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Synergistic microwave and structural studies of C-type $Ho_2Si_2O_7$

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ABSTRACT

$Ho_2Si_2O_7$ material exists in four polymorphs, a triclinic low temperature phase (type-B), a monoclinic modification (type-C), high temperature monoclinic (type-D), and high temperature orthorhombic modification (type-E). The structural properties are measured by XRD and the morphology is noted through scanning electron microscopy (SEM). The dc electrical resistivity (ρ) as a function of temperature and dielectric properties of C-type $Ho_2Si_2O_7$ in the microwave region is measured. The activation energy is calculated from ln ρ versus $1/k_BT$ plot. The activation energy is 0.119 ± 0.001 eV. Both the real (ε') and imaginary parts of permittivity (ε'') decrease slightly as the frequency increases up to 1.5 GHz, after that ε' increases while ε'' decreases as the frequency increases. At around 2.45 GHz, resonance is observed.

1. Introduction

Compounds containing rare-earth ions have a very important technological research interest on account of their magnetic, electrical and optical properties. The unique properties of these compounds are due to the $4f^n$ states. Recently, Maqsood [1] prepared all the four polymorphs of $Ho_2Si_2O_7$ by the heat treatment experiments (1350–1500 °C). These materials were characterized by the X-ray diffraction studies. The lattice constants along with the space groups are already published in the above reference. The present paper reports the dc electrical resistivity and dielectric properties of C-type $Ho_2Si_2O_7$ in the microwave region. Rare-earth disilicate structure C-type $Ho_2Si_2O_7$ [2] is the only one in the family of disilicate structures which is stable from room temperature up to the melting point of the compound. The wide range of stability of this structure type is likely to be explained by the nearly equal hexagonal packing of the oxygen containing rare-earth cations in the octahedra holes and silicon in the tetrahedra holes in the alternating parallel layers. The SiO_4 tetrahedra show very low degree of distortion as compared to other disilicate configurations.

The magnetic transition in rare-earth disilicate is reported [3] to be at low temperatures. The dc electrical resistivity (ρ) of C-type $Ho_2Si_2O_7$ in the temperature 300–600 K is reported. The electrical resistivity decreases with rise of temperature, showing a semiconductor like behavior. The permittivity of this compound in the microwave region at room temperature is also determined. It is the first attempt to make this type of experiments to our knowledge.

2. Experimental procedure

The C-type $Ho_2Si_2O_7$ material was prepared by the solid state reaction technique. The starting materials were rare-earth products 99.9% Ho_2O_3, BDH silica gel, 60–120 mesh. The SiO_2, which contained 12 wt% of H_2O was calcined at 1000 °C and after that kept in a desiccator. The starting composition was calculated from the formula, thoroughly mixed all the chemicals and then heated at 1450 °C for 48 h. This was the limit of the maximum temperature available in our laboratory. The material was checked by powder X-ray diffraction (XRD), using Cu Kα radiation. The obtained pattern is shown in Fig. 1. The X-ray diffraction pattern confirmed the formation of C-type $Ho_2Si_2O_7$ [1]. The SEM and EDS were made using a JEOL instrument (JSM-3-5-CF). For the resistivity measurements, the material was pressed with a load of 50 kN for 10 min and then sintered at 1000 °C for 24 h. The pallet was 13.02 mm in diameter and thickness was 2.60 mm. The measured density of the sample was 4.82 g-cm^{-3}.

The resistivity was measured using two probe method in the temperature range 300–600 K which was our home made apparatus. For permittivity measurement 'Agilent E4991A RF Impedance/Material Analyzer' was used in the frequency range 1 MHz to 3 GHz at room temperature.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the X-ray diffraction patterns for the sample under investigation. The X-ray data shows the formation of C-type $Ho_2Si_2O_7$ [JCPS-033-0594]. The lattice constants along with the calculated and measured densities are shown in Table 1.

3.2. SEM and EDS

Scanning electron microscopy can provide the morphology as well as the particle/grain size of the sample under investigation. Fig. 2(a) shows the particles are almost spherical and the size is of

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Table 1
Lattice parameter (a, b, c, α, β, γ), X-ray density (D_x), mass density (D_m), activation energy (E_a), correlation co-efficient (R).

Parameter	Value
a (A)	6.875 (3)
b (A)	8.962 (6)
c (A)	4.73 (5)
α	90°
β	101.68°
γ	90°
D_x (g-cm^{-3})	5.68
D_m (g-cm^{-3})	4.82
E_a (eV)	0.119 ± 0.001
R	0.9994

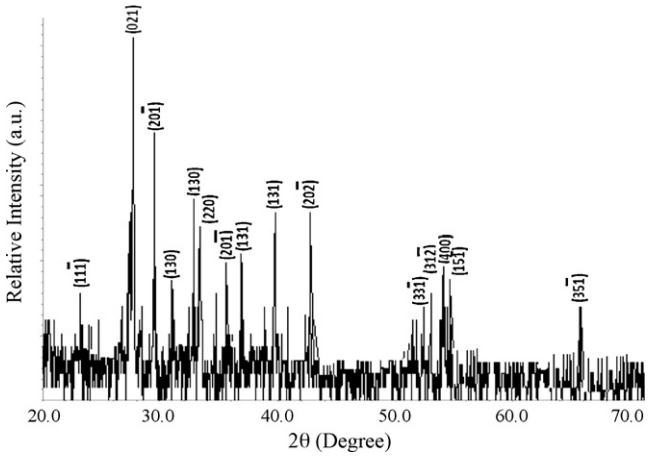

Fig. 1. Indexed X-ray diffraction pattern of C-type $Ho_2Si_2O_7$.

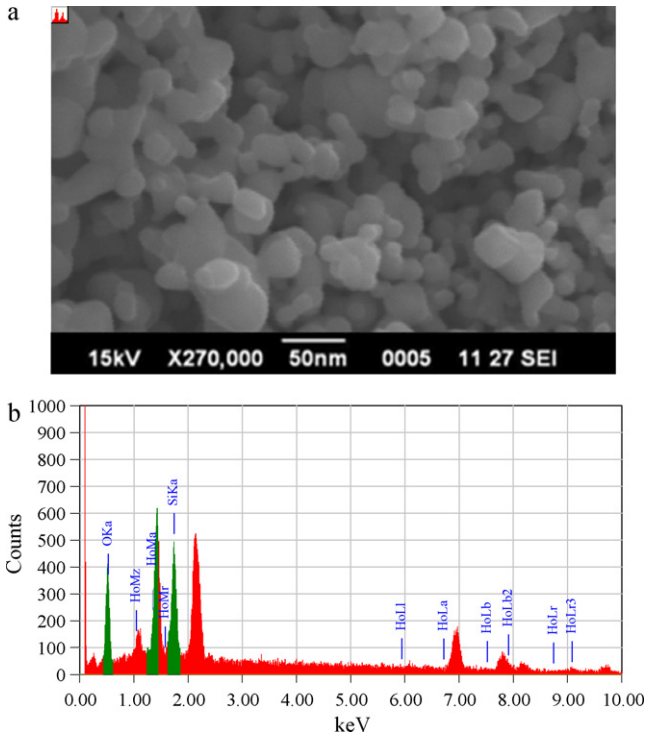

Fig. 2. (a) SEM morphology C-type $Ho_2Si_2O_7$. (b) EDS study of C-type $Ho_2Si_2O_7$.

Table 2
Dielectric constant (ε') at 3 MHz, 1 GHz, and 3 GHz, dielectric loss tangent (ε'') at 3 MHz, 1 GHz, and 3 GHz.

Parameters	Values
ε' at 3 MHz	2.1633
ε'' at 3 MHz	0.3371
ε' at 1 GHz	1.8083
ε'' at 1 GHz	−0.0291
ε' at 3 GHz	10.5315
ε'' at 3 GHz	5.0663

the order of 200 nm. From EDS results Fig. 2(b) the end composition of the compound agreed with the starting composition within the experimental errors.

3.3. Electrical resistivity

In general, the electrical properties of the materials depend upon chemical composition, methods of synthesis, sintering temperature and grain size.

The dc electrical resistivity as a function of temperature may be expressed [4].

$$\rho = \rho_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (1)$$

In the above equation ρ is the dc electrical resistivity at temperature T, ρ_0 is resistivity extrapolated to $1/T = 0$, E_a is the activation energy (shown in Table 2) and k_B is the Boltzmann's constant. Fig. 3(a) shows that the resistivity of this material in the temperature range 30–600 K. It is very high, behaving like an insulator at room temperature. By increasing temperature the resistivity of $Ho_2Si_2O_7$ decreases, indicating that the material has semicon-

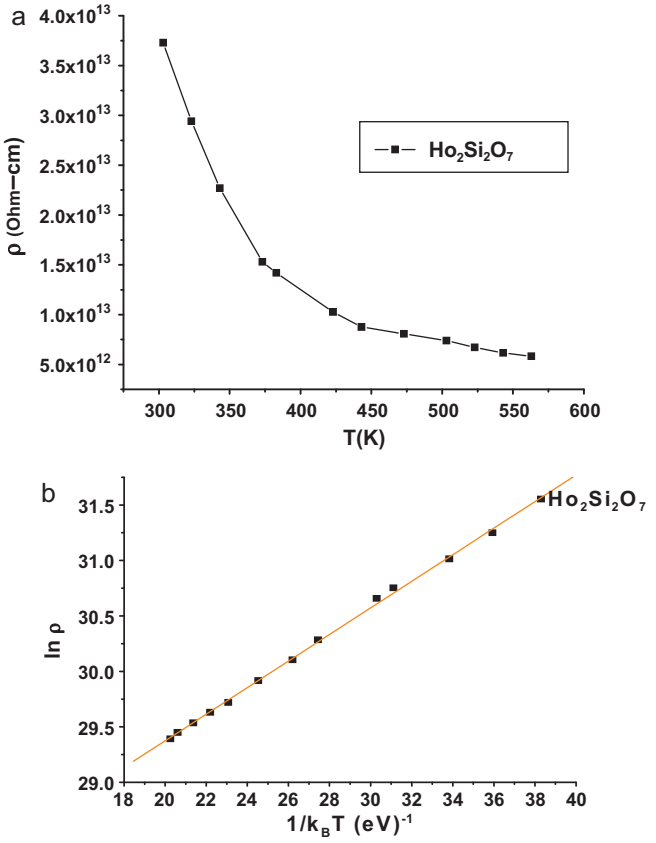

Fig. 3. (a) DC electrical resistivity of C-type $Ho_2Si_2O_7$ as a function of temperature. (b) The plot of ln ρ versus $1/k_BT$, the data are fitted to the linear equation $y = A + Bx$.

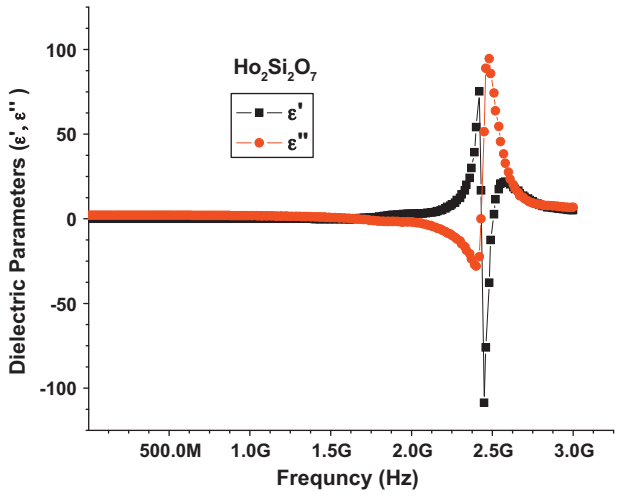

Fig. 4. Dielectric parameters of C-type $Ho_2Si_2O_7$ as a function of frequency ($\varepsilon_r = \varepsilon' - \varepsilon''$, $\tan\delta = \varepsilon''/\varepsilon'$).

ductor like behavior. The activation energy is calculated from $\ln\rho$ verses $1/k_BT$ and is shown in Fig. 3(b). The activation energy is 0.119 ± 0.001 eV as calculated for C-$Ho_2Si_2O_7$.

3.4. Microwave permittivity

The dielectric constant was calculated using the well known relation [5]

$$\varepsilon' = \frac{C_P t}{\varepsilon_o A} \tag{2}$$

where 'C_P' is the capacitance of the pallet in fared, t is the thickness of the sample in meter, A is the cross sectional area in m^2 and ε_o is the permittivity of free space.

The dielectric dissipation factor, $\tan\delta$ can be expressed in terms of the dielectric constant [5,6]

$$\tan\ \delta = D = \frac{\varepsilon''}{\varepsilon'} \tag{3}$$

The dielectric parameters of C-type $Ho_2Si_2O_7$ as a function of frequency are shown in Fig. 4. Both ε' and ε'' decrease slightly as the frequency increases up to 2.45 GHz, and then an abrupt increase occurred, as the frequency is further increased. A resonance behavior is noted at 2.45 GHz for $Ho_2Si_2O_7$. The permittivity of ceramics originates from space charge polarization, orientation polarization, ionic polarization and electronic polarization. Normally the resonance that is generated from vacancy or pores dominates in low-frequency regions, provided that there exist space charges in the materials. High frequency resonance is attributed to atomic and electronic polarization [6]. So we have observed a resonance peak in $Ho_2Si_2O_7$ at about 2.45 GHz, which appears to be an intrinsic property of our prepared material. The observation of negative permittivity is reported in nano materials by Zhu [7,8]. A loss less negative dielectric constant from quantum dot excitation polarization is theoretically explained by Fu et al. in detail [9]. The Debye relaxation (τ_o) [10,11] can be calculated from the resonance angular frequency (ω_o) and the width (γ) of the resonance peaks as

$$\tau_o = \frac{\gamma}{(w_o)^2} \tag{4}$$

From Fig. 4, the value of 'γ' is about 0.3 GHz, corresponding to 'τ' of 2.5×10^{-12} s. The observed relaxation times of ceramics are reported to be of same order [11–13]. Debye relaxation behavior is unique in the sense that all memory of excitation is instantaneously lost. Further research work is under progress.

4. Conclusions

The dc electrical resistivity as a function of temperature and dielectric constants are measured in the microwave region of C-type $Ho_2Si_2O_7$ polycrystalline material. By increasing temperature the conductivity of $Ho_2Si_2O_7$ increases, indicating that the material has semiconductor like behavior. A resonance is observed at about 2.45 GHz. This high frequency resonance is attributed to atomic and electronic polarization. This is the first report to our knowledge on rare-earth compounds.

Acknowledgements

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