Abstract
The segregation coefficient of $\text{Er}^{3+}$ and $\text{Yb}^{3+}$ ions in ErF$_3$ and YbF$_3$-doped calcium fluoride crystals has been determined using the optical absorption method. The RE-doped calcium fluoride crystals were grown by Bridgman method using the home–made crystal growth set-up. Taking into account the relationship between the optical absorption coefficient and the concentration of the impurities in the sample, the effective distribution coefficient of the $\text{Er}^{3+}$ and $\text{Yb}^{3+}$ ions has been calculated. The values of segregation coefficient obtained for these crystals are 1.03 for 0.83 mol% ErF$_3$ doped CaF$_2$ sample and 0.98 for 0.72 mol% YbF$_3$ doped CaF$_2$ crystals.

Keywords: segregation, calcium compounds, Bridgman technique.

1. Introduction
Various impurity-related centers in alkaline-earth fluorides have been the subject of several investigations since it was shown that these centers are laser-active. Interest in rare-earth (RE)–doped CaF$_2$ crystals used as laser materials is still growing due to the well-known good optical characteristics of the CaF$_2$ host. The charge compensation required when calcium fluoride is doped with trivalent rare earth ions determine a complex site structure leading to optical transitions having the form of broad bands that can be used for solid-state lasers. The ErF$_3$ and YbF$_3$ doped calcium fluoride have received an increasing interest in recent years as solid state laser materials for high power or ultra fast lasers [1].

The $\text{Er}^{3+}$ or $\text{Yb}^{3+}$-ions doped CaF$_2$ crystals are known as good laser material for IR spectral domain. The dopant distribution in laser crystals influences the optical properties and the efficiency of the laser material. The goal of this work is to investigate and evaluate the segregation coefficient of the dopant for CaF$_2$:0.83 mol% ErF$_3$ and CaF$_2$:0.72 mol% YbF$_3$ crystals using the optical absorption method. The segregation coefficient has been calculated using the absorption spectra for the characteristic absorption bands: 406nm for $\text{Er}^{3+}$ ions and 920nm for $\text{Yb}^{3+}$. 
2. Method and samples

Both investigated crystals, 0.83 mol% ErF$_3$ and 0.72 mol% YbF$_3$–doped calcium fluoride crystals have been grown in our crystals research laboratory using vertical Bridgman method. Supra-pure grade (Merck) CaF$_2$, ErF$_3$ and YbF$_3$ were used as starting materials. Transparent crystals (pink color for ErF$_3$ doped and colorless for YbF$_3$ doped CaF$_2$) of about 10mm in diameter over 6-7cm long were obtained in graphite crucible in vacuum ($\sim$ 10$^{-1}$ Pa) using a shaped graphite furnace [2]; the pulling rate was 4mm/h. In order to investigate the dopant concentration distribution along the crystals and to determine the segregation coefficient the optical absorption method has been used [3]. The crystals were cut from bottom to the top into 14-17 slides of ~ 2mm thickness and optically polished. The absorption coefficient $\alpha(i)$ of every slice (i) was calculated from the absorption spectra using the 406nm characteristic absorption peak for Er$^{3+}$ ions and the 920nm peak for ytterbium ions. The segregation coefficient is defined by $k = C_S/C^0_L$, where $C_S$ is the RE ions concentration at the bottom of the as-grown crystal and $C^0_L$ is the dopant concentration in the initial melt. The value of $C_S$ can be measured by various methods, or calculated from optical absorption measurements [3-5]. The RE ions concentration can be calculated using the measured optical density (OD) from $C_S = \ln (10) \, \text{OD} / \alpha$, where $\alpha$ is the absorption coefficient using a reference sample. The RE ions concentration of the other cut samples from the crystal, $C_{iS}$, can be determined from $C_{iS} = C^0_L \, k \, (1-g)^{k-1}$, where $g = Vt/L$ is the fraction of the crystallized melt, $V$ is the crystal growth rate, $t$ is the growth time, $L$ is the crystal length. The segregation coefficient, $k$, can be calculated from the slope of the variation of the absorption coefficient along the length of the crystals, $\alpha(z)$, described by the relation:

$$\lg \, \alpha(z) = (k-1) \, \lg \, (1-g) + \lg \, (k \, N \, \alpha (0)),$$

where $\alpha(0)$ corresponds to the absorption coefficient of the sample $i=1$. 

3. Results and Discussions

Room-temperature absorption spectrum of the 0.83 mol% ErF$_3$– doped CaF$_2$ crystal is shown in Fig. 1a. This spectrum reveal the characteristic bands of the Er$^{3+}$ ions. The absorption coefficient $\alpha(z)$ of every slice was calculated from the absorption spectra for the characteristic absorption band at 406nm corresponding to the electronic transition between $^4I_{15/2}$ ground state and $^2H_{11/2}$ excited state of the Er$^{3+}$ ions (see inset of Fig. 1a). The segregation coefficient was calculated from the slope of the fitting line of $\lg(\alpha)$ versus $\lg (1-g)$ (Fig. 1b).
The room temperature absorption spectrum of Yb$^{3+}$ ions in CaF$_2$ crystal in the near-IR spectral region is shown in Fig. 2a. This spectrum is related to the electronic transition from $^{2}F_{7/2}$ ground state to the $^{2}F_{5/2}$ excited state of the Yb$^{3+}$ ions and is characterized by a very broad band. The structure of this bands is due to various crystal field symmetries, generated by several types of charge compensation. The characteristic absorption peak at 920nm observed in this work was obtained by deconvolution of this broad band using the gaussian
multi-peaks method. For calculate the segregation coefficient of the Yb$^{3+}$ ions in CaF$_2$ host it was used method already described in the case of Er$^{3+}$ ions.

For both investigated crystals the segregation coefficient is closed to the unity; this means that the trivalent ions studied in this work (Er$^{3+}$ and Yb$^{3+}$) are distributed homogeneously along the crystals. The obtained values of the segregation coefficient are $k=1.03$ for the CaF$_2$:0.83 mol% ErF$_3$ and $k=0.98$ for the CaF$_2$:0.72 mol% YbF$_3$. These values are in good agreement with those reported for CaF$_2$:1.96 at% YbF$_3$ ($k=1.07$) by L. Su [6].

4. Conclusions

From the investigated crystals, obtained using the vertical Bridgman method, results that the segregation coefficient slightly depends on the type of the trivalent RE impurity in CaF$_2$. The value of segregation coefficient is 1.03 for CaF$_2$: 0.83 mol% ErF$_3$ and 0.98 for CaF$_2$: 0.72 mol% YbF$_3$ crystal.

Acknowledgements

This work was supported by the National Agency for Scientific Research, Romania, Grant CEEX no.72/3758/2006.

References