study of  $\text{SrF}_2$  crystals the absorption bands at 4 eV and 5 eV appear at the same temperatures as in  $\text{CaF}_2$  crystals, and the band energies lie within the same spectral range of  $\text{Nd}^{2+}$  absorption. However the ratio of band intensities is different. The infrared band (peak1) has a higher optical density than the analogous band in  $\text{CaF}_2$  spectrum. Besides, the distance between bands diminishes in the visible spectral range (peaks 2 and 3). Furthermore, an essential increase of the absorption band at 6 eV in the spectra of all three crystals is observed (curve 2).

Fig. 2 shows the thermal decay of  $\text{Nd}^{2+}$  absorption in  $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$  doped with  $\text{Nd}^{3+}$ . Upon irradiation of the crystals at 300 K and its subsequent heating to 570 K ( $\text{CaF}_2$ ), 523 K ( $\text{SrF}_2$ ) and 470 K ( $\text{BaF}_2$ ) the absorption of  $\text{Nd}^{2+}$  decays. There is an early investigation of photoreduction of  $\text{Nd}^{3+}$  ions to  $\text{Nd}^{2+}$  in  $\text{CaF}_2$  crystals affected by powerful light pulses generated by an exciting lamp (Batygov and Kaminskii, 1968). It has been shown that the inverse process of thermal oxidation  $\text{Nd}^{2+} - \text{Nd}^{3+}$  proceeds at annealing temperatures above 50–70 °C. In some sense this fact contradicts available results. We suspect that low temperature stability of photo-induced  $\text{Nd}^{2+}$  centers may be due to the closely spaced electron and hole centers (Arkhangel'skaya, 1967) formed in charge-transfer process under photo-reduction.

Fig. 3 displays thermal decay of absorption bands of x-irradiated  $\text{CaF}_2\text{-Nd}$  at room temperature. It was shown that both absorption bands of  $\text{Nd}^{2+}$  centers (0.8 eV, 2.1 eV, 2.8 eV, 4.2 eV and 5.2 eV) and absorption band at 6 eV-centers decay at the same temperature. All bands of  $\text{Nd}^{2+}$  are shifted to shorter wavelengths by few nm and splitting of bands in the visible range is decreased in the row from



**Fig. 2.** Thermal decay of  $\text{Nd}^{2+}$  in  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  doped with  $\text{NdF}_3$  crystals irradiated at room temperature. Absorption was controlled in the maximum of the absorption bands at 0.8 eV ( $\text{CaF}_2$ ), 0.9 eV ( $\text{SrF}_2$ ), 1.2 eV ( $\text{BaF}_2$ ).



**Fig. 3.** Thermal decay of absorption bands of  $\text{CaF}_2$  doped with  $\text{NdF}_3$  after x-irradiation at 300 K. Curve 1 is the absorption after irradiation at 300 K, 2- heating crystals to 323 K, 3–373 K, 4–473 K, 5–523 K, 6–573 K. Absorption spectra were measured after cooling to 300 K.

$\text{CaF}_2$  to  $\text{BaF}_2$ . The shift of the absorption of 4f–5d bands in the row from  $\text{CaF}_2$  to  $\text{BaF}_2$  is also the case for some other rare-earth ions. It is caused by decrease of a crystal field splitting of 5d levels (Radzhabov and Nepomnyashchikh, 2008). Behavior of the absorption band at about 6 eV in the row from  $\text{CaF}_2$  to  $\text{BaF}_2$  is different from bands related to  $\text{Nd}^{2+}$  centers. Radzhabov et al. (Radzhabov, 2016; Figura et al., 1989). identified the absorption band at about 6 eV in the spectra of irradiation-colored  $\text{CaF}_2$ -Tm, Dy and  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  doped with Yb crystals. The study proved this band to belong to hole  $\text{F}_3^-$  centers. In the irradiated  $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$  doped with Nd crystals, the strong absorption bands in ultraviolet region at about 6 eV could be attributed to absorption of  $\text{F}_3^-$  centers. Hereby, recombination between a hole of  $\text{F}_3^-$  and an electron of  $\text{Nd}^{2+}$  centers takes place at the heating.

#### 4. Conclusion

After x-irradiation at 80 K the optical absorption of  $\text{V}_k$  centers and  $\text{Nd}^{2+}$  ions are observed in  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  doped with  $\text{NdF}_3$ . Several bands of inter-configuration  $4f^m-4f^{m-1}-5d^1$  transitions of  $\text{Nd}^{2+}$  were recorded: 0.8 eV, 2.1 eV, 2.8 eV, 4.2 eV and 5.2 eV – for  $\text{CaF}_2$ ; 0.9 eV, 2.2 eV, 2.8 eV, 4 eV and 5 eV –for  $\text{SrF}_2$  and 1.2 eV, 2.2 eV, 2.5 eV, 3.9 eV –for  $\text{BaF}_2$ .

The charge reduction of Nd by irradiation is not temperature-stable, and the ion reoxidation ( $\text{Nd}^{2+} \rightarrow \text{Nd}^{3+}$ ) occurs under heating to 570 K in  $\text{CaF}_2$ , 520 K in  $\text{SrF}_2$  and 470 K in  $\text{BaF}_2$ .

The strong absorption bands in ultraviolet region at about 6 eV  $\text{CaF}_2$ ,  $\text{SrF}_2$  and  $\text{BaF}_2$  doped with Nd could be attributed to absorptions of  $\text{F}_3^-$  centers.

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