

Dielectric spectrum of rare-earth-doped calcium fluoride crystals

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Abstract

Calcium fluoride crystals doped with ErF_3 and YbF_3 have been grown using the vertical Bridgman method. The real and imaginary parts of the complex dielectric constant, ϵ' and ϵ'' , have been measured at five audio-frequencies (1–100 kHz) over the temperature range 150–300 K. From the observed relaxation processes the activation energy for dipole reorientation and the relaxation time constant, τ_0 , have been determined. A comparison of our results with those obtained by other authors is also given.
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1. Introduction

The alkaline-earth fluorides (MF_2 , $M = \text{Ca}$, Ba , Sr) crystals doped with rare-earth fluorides (RF_3 , $R = \text{La}$, Er , Yb , etc.) are good laser crystals. The R ions are trivalent; consequently an additional charge-compensating defect must occur. Charge compensation in calcium fluoride doped with trivalent rare-earth cations is effected by interstitial anions. Local compensations by pairing of trivalent cations with interstitial anions create electric dipoles whose relaxation may be observed as dielectric absorption. There are different experimental techniques for studying the defects responsible for the diffusive motions as well as the motions themselves. The static techniques (EPR, optical absorption, ENDOR) provide information about the nature and site symmetry of the defects. The dynamic techniques, such as ionic conductivity, ionic thermocurrent (ITC), dielectric relaxation, NMR relaxation, tend to measure defect properties such as diffusion constant and activation energy. Temperature and frequency dependence of the complex dielectric constant give information about the relaxation processes and permits the determination of the activation energy and the reciprocal frequency factor, τ_0 , of the relaxation time, τ [1–5]. At least five dielectric

relaxations (denoted by R_I , R_{II} , R_{III} , R_{IV} and R_V) are associated with the $\text{CaF}_2\text{:RE}$ system [1–3].

In this paper we report a study of some relaxation regions in samples of calcium fluoride crystals doped with various concentrations of ErF_3 and YbF_3 using the dielectric relaxation technique. Temperature and frequency dependence of the complex dielectric constant have been measured and the activation energy and relaxation time constant have been calculated.

2. Experiment


Calcium fluoride crystals doped with various concentrations of ErF_3 and YbF_3 have been grown using the vertical Bridgman method [6]. Chemically pure grade (99.9%) RF_3 reagent and suprapure grade Merck, calcium fluoride were used as the starting materials. Transparent single crystals have been grown in graphite crucibles in vacuum ($\sim 10^{-3}$ Pa); the addition of 4 wt% PbF_2 was used as scavenger of oxygen impurities. The as-grown single crystals are shown in Fig. 1. The rate of the crucible lowering was 4 mm/h.

Capacitance C , conductance G , dielectric loss D and θ measurements were performed on the samples using a RLC Meter type ZM2355, NF Corporation, Japan, over the temperature range 150–300 K, at five audio-frequencies 1, 10, 20, 60 and 100 kHz. The real part of the dielectric

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