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EFFECT OF THE SURFACE ORIENTATION ON THE DIELECTRIC SPECTRA OF ErF_3 –DOPED CaF_2 CRYSTALS

Irina Nicoara, M. Munteanu, E. Preda, G. Buse and M. Stef

West University of Timisoara, Dept. of Physics, Bd. V. Parvan nr 4, Timisoara, Romania

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_I 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) CaF_2, ErF_3 and PbF_2 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 4mm/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 ε_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 ε_2 spectra (fig. 2).

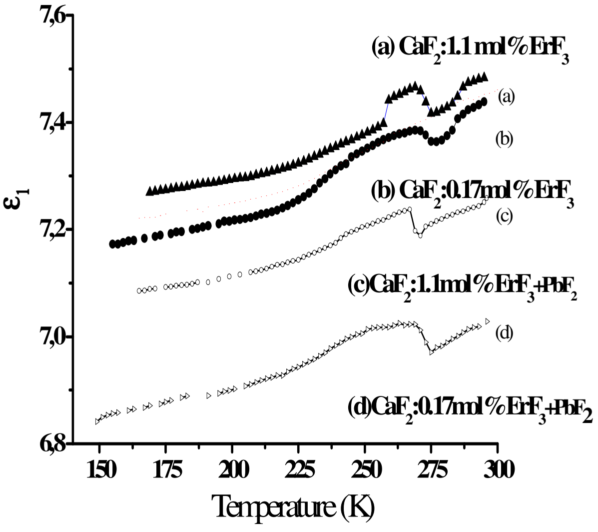

Fig.1.Influence of dopant concentration and surface orientation on ε_1 spectra; (a,c,d) cleavage and (b) cut plane.

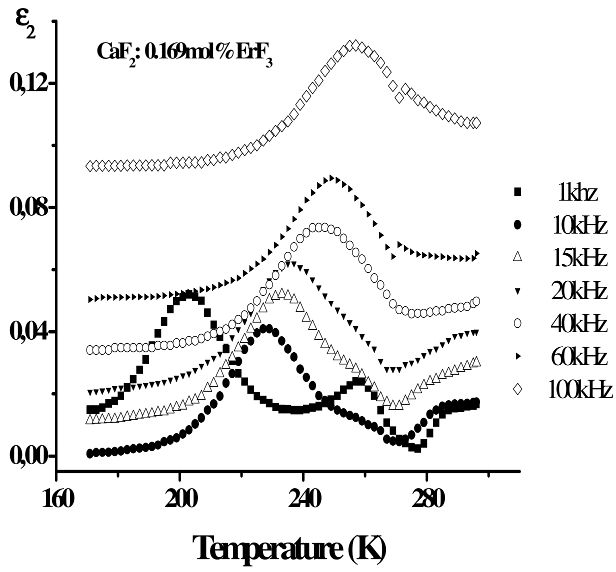

Fig. 2.Temperature and frequency dependence of the imaginary part of the complex dielectric constant.

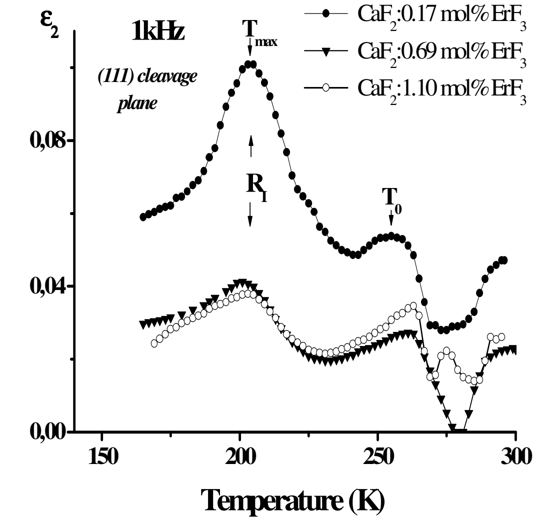

Fig. 3.Influence of dopant concentration.

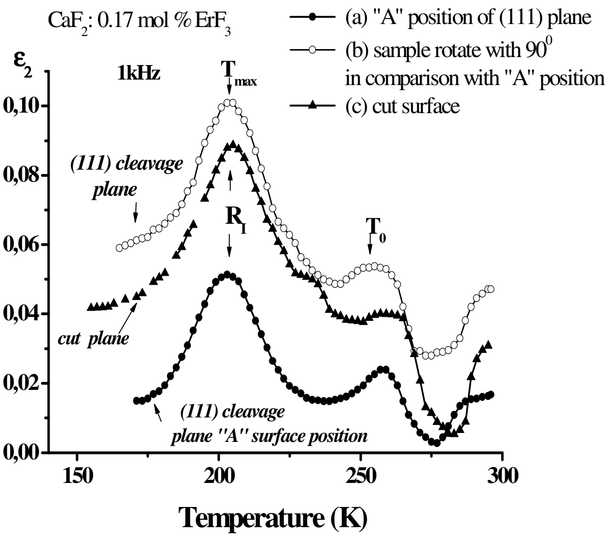

Fig. 4. Effect of surface orientation.

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 ε_1 are shown in Figs. 5, 6. The loss tangent has a maximum at a slightly lower temperature than the ε_1 maximum and a sharp minimum at a slightly higher temperature.. We can observe that the slopes of the ε_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].

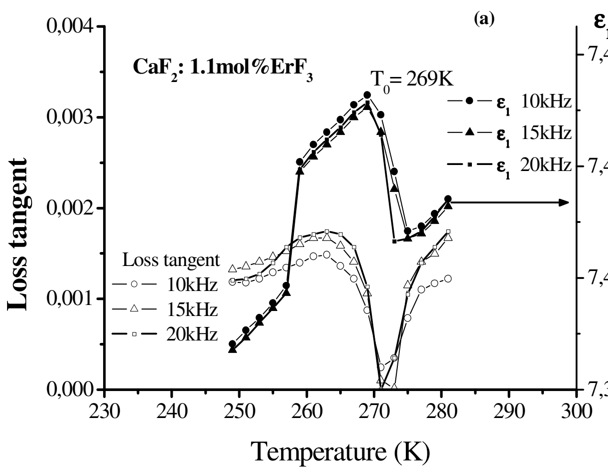

Fig. 5. Temperature dependence of the real dielectric constant and of loss tangent.

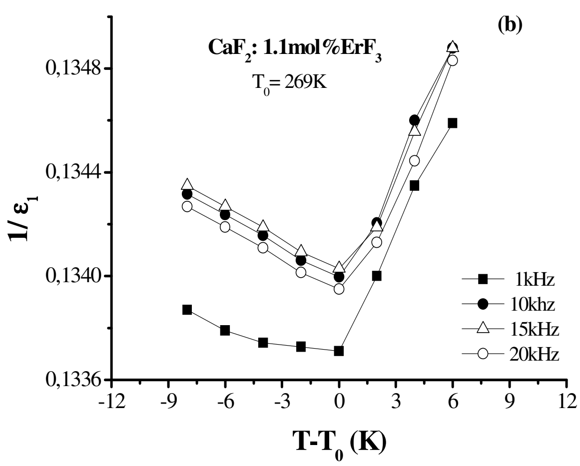

Fig. 6. Temperature dependence of the reciprocal dielectric constant.

Table 1. Relaxation parameters

ErF_3 (mol%)	Sample type	$\mathbf{R_I}$			$\mathbf{R_{IV}}$	
		E (eV)	τ_0 (10^{-14} s)	other works *E(eV)*; τ_0 (10^{-14})	*E* (eV)	τ_0 (10^{-15} s)
0.17	cleaved (A)	0.381	5.5	–	0.68	0.04
	cleaved R	0.38	6.03	–	other works [2, 4]	
	cut	0.395	2.9	0.406; 1.88 [2]	0.54	0.05
$+PbF_2$	cleaved	0.388	5.3	–	0.527	0.18
0.69	cleaved	0.349	29	–	–	–
	cut	0.353	22	0.4; 1.97 [1]	–	–
1.1	cleaved	0.36	18.5	–	–	–
	cut	0.368	12	0.401; 2.65 [1]	–	–
$+PbF_2$	cleaved	0.394	3.5	–	0.651	0.03

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_I and R_{IV}, characteristic for RE doped CaF_2, 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 ε_1 has been not reported before.

Acknowledgements

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References

1. J. Fontanella and C. Andeen, J. Phys. C9 (1976) 1055,
2. C. Andeen, D. Link and J. Fontanella, Phys Rev. B16 (1977) 3429, 3762,
3. J. Fontanella, D.J. Treacy, J. Chem. Phys. 72 (1980) 2235,
4. C. Andeen, G.E. Matthews, M.K. Smith and J. Fontanella, Phys. Rev. B19 (1979) 5293,
5. D. Nicoara and I. Nicoara, Mater. Science and Eng. A 102 (1988)L1,
6. B. A. Strukov, A.P. Levanyuk, *Ferroelectric Phenomena in crystals*, Springer, Berlin, 1998,