Measurements of thermal properties of crystals CaF$_2$: Ce$^{3+}$ activated Yb$^{3+}$ and Lu$^{3+}$ ions.

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Abstract. Aim of this work was to investigate parameters of thermal expansion, thermal conductivity, and the temperature coefficient of the refractive index. These data are very important in the development of optical systems of lasers. Measurements of thermal conductivity were carried out using absolute stationary method of longitudinal heat flux. Parameters of thermal expansion and temperature coefficient of the refractive index were obtained by Jamin and Michelson interferometers.

1. Introduction

Solid solutions with fluorite structure are key components of many nano, poly and nanocrystalline materials, including active and passive photonic materials (solid lasers, scintillators, IR and UV block optics, holography, photolithography and anti-glare coating) and solid electrolytes [1 - 3].

One of the main advantages of fluorite crystals is large spectral large spectral range of transparency which extends to vacuum UV. Good thermal conductivity and low maximum phonon energy provide low probability of nonradiative transitions. The drawback is that charge compensation is needed then doping by trivalent rare earth ions. This could lead to higher probability of defects formation and multiple impurity sites character of crystallization. From another hand this drawback provides an opportunity to achieve larger gain spectrum due to inhomogenous broadening or varying of optical properties [4, 5]. Also it is known that all the rare earth ions exhibit trend to cluster in the fluorite structure. The presence of a large number of clusters of rare earth ions in the doped CaF$_2$ could be advantageous [6, 7] and is being used to develop an effective system of high power amplifiers and femtosecond lasers [8, 9]. Generally a heterovalent activation nature and clusterization of dopants worsens thermal physical properties of the materials.

Parameters of thermal expansion, thermal conductivity, and the temperature coefficient of the refractive index are the fundamental characteristics of any material. Thermal conductivity determines the temperature distribution over the cross section and over the length of the active element and, consequently, induced thermal lens shape defining the divergence of the laser beam. Particularly it is important to know the thermal conductivity values for evaluating the possibility of applying the crystalline material in a continuous solid state lasers, and pulsed lasers operating at high power levels, due to the problem of heat removal from the active element. In this paper, we present an experimental study of thermal conductivity and temperature coefficient of the refractive index for crystals CaF$_2$ and solid solutions CaF$_2$-LuF$_3$ doped by Yb$^{3+}$ ions.
2. Experimental equipment and measurement technique

Measurements of thermal conductivity were carried out in Bryansk State University named after academician I. G. Petrovsky. As the basis for the design of experimental setup the state special standard unit of thermal conductivity was taken [10]. The scheme of the measuring chamber of the apparatus used in the present work is shown in Figure 1.

![Figure 1](image_url)

**Figure 1.** Scheme of the measuring chamber: 1 – investigated sample; 2, 4, 8, 11 - thermocouple; 3,7,9 - heaters; 5 - bushing for mounting the sample; 6 - radiation shield; 10 – heat output; 12 - flange; 13 - evacuation tube; 14 - coal getter; 15 - liquid nitrogen; 16 - radiator for wiring; 17 - thermal resistance

Absolute stationary method of longitudinal heat flux was used in the measurements of thermal conductivity. The samples were prepared in the form of cylinders and were connected to heater and heat output reservoir at the opposite sides. Liquid nitrogen was used as a refrigerant. The heat flux was measured along the sample by means of thermocouple attached to two points of the sample. Measurement procedure is described in detail in [11; 12]. Error in determining the value of thermal conductivity does not exceed ± 5%.

Also, we have determined the temperature coefficient of the refractive index and the coefficient of linear thermal expansion. The scheme of experimental setup utilized is shown in Figure 2.

In order to separate peculiarities arising from thermal expansion of the samples and refractive index change we have utilized the setup consisting of both Michelson and Jamin interferometers.

When illuminating Jamin interferometer with monochromatic light (1 at fig. 2) there are lines of equal inclination at the place of CCD camera 5 appearing due to interference of light beams of branches A and B (see fig. 2). If the wavefront of the light beam is almost flat, the width of the interference fringes exceeds the cross-section diameter of the light beam and the interference pattern illuminates the field uniformly. To observe the interference pattern, the sample is placed in the working beam A.
Figure 2. Scheme of interference measurement setup for measuring temperature coefficient of the refractive index and the coefficient of linear thermal expansion: 1 – DPSS laser at 532 nm; 2, 4 – thin (~ 2 cm) plane parallel plates, 6 - plane - parallel plate; 3 - the sample; 5,8 - CCD cameras; 7 - mirror; 9 – He-Ne laser with a wavelength of 632.8 nm, A and B – the working beam and reference beam of Jamin interferometer correspondingly.

Optical path of the laser beam transmitted through the crystal increases when heating the crystal due to its expansion and refractive index changes. When the sample is heated from temperature $T_1$ to $T_2$, the optical path length change could be written as follows:

$$
\Delta l = n_2(h_1 + dh) - n_1h_1 - dh
$$

where $n_1$ and $h_1$ are refractive index and thickness of the sample correspondingly at $T_1$, $n_2$ is the refractive index at $T_2$, $dh$ is the value of expansion of the crystal due to temperature change. Because of the change in length of optical path the phase difference between the working and reference beam is varying. This leads to a shift of interference fringes. Number of fringes passed through the field of view of CCD camera due to shift in Jamin interferometer can be determined as:

$$
X = \frac{n_2(h_1 + dh) - n_1h_1 - dh}{\lambda}
$$

here $X$ - number of shifted bands, $\lambda$ - the wavelength of the light. $X$ could be estimated from counting the number of displaced fringes in the interference pattern, which was filmed by the CCD camera. The refraction index $n_1$ was determined using a microscope. Contribution of thermal expansion $dh$ was determined using a Michelson interferometer. Here we utilized interference of beams reflected from mirror 7 and polished side of the sample 3 (see fig. 2). The sample 3 was mounted at the heater in such a way that one of its polished sides was glued to the heater and other stayed free so that expansion of the sample was equal to the shortening of one of the shoulders of Michelson interferometer.

Heat expansion $dh$ of the sample to the value $\frac{\lambda_0}{4}$ (where $\lambda_0$ is the wavelength of the He-Ne laser 9) is accompanied by shift of interference pattern and mutual change of places of maximum and minimum intensity. Determining the number of such displacements $N$ we can determine the expansion of the sample

$$
dh = N \frac{\lambda_0}{4}
$$

Unknown member $n_2$ in formula (2) could be derived from:

$$
n_2 = \frac{(X \lambda + n_1h_1 + dh)}{h_1 + dh}
$$
The temperature coefficient of the refractive index and coefficient of linear thermal expansion are determined by the following formulas:

\[ n_T = \frac{(n_2 - n_1)}{dT} \]  \hspace{1cm} (5)

\[ \alpha_T = \frac{dh}{h_1dT} \]  \hspace{1cm} (6)

Temperature of the sample was measured by means of heat-variable resistor.

3. Results

Figure 3 shows the results of measurement of thermal conductivity of the samples. It is seen from the graph that the samples are in the behavior of the thermal conductivity characteristic to glasses, i.e. increase in thermal conductivity with increasing temperature.

![Graph showing thermal conductivity of CaF₂-LuF₃ crystals doped with Ce³⁺ and Yb³⁺ ions.](image)

**Figure 3.** Thermal conductivity \( k \) of samples of CaF₂-LuF₃ crystals doped with Ce³⁺ and Yb³⁺ ions.

Low thermal conductivity and the weakness of its temperature dependence indicate the presence of inhomogeneities of the crystal structure and other centers of phonon scattering [13, 14]. It also shows that with increasing concentration of LuF₃ thermal conductivity reduces, which is a negative characteristic for the laser material.

**Table 1.** Temperature coefficient of the refractive index and the coefficient of linear thermal expansion measured for CaF₂-LuF₃ crystals doped with Ce³⁺ and Yb³⁺ ions and CaF₂ table data

|                | \( n_T \)          | \( \alpha_T \)        |
|----------------|--------------------|-----------------------|
| CaF₂ (from ref)| -1,0±0,1*10⁻⁵      | 1,8±0,3*10⁻⁵          |
| CaF₂: Ce (1 %) | -1,4±0,1*10⁻⁵      | 1,08±0,02*10⁻⁵        |
| CaF₂: Ce (0,2 %)+Yb (0,05 %) | -1,5±0,1*10⁻⁵ | 1,24±0,02*10⁻⁵ |
| CaF₂-LuF₃ (20%): Ce (1 %) | -2,1±0,4*10⁻⁵ | 1,43±0,07*10⁻⁵ |

In the Table 1 the results of measuring the temperature coefficient of the refractive index and the coefficient of linear thermal expansion are shown. Obtained data show that these parameters experience significant changes when host lattice is doped with RE ions. Although doping level was not high in our samples the temperature coefficient of the refractive index decreases in 1,5 times for Ce³⁺ and Yb³⁺ doped crystals compared to CaF₂ crystal host. It is known that doping CaF₂ crystal by RE ions at levels higher than 0,1 at. % provides significant probability of impurity clusters formation.
4. Conclusion
In present work we have investigated thermal conductivity in the range 50 – 300 K and have estimated temperature coefficient of the refractive index and the coefficient of linear thermal expansion of CaF$_2$ crystals doped by Ce$^{3+}$ and Yb$^{3+}$ ions and CaF$_2$-LuF$_3$ mixed crystal. Thermal conductivity of the investigated materials appears to be lower than that of pure CaF$_2$ and shows behavior characteristic to glasses, which is the evidence of presence of inhomogeneities of the crystal structure and other centers of phonon scattering due to impurities. The temperature coefficient of the refractive index is also 1.5 times lower for Ce$^{3+}$ and Yb$^{3+}$ doped crystals compared to CaF$_2$ crystal host. These data are very important in the development of optical systems of lasers.

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