

## SOME OPTICAL AND DIELECTRIC PROPERTIES OF YbF<sub>3</sub> – DOPED CaF<sub>2</sub> CRYSTALS

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### **Abstract**

Pure and YbF<sub>3</sub>-doped calcium fluoride crystals have been grown using the vertical Bridgman method. The influence of the X-ray irradiation on the optical properties has been investigated. The real and imaginary parts of the complex dielectric constant have been measured at five audio-frequencies over the temperature range 150–300 K. From the observed relaxation processes the activation energy for various structural defects has been determined.

**Keywords:** Defects, Calcium compounds, Dielectric materials, Optical properties.

### **1. Introduction**

The alkaline-earth fluorides crystallize in the cubic structure and constitute an important class of relatively simple ionic crystals whose optical and lattice-dynamical properties have theoretical and experimental interest. The alkaline-earth fluorides (MF<sub>2</sub>, M=Ca, Ba, Sr) crystals doped with rare-earth fluorides (REF<sub>3</sub>, RE=La, Er, Yb, etc.) are a good laser crystals. The RE ions are trivalent, consequently an additional charge compensating defect must occur. When an impurity ion substitutes for a host ion of different charge in an ionic crystal, compensation is usually accomplished by the incorporation of the lattice vacancies, interstitial host ions, another species of impurity ion in interstitial or substitutional sites or a combination thereof. Many investigators have published observations of the behavior of the trivalent Yb ions as an impurity ion in the CaF<sub>2</sub> lattice. Although RE ions are most easily stabilized as trivalent ions in these crystals, the divalent state has certain distinct advantages for laser applications. The change of valence, i.e. reduction, has been attained by exposing the crystals to ionising radiation, baking them in a suitable atmosphere or electrolytic annealing [1-5]. This work is concerned with reduction of Ytterbium ions in CaF<sub>2</sub> during the crystal growth process.

In order to characterize the various YbF<sub>3</sub>- concentrations doped CaF<sub>2</sub> crystals, obtained by Bridgman method, the following properties have been studied in this paper: the influence of Ytterbium ions on the absorption and dielectric spectra, the effect of the X-ray irradiation

on the absorption spectrum, the temperature and frequency dependence of the complex dielectric constant  $\varepsilon^* = \varepsilon_1 + i\varepsilon_2$  in order to calculate the activation energy and the reciprocal frequency factor of the observed relaxations.

## 2. Method and samples

Pure CaF<sub>2</sub> Crystals and doped with 0.17, 1.2 and 1.7 mol% YbF<sub>3</sub> have been grown in our crystal research laboratory using vertical Bridgman method [6]. A chemically pure grade (99,9%) RF<sub>3</sub> reagent and suprapure grade Merck calcium fluoride were used as the starting materials. Transparent single crystals were grown by the Bridgman techniques in graphite crucible in vacuum ( $\sim 10^{-3}$  torr). The rate of the crucible lowering was 4 mm/h. A special crystal growth process has been developed in order to obtain efficient Yb<sup>3+</sup> charge conversion to Yb<sup>2+</sup>. The optical absorption spectra at room temperature have been recorded using a Shimadzu 1650PC spectrophotometer. The dependence of the dielectric constant with frequency and temperature of the crystals have been measured using a LCR Meter type ZM 2355, NF Corporation, Japan. Linear heating rates of 3 K/min were employed from liquid nitrogen to room temperature.

## 3. Results and discussions

### *Optical properties*

The absorption spectra of YbF<sub>3</sub> -doped crystals are shown in Fig.1. Before X-ray irradiation the crystals exhibit peaks in UV region characteristic for Yb<sup>2+</sup> ions at: A<sub>i</sub> = 365, 275, 263 and 230 nm and in near IR characteristic for Yb<sup>3+</sup> ions: B<sub>i</sub> = 922, 944, 967 and 978 nm; these values vary with the sample concentration. The near IR spectrum is characterized by a very broad band, corresponding to the <sup>2</sup>F<sub>7/2</sub> (ground state) and <sup>2</sup>F<sub>5/2</sub> (excited state) transition; the structure of the band is due to different charge compensation mechanism which leads to various crystal field symmetries of the incorporated Yb<sup>3+</sup> ions. The UV absorption bands at A<sub>1</sub>, A<sub>3</sub>, and A<sub>4</sub> were attributed to <sup>2</sup>F<sub>7/2</sub> -5d(e<sub>g</sub>)4f<sup>13</sup>, <sup>2</sup>F<sub>5/2</sub>-5d(e<sub>g</sub>)4f<sup>13</sup> and <sup>2</sup>F<sub>7/2</sub> -5d(t<sub>2g</sub>)4f<sup>13</sup> energy levels of Yb<sup>2+</sup> ions, probably in cubic symmetry; the A<sub>2</sub> band can be assigned as <sup>2</sup>F<sub>7/2</sub> -5d(e<sub>g</sub>)4f<sup>13</sup> of Yb<sup>2+</sup> ions surrounded by Yb<sup>3+</sup> ions [5,7,8].

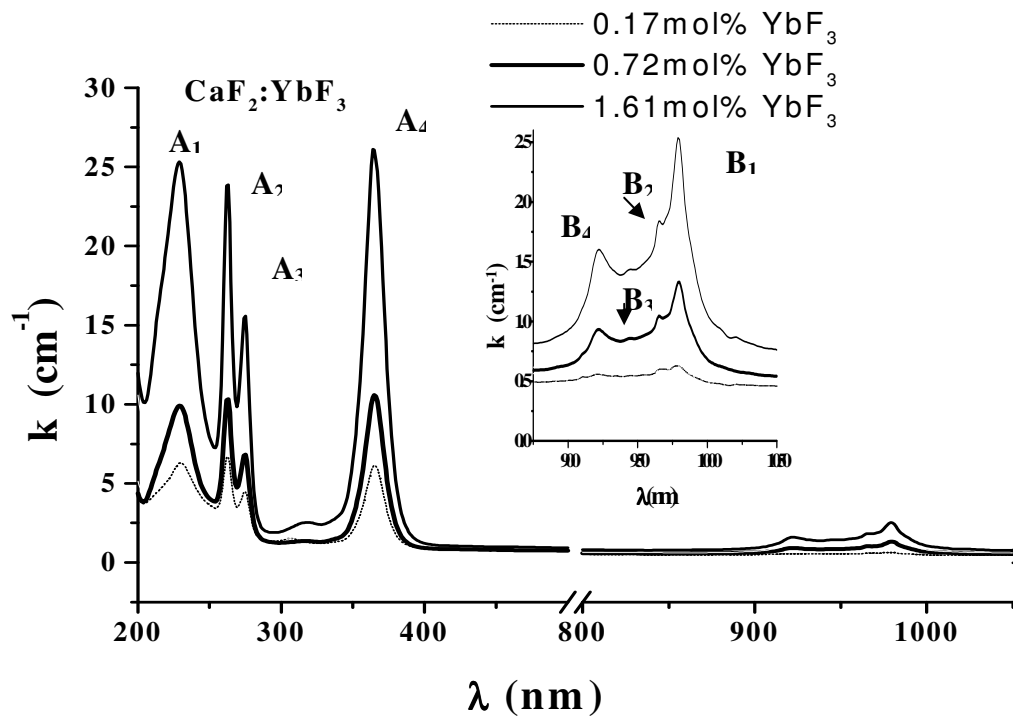


Fig.1. Absorption spectra of various  $\text{YbF}_3$ -doped  $\text{CaF}_2$  crystals.

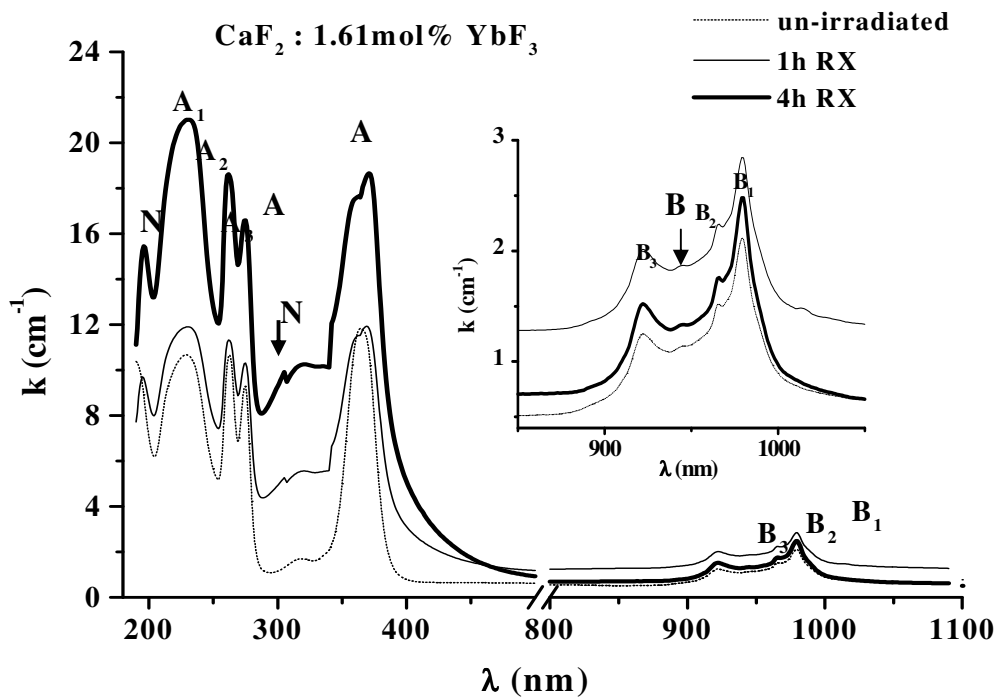


Fig. 2. Absorption spectra after X-ray irradiation.

After X-ray irradiation two new absorption bands appear at  $N_i = 194$  and  $305$  nm, the  $365$  enlarges and splits (Fig.2.). For high  $\text{YbF}_3$  concentration the absorption coefficient in UV bands increases with the irradiation time. The absorption coefficient ( $k$ ) in the near IR bands first increases with the irradiation time but after 4hours have a little higher value than before irradiation. For low concentration samples, in the UV region,  $k$  decreases with irradiation time in contrast with the IR region where the absorption coefficient increases with X-ray dose. All these behavior are related with the charge conversion of the Yb ions.

### Dielectric spectra

After doping  $\text{CaF}_2$  with  $\text{YbF}_3$  some dipolar complex appear which can reorient (relax) by “jump” of the charges to other lattice sites. Such dipoles are usually characterized by a relaxation time:  $\tau = \tau_0 \exp(E/kT)$  [9-11]. In order to determine the activation energy for reorientation,  $E$ , and the reciprocal frequency factor  $\tau_0$ , the complex dielectric constant  $\epsilon^*(\omega, T) = \epsilon_1 + i\epsilon_2$  has to be determined. The dielectric constant  $\epsilon_1$  has been calculated from the measured capacitance  $C$ . The imaginary part of the dielectric constant,  $\epsilon_2$ , has been calculated from:  $D = \tan \theta = \epsilon_2 / \epsilon_1$ . Temperature and frequency dependence of  $\epsilon_2$  for  $0.17$  mol%  $\text{YbF}_3$  doped  $\text{CaF}_2$  is shown in Fig.3.

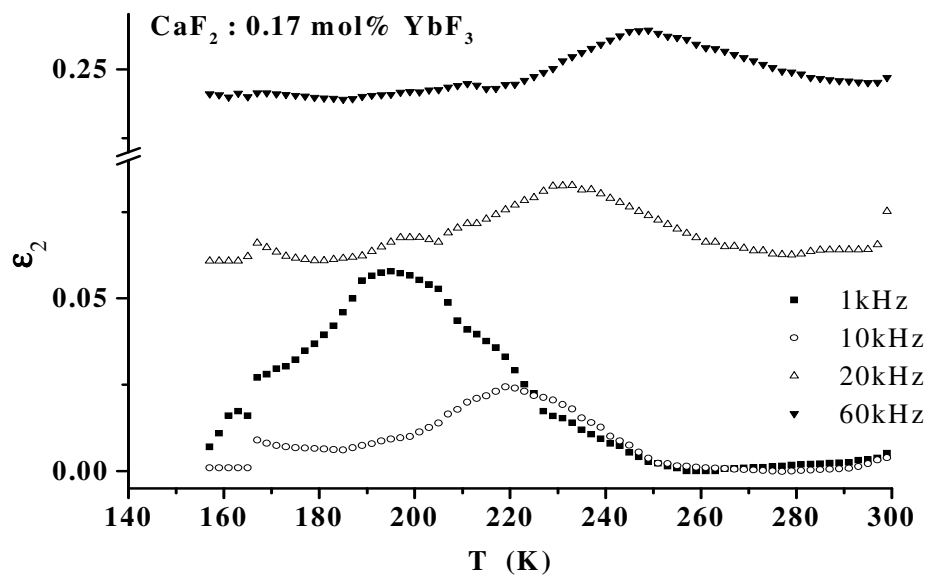


Fig.3. Temperature and frequency dependence of  $\epsilon_2$ .

The  $\varepsilon^*(\omega, T)$  obeys the Debye equations. Since  $\varepsilon_2$  has a maximum for  $\omega\tau = 1$ , it follows that:  $\ln \omega = E/kT_{\max} + \ln \tau_0$ , where  $T_{\max}$  is the temperature at which  $\varepsilon_2$  has a maximum at a given frequency.  $E$  and  $\tau_0$  can be determined from the slope and intercept of the plot of  $1/T_{\max}$  versus the  $\ln \omega$  (see Fig.4.). The value of the activation energy for the observed relaxations is shown in the Table 1.

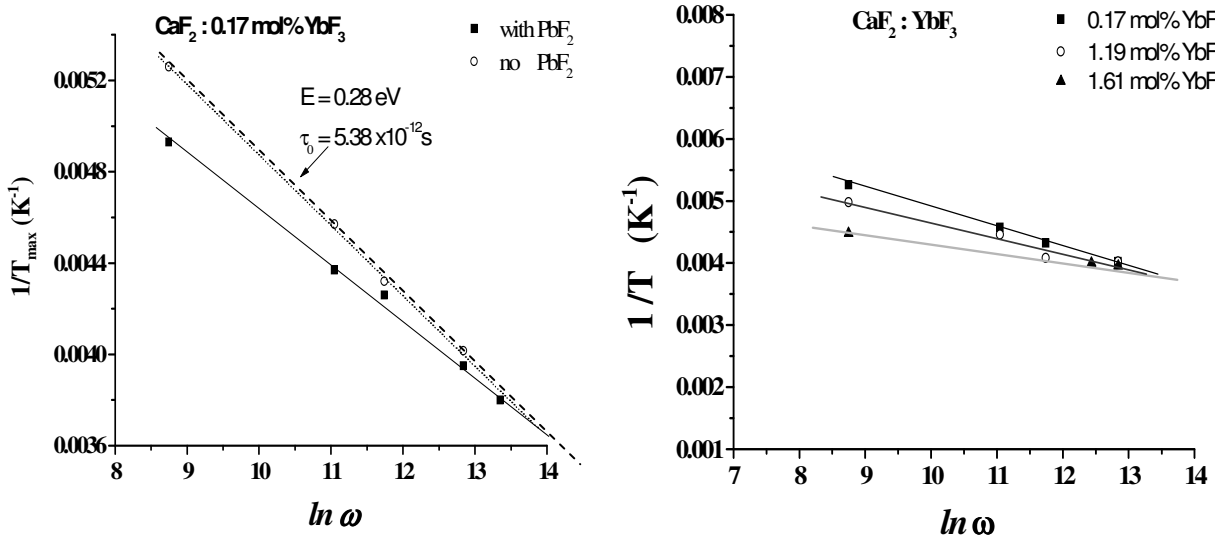


Fig. 4. Dependence of the  $T_{\max}^{-1}$  on the  $\ln \omega$ .

Table 1. Activation energy of the single observed relaxation.

| Crystal                        | CaF <sub>2</sub> :YbF <sub>3</sub>                           |                        |                        |
|--------------------------------|--|------------------------|------------------------|
| YbF <sub>3</sub> concentration | 0.17 mol%  | 1.2 mol%               | 1.6 mol%               |
| $E$ (eV)                       | 0.281  | 0.348                  | 0.688                  |
| $\tau_0$ (s)                   | $5.38 \times 10^{-12}$                                       | $3.08 \times 10^{-13}$ | $1.2 \times 10^{-19}$  |
|                                | CaF <sub>2</sub> :YbF <sub>3</sub> + 1 mol% PbF <sub>2</sub> |                        |                        |
| $E$ (eV)                       | 0.356  |                        | 0.648                  |
| $\tau_0$ (s)                   | $5.5 \times 10^{-14}$  |                        | $1.17 \times 10^{-13}$ |

The main observed relaxations are associated with substitutional Yb ion and a nearest-neighbour F<sup>-</sup> vacancy.

#### **4. Conclusions**

Various concentrations YbF<sub>3</sub>-doped CaF<sub>2</sub> have been obtained with high concentration divalent Ytterbium, using a special growth process. Some optical and dielectric properties have been studied. After X-ray irradiation two weak new absorption bands appear in UV. For high YbF<sub>3</sub> concentration the absorption coefficient of all the UV bands increase in contrast for the lower YbF<sub>3</sub> concentration samples. Preliminary emission experiments reveal a high emission in near UV domain due to the divalent Ytterbium. The main observed relaxations are associated with substitutional Yb ion and a nearest-neighbour F- vacancy.

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