EFFECT OF THE SURFACE ORIENTATION ON THE DIELECTRIC SPECTRA OF ErF$_3$–DOPED CaF$_2$ CRYSTALS

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Abstract

Some ErF$_3$-doped calcium fluoride crystals have been grown using the vertical Bridgman method. Temperature and frequency dependence of the complex dielectric constant have been studied over the temperature range of 150-300K. The effect of the sample surface orientation on the dielectric relaxation has been revealed for the first time.

Keywords: Defects, Relaxation processes, Dielectric materials.

1. Introduction

The CaF$_2$ crystals doped with Er$^{3+}$ ions are good laser materials. In order to use the laser properties of the crystals it is necessary to study the influence of the various types of defects on the properties of the crystals. Information on impurity-defect aggregates can be obtained from spectroscopic and dielectric relaxation techniques, the last being sensitive to aggregates with a dipole moment which can reorientate through migration of the anions. The extra positive charge of the Erbium ions are usually compensated by interstitial F$^-$ ions in various positions in the CaF$_2$ lattice. Besides, the tetragonal (C$_{4v}$) symmetry of the predominant dipolar complex (NN or R$_1$ type dipole), many other simple or cluster configurations appear. The resultant dipolar complexes can reorient (relax) by “jump” of one of the charges to other lattice sites. Temperature and frequency dependence of the complex dielectric constant (dielectric spectra) give information about the relaxation processes and permits the determination of the activation energy and the reciprocal frequency factor of the relaxation time [1-4].

The objectives of the paper are to analyze the effect of the sample surface orientation, cleaved or cut from the crystal, on the dielectric spectra and to determine the corresponding activation energies and the relaxation time constant. Temperature and frequency dependence of the complex dielectric constant have been measured at seven audio frequencies over the temperature range of 150-300K.
2. Method and samples

Pure and various concentrations ErF3–doped CaF2 crystals have been grown using vertical Bridgman method [5]. Supra-pure grade (Merck) CaF2, ErF3 and PbF2 were used as starting materials. Transparent single crystals have been grown in graphite crucible in vacuum (~10⁻¹ Pa); the rate of the crucible lowering was 4 mm/h. The orientation of the (111) cleavage plane with respect to the growth direction varies from sample to sample because we did not use seed in order to obtain special oriented crystals.

Capacitance (C), $\varepsilon_1 = C / A$, $A$ is a geometrical factor, and dielectric loss ($D$) measurements were performed on the samples using a RLC Meter type ZM2355, NF Corporation, Japan, over the temperature range 150–300 K at seven audio-frequencies; the imaginary part of the dielectric constant has been calculated by $\varepsilon_2 = D \varepsilon_1$. The measurements were performed both, on (111) cleavage plane and on cut surface in order to characterize the observed relaxations.

3. Results and Discussions

The temperature dependence of the real part of the complex dielectric constant is approximately linear (Fig. 1), with higher slope for temperatures >230K than for lower temperatures; around $T_0 = 269K$ an anomaly of $\varepsilon_1$ behavior (Figs. 1, 3, 4) has been observed (not reported before) which can be assigned with a phase transition of the order-disorder type. The relaxation parameters have been calculated from $\varepsilon_2$ spectra (fig. 2).

![Fig. 1. Influence of dopant concentration and surface orientation on $\varepsilon_1$ spectra; (a,c,d) cleavage and (b) cut plane.](image1)

![Fig. 2. Temperature and frequency dependence of the imaginary part of the complex dielectric constant.](image2)
The observed anomaly in dielectric spectra at $T_0$, depends on the surface orientation of the sample and on the impurity concentration (figs. 1, 3, 4). The maximum effect has been observed for 1.1mol%ErF$_3$-doped cleaved sample. The temperature dependence of the loss tangent and of the reciprocal of $\varepsilon_1$ are shown in Figs. 5, 6. The loss tangent has a maximum at a slightly lower temperature than the $\varepsilon_1$ maximum and a sharp minimum at a slightly higher temperature.. We can observe that the slopes of the $\varepsilon_1^{-1} (T)$ plots are different on both sides of $T_0$. These types of anomalies in the dielectric properties have been observed for some perovskite-type compounds and are assigned with an order-disorder type phase transition [6].

Fig. 3. Influence of dopant concentration.  
Fig. 4. Effect of surface orientation.

Fig. 5. Temperature dependence of the real dielectric constant and of loss tangent.  
Fig. 6. Temperature dependence of the reciprocal dielectric constant.
Table 1. Relaxation parameters

<table>
<thead>
<tr>
<th>ErF₃ (mol%)</th>
<th>Sample type</th>
<th>( E ) (eV)</th>
<th>( \tau₀ ) (10⁻¹⁴ s)</th>
<th>( E(eV) ); ( \tau₀ ) (10⁻¹⁴)</th>
<th>( E ) (eV)</th>
<th>( \tau₀ ) (10⁻¹⁵ s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.17</td>
<td>cleaved (A)</td>
<td>0.381</td>
<td>5.5</td>
<td>–</td>
<td>0.68</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>cleaved R</td>
<td>0.38</td>
<td>6.03</td>
<td>–</td>
<td>other works</td>
<td>[2, 4]</td>
</tr>
<tr>
<td></td>
<td>cut</td>
<td>0.395</td>
<td>2.9</td>
<td>0.406; 1.88 [2]</td>
<td>0.54</td>
<td>0.05</td>
</tr>
<tr>
<td>+PbF₂</td>
<td>cleaved</td>
<td>0.388</td>
<td>5.3</td>
<td>–</td>
<td>0.527</td>
<td>0.18</td>
</tr>
<tr>
<td>0.69</td>
<td>cleaved</td>
<td>0.349</td>
<td>29</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>cut</td>
<td>0.353</td>
<td>22</td>
<td>0.4; 1.97 [1]</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1.1</td>
<td>cleaved</td>
<td>0.36</td>
<td>18.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>cut</td>
<td>0.368</td>
<td>12</td>
<td>0.401; 2.65 [1]</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>+PbF₂</td>
<td>cleaved</td>
<td>0.394</td>
<td>3.5</td>
<td>–</td>
<td>0.651</td>
<td>0.03</td>
</tr>
</tbody>
</table>

cleaved R- cleaved and rotate with \( \pi/2 \) in comparison with A position of the sample,

4. Conclusions

In the temperature range studied (150-300 K) our investigation reveals the two types of relaxations, \( R_1 \) and \( R_{IV} \), characteristic for RE doped CaF₂, approximately at the same temperature and activation energy as reported in other published works. The observed influence of the sample surface orientation on the dielectric properties and the anomaly in temperature dependence of the \( \varepsilon_i \) has been not reported before.

Acknowledgements

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References

2. C. Andeen, D. Link and J. Fontanella, Phys Rev. B16 (1977) 3429, 3762,