

# Growth and mid-infrared emission properties of "mixed" fluorite-type Er:(Ca,Sr)F<sub>2</sub> and Er:(Ba,Sr)F<sub>2</sub> crystals

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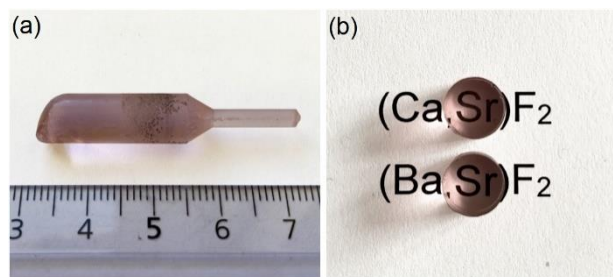
**Abstract.** Fluorite-type 5 at.% Er<sup>3+</sup>:(M<sub>1</sub>,M<sub>2</sub>)F<sub>2</sub> (M<sub>1</sub> = Ca, Ba; M<sub>2</sub> = Sr) crystals were grown by the conventional Bridgman technique and a comparative study of their spectroscopic properties was performed. The vibronic properties of the fluorite-type crystals were studied by Raman spectroscopy. The Er:(M<sub>1</sub>,M<sub>2</sub>)F<sub>2</sub> crystals exhibited a slightly inhomogeneous broadening of mid-infrared luminescence spectra as compared to the 'parent' compound, Er:SrF<sub>2</sub>. The luminescence lifetimes of the <sup>4</sup>I<sub>11/2</sub> and <sup>4</sup>I<sub>13/2</sub> manifolds were measured, e.g., for the Er:(Ca,Sr)F<sub>2</sub> crystal, the luminescence lifetimes were estimated to be 8.64 ms and 5.64 ms, respectively, representing a favorable ratio for mid-IR laser operation.

## 1 Introduction

Calcium fluoride (CaF<sub>2</sub>) also called fluorite when appearing in the mineral form is an attractive host matrix for doping with laser-active rare-earth ions (RE<sup>3+</sup>). This is because of a combination of good thermal properties of the host matrix and a unique spectroscopic behavior of the dopant RE<sup>3+</sup> ions, namely, very strong inhomogeneous spectral broadening arising from ion clustering observed even at low doping levels [1]. In particular, fluorite-type solid-solution crystals, (M<sub>1</sub>,M<sub>2</sub>)F<sub>2</sub> (where M<sub>1</sub>, M<sub>2</sub> = Ca, Sr, and Ba) provide modification of the spectroscopic properties of RE<sup>3+</sup> ions in the form of inhomogeneous broadening of the absorption and emission bands, which is attractive for broadly tunable and mode-locked lasers [2,3]. Erbium ions are attractive for developing mid-infrared lasers at 2.8 μm according to the <sup>4</sup>I<sub>11/2</sub> → <sup>4</sup>I<sub>13/2</sub> transition [4]. In the present work, we report on the growth and a comparative spectroscopic study of Er<sup>3+</sup>-doped (Ca,Sr)F<sub>2</sub> and (Ba,Sr)F<sub>2</sub> crystals.

## 2 Crystal growth

The crystals of 5 at.% Er<sup>3+</sup>:(M<sub>1</sub>,M<sub>2</sub>)F<sub>2</sub> (M<sub>1</sub> = Ca, Ba; M<sub>2</sub> = Sr) crystals were grown by the conventional Bridgman technique using MF<sub>2</sub> and ErF<sub>3</sub> powders with high purity (4N) in a graphite crucible. As an example of an as-grown crystal, the Er<sup>3+</sup>:SrF<sub>2</sub> boule crystal is shown in Fig.1(a). The as-grown crystals were of high optical quality without cracks and inclusions and had a slight rose coloration, Fig. 1(b).



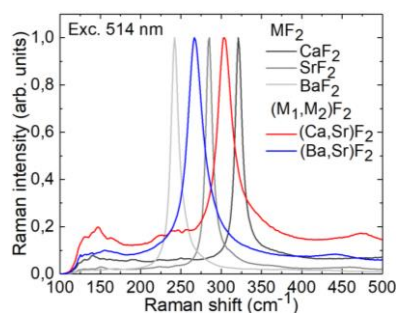
**Fig. 1.** (a) A photograph of an as-grown Er<sup>3+</sup>:SrF<sub>2</sub> crystal boule; (b) a photograph of laser-quality polished Er<sup>3+</sup>:(M<sub>1</sub>,M<sub>2</sub>)F<sub>2</sub> crystals

## 3 Optical spectroscopy

### 3.1. Raman spectra

The vibronic properties of the fluorite-type crystals were studied by Raman spectroscopy, Fig. 2. The Raman spectra were measured with an excitation of 514 nm. The factor group analysis predicts the following irreducible representations for the optical and acoustical modes at the  $\Gamma$ -point ( $\mathbf{k} = 0$ ):  $\Gamma_{\text{total}} = 1F_{2g} + 2F_{4u}$ , of which 1 mode ( $F_g$ ) is Raman active and 2 modes ( $F_u$ ) are IR-active [5]. For the 'parent' fluoride crystals, MF<sub>2</sub>, the single modes are observed at 242, 285 and 321 cm<sup>-1</sup> for BaF<sub>2</sub>, SrF<sub>2</sub> and CaF<sub>2</sub>, respectively. Raman spectra of the 'mixed' fluorides, (M<sub>1</sub>,M<sub>2</sub>)F<sub>2</sub> are significantly broadened as compared to that of the 'parent' ones. Their Raman peaks are located at 285 and 321 cm<sup>-1</sup> (for (Ba,Sr)F<sub>2</sub> and (Ca,Sr)F<sub>2</sub>, respectively) occupying the intermediate positions between those for 'parent' ones.

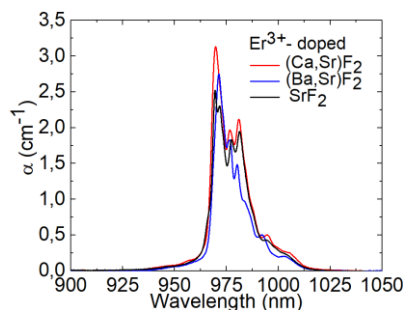
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**Fig. 2.** Unpolarized Raman spectra of the MF<sub>2</sub> and (M<sub>1</sub>,M<sub>2</sub>)F<sub>2</sub> crystals,  $\lambda_{exc}$ = 514 nm

### 3.2 Absorption

The absorption spectra of the Er:(M<sub>1</sub>,M<sub>2</sub>)F<sub>2</sub> and Er:SrF<sub>2</sub> crystals corresponding to the  $^4I_{15/2} \rightarrow ^4I_{11/2}$  Er<sup>3+</sup> transition are shown in Fig. 3. The spectra of ‘mixed’ fluorides are slightly broader than that of Er:SrF<sub>2</sub>, e.g., for Er:(Ca,Sr)F<sub>2</sub>, the peak absorption is at 969.8 nm and the absorption bandwidth is 16 nm, which is attractive for pumping of these crystals using commercial InGaAs laser diodes.

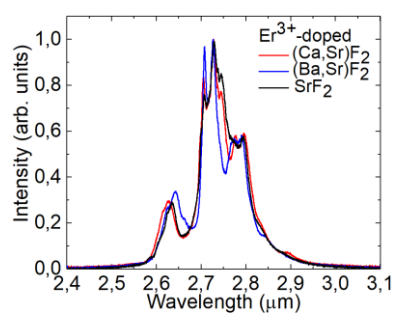


**Fig. 3.** Absorption spectra for the  $^4I_{15/2} \rightarrow ^4I_{11/2}$  transition of the Er:(M<sub>1</sub>,M<sub>2</sub>)F<sub>2</sub> and Er:SrF<sub>2</sub> crystals

### 3.3 Mid-IR luminescence

The spectra of mid-IR luminescence Er<sup>3+</sup>-doped (Ba,Sr)F<sub>2</sub> and (Ca,Sr)F<sub>2</sub> crystals and Er:SrF<sub>2</sub> crystal studied for comparison are shown in Fig. 4. The spectra span from 2.5 to 3.05  $\mu$ m, the luminescence is assigned to the  $^4I_{11/2} \rightarrow ^4I_{13/2}$  Er<sup>3+</sup> transition. For ‘mixed’ crystals, the luminescence spectra are slightly broadened as compared to those for the ‘parent’ compound due to the inhomogeneous spectral broadening arising from the compositional disorder.

The luminescence lifetimes of the upper and lower laser levels,  $^4I_{11/2}$  and  $^4I_{13/2}$  were measured using finely powdered samples to avoid the effect of reabsorption. For the Er:(Ca,Sr)F<sub>2</sub> crystal, they amount to 8.64 ms ( $^4I_{11/2}$ ) and 5.64 ms ( $^4I_{13/2}$ ), and for the Er:(Ba,Sr)F<sub>2</sub> crystal, 8.72 ms and 6.32 ms, respectively. In contrast, the lifetime ratio for the Er:SrF<sub>2</sub> crystal is 8.96 and 8.87 ms, respectively. Significantly reduced lower laser level lifetime in ‘mixed’ fluorides allows to achieve low laser thresholds, as well as overcoming the ‘bottleneck’ effect inherent to the  $^4I_{11/2} \rightarrow ^4I_{13/2}$  Er<sup>3+</sup> transition thus leading to continuous-wave laser operation at 2.8  $\mu$ m.



**Fig. 4.** Mid-infrared luminescence spectra for the  $^4I_{11/2} \rightarrow ^4I_{13/2}$  transition,  $\lambda_{exc}$  = 970 nm

## 4 Conclusion

To conclude, we report on a comparative spectroscopic study of two Er<sup>3+</sup>-doped fluorite-type (M<sub>1</sub>,M<sub>2</sub>)F<sub>2</sub> crystals (M<sub>1</sub> = Ca, Ba; M<sub>2</sub> = Sr). They provide inhomogeneously broadened emission bands in the mid-infrared and a favorable ratio of the  $^4I_{11/2}$  and  $^4I_{13/2}$  level lifetimes making them attractive for 2.8  $\mu$ m lasers. In particular, Er:(Ca,Sr)F<sub>2</sub> appears promising because of its high thermal conductivity compared to CaF<sub>2</sub> and SrF<sub>2</sub> crystals, low phonon energies and long luminescence lifetimes of Er<sup>3+</sup> ions. Further work will focus on demonstration of laser performances in Er:(M<sub>1</sub>,M<sub>2</sub>)F<sub>2</sub> crystals.

## 5 Acknowledgement

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