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Interactive microwave and structural studies of C–$Er_2Si_2O_7$

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ABSTRACT

$Er_2Si_2O_7$ compound exists in three polymorphs, low temperature polymorph (type-B), monoclinic (type-C) and the high temperature monoclinic modification (type-D). The polymorphic $Er_2Si_2O_7$ is synthesized by solid state double sintering method. The crystal structure and surface morphology of the calcined samples were characterized by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM). The electromagnetic properties are measured through network analyzer (Agilent 8722ET). The dc electrical characterization is also performed in the microwave region and electrical transport data are analyzed according to Mott's variable-range hopping. The activation energy ($\Delta E = 0.119 \pm 0.001$ eV) is calculated from $ln\rho$ versus $1/k_BT$ plot. Furthermore, the microwave electromagnetic properties of the samples were also studied at the frequency range from 20 Hz to 3 GHz on room temperature. It can be observed that C-type $Er_2Si_2O_7$ exhibit dielectric dispersion where both ε' and ε'' decrease slightly with increasing frequency up to 2.43 GHz, and then a resonance occurs around 2.85 GHz. This is the first kind of measurement on C–$Er_2Si_2O_7$ as far as our knowledge goes.

1. Introduction

The compound containing rare earth materials specially their silicates are promising materials for future microelectronics because of their high dielectric constant and low losses as a replacement for traditional SiON/poly-Si electrodes. Modern solid state technology has recently made use of rare earth compounds in microwave devices, semiconductors, ferromagnetic, ferroelectric, laser and phosphors. Dielectric phenomenon in rare earth containing materials has been recently extensively studied [1]. Currently the dielectric spectroscopic measurements have been performed and charge transport mechanisms are analyzed by many authors [2–4] for various rare earth formulations.

Worldwide, researchers are analyzing various rare earth formulations specially their oxides and silicates for transistor scaling as being high dielectric materials for 22 nm node and beyond [5]. The unique properties of this group of compounds, which also include rare-earth silicates/disilicates, are due to their special $4f^n$ electronic states and the general shielding of these orbitals by higher orbitals in the rare earth ions [6].

A number of investigations have been reported for studying of this group of compounds. Maqsood et al. [7] prepared this material in form of both poly- and single crystals. The material was characterized by X-ray diffraction. The lattice constants and possible space groups were determined by the same authors. The high temperature polymorph forms a monoclinic structure with lattice constants, $a = 4.68$ Å, $b = 5.56$ Å and $c = 10.79$ Å, $\gamma = 96$ with four atoms per unit cell. The space group is $P2_1/b$ [8–10]. The magnetic susceptibility on the single crystals of this compound showed the aniferromagnetic behavior at 1.9 ± 0.1 K [11]. The mechanical and thermal transport properties of these crystals have been reported by Maqsood et al. [12,13].

In this paper, the dc electrical resistivity (ρ) of C-type $Er_2Si_2O_7$ in the temperature 300–600 K is reported. The electrical resistivity decreases with rise of temperature, showing a semiconductor like behavior. The electrical transport data are also analyzed according to Mott's variable-range hopping. Furthermore, the permittivity of this compound in the microwave region at room temperature is also determined. It can be observed that C-type $Er_2Si_2O_7$ exhibit dielectric dispersion where both ε' and ε'' decrease slightly with increasing frequency up to 2.43 GHz, and then a resonance occurs around 2.85 GHz. It is the inaugural attempt to make this type of experiments on $Er_2Si_2O_7$ to our knowledge.

2. Experimental procedure

The material was prepared by solid state reaction method. Precursors taken were 99.9% Er_2O_3, BDH silica gel of 60–120 mesh. The SiO_2, containing 12 wt% of H_2O was calcined at 1000 °C and then kept in a desiccator. Composition is calculated from formula was well mixed and heated at 1450 °C for 24 h and then kept at this temperature for 24 h. After that furnace was switched off. On cooling, material was remixed thoroughly and same process was repeated.

3. Measurements

C-type $Er_2Si_2O_7$ material was checked by powder X-ray diffraction (XRD), using Cu Kα radiation. The X-ray diffraction pattern

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confirmed the formation of C-type $Er_2Si_2O_7$. The end product agreed with structure of C–$Er_2Si_2O_7$ (ASTM card no. 82-0733). Lattice constants were in agreement with earlier reports [7]. SEM and EDS were made using a JEOL instrument (JSM-3-5-CF). For resistivity measurements, prepared material was pressed with a load of 50 kN for 10 min and then sintered at 1000 °C for 24 h. The pallet was 13.01 mm in diameter and thickness was 3.5 mm. The measured density of the sample was 4.82 g cm^{-3}. Resistivity was measured using two probe method in temperature range 300–600 K which was our home made apparatus. Permittivity measurement 'Agilent E4991A RF Impedance/Material Analyzer' was used in frequency range 1 MHz to 3 GHz at room temperature. Furthermore, from experimental data Debye relaxation time is also measured [2].

4. Results and discussion

4.1. Structural properties

X-ray diffraction for C–$Er_2Si_2O_7$ in powder identifies that bulk sample be the polycrystalline nature. Results are analyzed with card No. ASTM 82-0733 and it proves that the resulted structure is the C-phase of $Er_2Si_2O_7$ with lattice constants in agreement with previous reports [7] as shown in Fig. 1. High temperature polymorph forms a monoclinic structure with lattice constants, $a = 6.849$ Å, $b = 8.939$ Å and $c = 4.722$ Å, $\beta = 101.8$. Scanning electron microscopy (SEM) shows morphology of particle as shown in Fig. 2a. Fig. 2b shows the EDS compositional analysis which confirms that resulting Er: Si ratio was 7: 1 in agreement with composition.

4.2. Electrical resistivity

Temperature dependence of dc electrical conductivity of C–$Er_2Si_2O_7$ is measured as a function of temperature in range of 450–535 K. The obtained behavior of C–$Er_2Si_2O_7$ compounds is like a semiconductor material in case of dc electrical conductivity, expressed by the relation [14].

$$\sigma_c = \sigma_o \exp(-\Delta E/k_B T) \quad (1)$$

where σ_o is pre-exponential factor, ΔE is activation energy for conduction and k_B is Boltzmann constant. By using Eq. (1), activation energy can be calculated from slope of $ln\sigma_{dc}$ vs $1/k_BT$ plot as shown in Fig. 3a. Activation energy comes out to be 0.349 ± 0.01 eV and

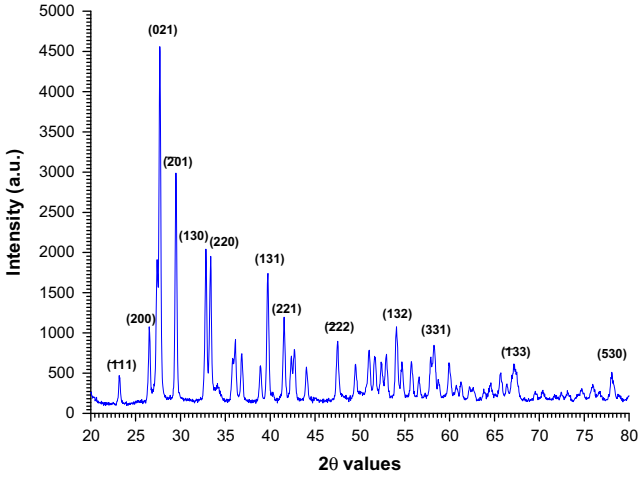

Fig. 1. X-ray diffraction pattern for C–$Er_2Si_2O_7$.

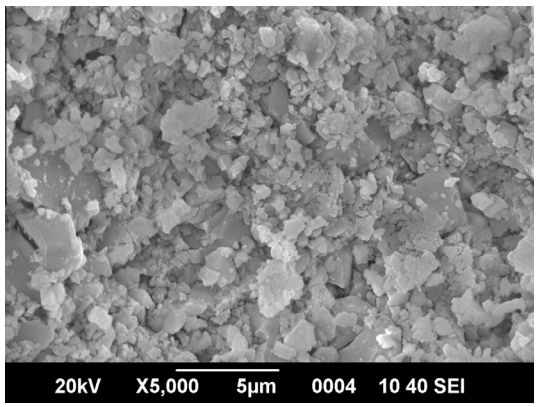

Fig. 2a. SEM micrograph.

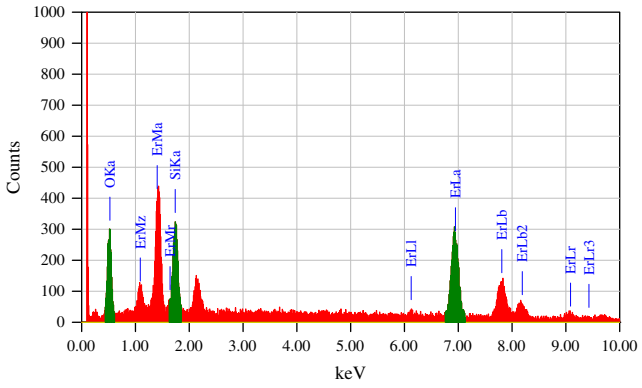

Fig. 2b. EDS analysis.

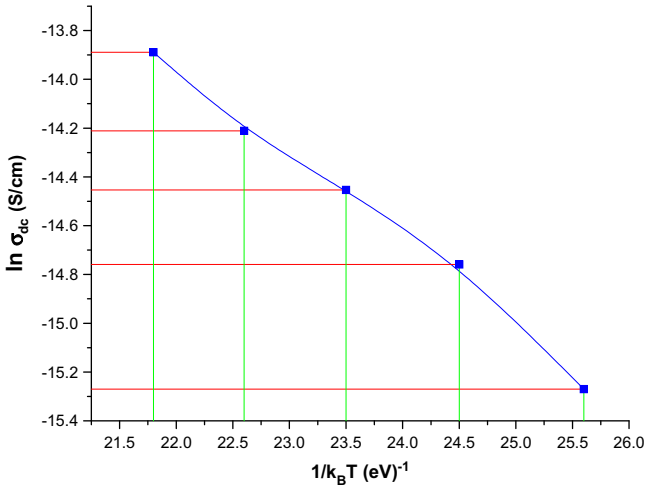

Fig. 3a. Arrhenius plot for C–$Er_2Si_2O_7$.

value of room temperature dc electrical conductivity is 1.1×10^{-5} S/m.

Magnitude of pre-exponential factor σ_o is indicative of fact that whether conduction is caused by extended states or is due to localized states [15]. It is well known that for extended state conduction, value of σ_0 should lie between 10^3–10^4 S/cm [16] and there should be a smaller value for conduction by hopping of charge carriers between different states. In C–$Er_2Si_2O_7$ sample, value of pre-exponential factor σ_o is 10^{-3} S/cm, which is fairly small. Such a small value confirms that the conduction takes place by hopping