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Growth and electrical properties of doped $Bi_4Ge_3O_{12}$ single crystals

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The optimal conditions for $Bi_4Ge_3O_{12}$ single crystals doped with Mn grown by the Czochralski technique have been established. The dielectric constant and the dielectric losses have been measured in the frequency range 10^2-10^5 Hz at temperatures of 300-600 K. Some studies of the a.c. conductivity and the behaviours of the real and imaginary parts of a.c. conductivity have been performed.

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1. Introduction

Bismuth germanate ($Bi_4Ge_3O_{12}$) is of interest due to its potential as voltage and electric field sensors, in which precision is more important than sensitivity [1]. Doping of $Bi_4Ge_3O_{12}$ crystals with Mn allows the formation of space charges, induced when illuminating the crystals with modulated light of 514 nm wavelength. The spatial charge distribution and the presence of a strong linear elector-optic effect in these materials result in the formation of transient spatial gratings, due to the optically induced redistribution of electrons and holes between impurity levels [2]. Such processes make Mn-doped $Bi_4Ge_3O_{12}$ a promising material for the storage of optical information.

Impedance or dielectric spectroscopy uses an a.c. signal to probe a material [3,4]. This is generally done in a parallel plate capacitor system. By applying a current and measuring the output voltage and the phase angle at different frequencies, an abundance of information about a material can be determined. Commonly, the capacitance and tan δ or impedance and phase angle are measured. AC signals are highly affected by interfaces, whether they are between a material and the electrodes, different grains, or different phases in a material. Different types of interfaces affect different frequency ranges; therefore, by looking at an impedance spectrum many interfacial properties can be distinguished and determined [5].

In this paper, we report experimental results on the growth of doped $Bi_4Ge_3O_{12}$ and the influence of the Mn impurities on the temperature (300K to 576K) and frequency (10^2 Hz to 10^5 Hz) dependence of the AC conductivity in pure and Mn doped crystals.

2. Experiment

Crystals of $Bi_4Ge_3O_{12}$ were grown from stoichiometric melts using the Czochralski method. The melting point was approximately 1050^0C. A platinum crucible and atmospheric environment were used. The pulling and rotation rates employed were 0,8-1 mm/h and 15 rpm, respectively. The starting materials were 99.999% pure Bi_2O_3 and GeO_2, mixed in the stechiometric ratio 2:3. Transition-metal ions of Mn were added to the melt as MnO_2. Several green crystals were prepared. The pulling direction was chosen to be along one of the cubic axes <110>.

The impurity contents were determined by flame analysis with a Pye Unicom 1950. absorption spectrophotometer Four samples were investigated: a pure crystal of $Bi_4Ge_3O_{12}$, and doped $Bi_4Ge_3O_{12}$ crystals with three different concentrations of Mn: BGOMn1 (0.899×10^{18}atoms.cm^{-3}), BGOMn2 (0.476×10^{18}atoms.cm^{-3}) and BGOMn3 (0.094×10^{18} atoms.cm^{-3}).

Samples with diameter of 10 mm and thickness of 1 mm were prepared for the AC measurements. On these samples, Au contacts were coated by vacuum evaporation. A planar capacitor was thus formed. The AC conductivity measurements were done using a Hewlett Packard 4275 multy-frequency bridge. Frequencies from 10^2 Hz to 10^5 Hz were used. The capacitance, tan δ, impedance and phase angle were measured in the temperature range 300 K to 600 K. The dielectric constant was obtained from the capacitance and the geometry of the sample.

By studying the dielectric constant and the real part of the conductivity as a function of frequency, different processes can be highlighted.

3. Results

The dielectric constants as a function of frequency for the pure sample and those doped with three different concentrations of Mn are plotted in Fig. 1. The dielectric constant reported in the literature for $Bi_4Ge_3O_{12}$ is 16 at low frequencies [6]. The values obtained at room temperature were somewhat less than this. At high temperature (T=576 K), the dielectric constants of the doped samples BGOMn2 and BGOMn3, at low frequency are higher that those of pure BGO and BGOMn1. The frequency dependence of the dielectric constant of the sample with the highest concentration of Mn is the same as that of the pure sample.

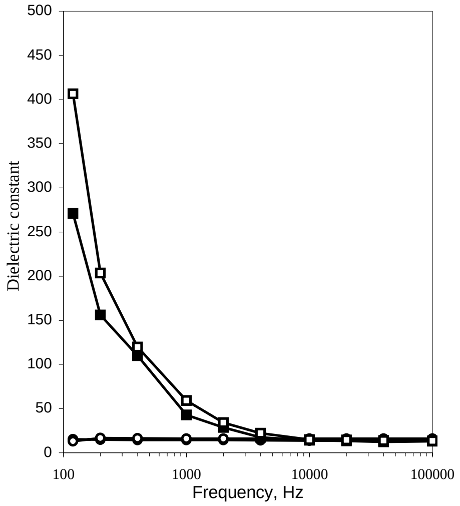

Fig.1. The dielectric constant as a function of the frequency at 576 K

The dielectric loss of the pure and Mn doped $Bi_4Ge_3O_{12}$ crystals, as a function of temperature, at a frequency of 10 kHz is plotted in Fig. 2.

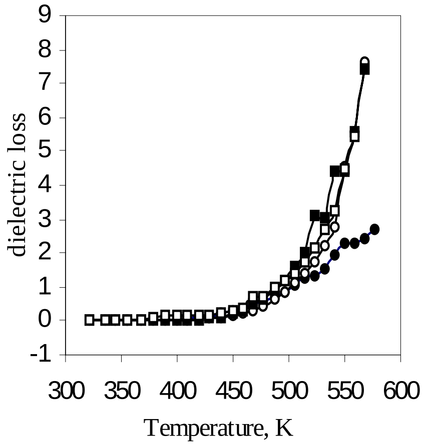

Fig. 2. The temperature dependence of the dielectric loss at 10 kHz

The values of tan δ are nearly zero until about 450K, and increase rapidly in the temperature range 450-600 K. For the doped sample, the slope of the curve is bigger than for the pure sample. In the temperature dependence of the dielectric loss for sample BGOMn3, on observes weak peaks at temperatures of about 523 K and 541 K.

Figs. 3a and 3b show the temperature dependence of the real part of the AC conductivity of pure BGO single crystals and of samples doped with different concentrations of Mn, at 10 kHz and 100 kHz.

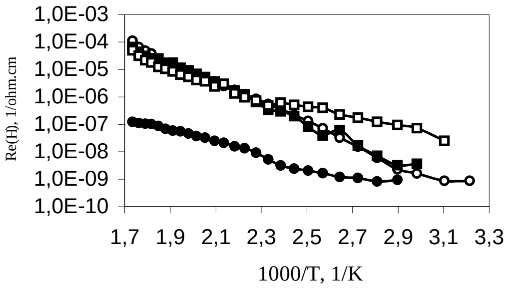

Fig.3a. The temperature dependence of the real sigma at 10 kHz

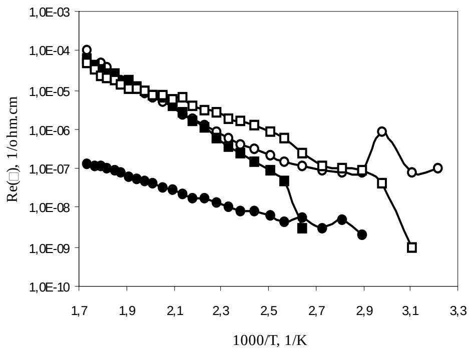

Fig.3b. The temperature dependence of the real sigma at 100 kHz

The doping leads to a considerable increase in the real part of the conductivity, σ, in the temperature range 300 K to 600 K. In the temperature dependence of the conductivity of sample BGOMn1, on observes a peak at a temperature of about 335 K at 100 kHz. There is a weak peak at 378 K in the curve at 10 kHz for sample BGOMn2.

The effective activation energies, E, were obtained using the equation $\sigma=\sigma_0\exp(-E/kT)$ and are summarized in Table 1. The activation energies of the doped samples increase with increasing impurity concentration.

Table 1. The activation energies of the samples

Sample	Activation energy, eV	
	at 10^4 Hz	at 10^5 Hz
BGO pure	0,234	0,352
BGOMn1	0,796	0,725
BGOMn2	0,749	0,749
BGOMn3	0,621	0,390

4. Discussion

According to some theoretical investigations [7], if the condition $\sigma(\omega) = \omega^s$ is satisfied and the charges are assumed to be transferred by hopping between localized states, the transfer process can be described by two mechanisms: hopping near the edge of the conduction or valence band, characterized by a strong temperature dependence of exponential form, and hopping between localized states with energies close to the Fermi level, in which a weak temperature dependence is observed. Figs. 3a and 3b illustrate the temperature dependence of Re (σ) at 10 kHz and 100 kHz respectively. At high temperatures, an exponential increase is observed. In this case, it may be suggested that the mechanism of hopping conductivity between localized states near the valence or conduction bands prevails.

5. Conclusions

This preliminary characterization shows that impedance spectroscopy is an appropriate tool for studying $Bi_4Ge_3O_{12}$ single crystals. In an electron paramagnetic resonance study of the Mn^{2+} ion in $Bi_4Ge_3O_{12}$, it has been determined that the Mn^{2+} ion enters the Bi^{3+} trigonal site without local charge compensation [8]. In this work, it has been established that the presence of transition metal ions (Mn^{2+}) in the BGO crystal lattice increases the conductivity of sample. The changes are expected to be due to microstructure variations, including the presence of impurity ions. Doped and undoped samples show distinctions between their dielectric spectra, due to anisotropy distribution of the Mn atoms in the $Bi_4Ge_3O_{12}$ lattice. The experimental results obtained from investigations of the AC conductivity reveal that impurity conduction is present in these crystals, on the basis of hopping of charge carriers involving impurity centres.

Acknowledgments

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