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Archives of Physics Research, 2010, 1 (4):146-150
(http://scholarsresearchlibrary.com/archive.html)

Scholars Research Library
ISSN 0976-0970
CODEN (USA): APRRC7

Structural and electrical properties of heavy rare-earth zirconate

Priyanka Rani, A.N.Thakur, Pooja Raghuvanshi and A.Kumar

Department of Physics, Tilak Dhari Post Graduate College Jaunpur-222002, India.

ABSTRACT

The synthesis, characterization and electrical properties of $Tb_2Zr_2O_7$ compound have been studied. The heavy rare earth zirconate were prepared by solid state reaction technique and characterized by XRD, differential thermal analysis (DTA), thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG). The XRD characterization shows the formation of single phase orthorhombic structure at room temperature. The electrical conductivity of $Tb_2Zr_2O_7$ compound was measured in the temperature range 300-1125 K at an internal frequency of 1kHz. The logσ vs $10^3/T$ plot yield two different slopes separated by break temperature (T_1). The activation energy below and above this break temperature have been estimated as 0.13eV and 3.4eV respectively. Hence the electrical conduction below T_1 is essentially extrinsic always associated with impurities, defects and interstitials and conduction above T_1 is essentially intrinsic due to the change in conduction mechanism.

Keywords: electrical conductivity; XRD; DTA; TGA; DTG; $Tb_2Zr_2O_7$.

INTRODUCTION

Rare-earth zirconate ($R_2Zr_2O_7$, R = rare earth) have received considerable attention in recent years [1, 2], due to their excellent properties, such as metal-insulator transitions, ferroelectric properties, fluorescent and phosphorescent properties [3]. The electrical properties of these materials make them promising candidates for fuel-cell applications where high ionic conductivity and low activation energy are desired [4, 5].

In this paper, we discussed the synthesis, characterization and electrical properties of $Tb_2Zr_2O_7$ compound. The literature survey showed that only limited studies are reported on heavy rare earth zirconate compounds. These studies are related with their preparation, characterization and photocatalytic properties [6, 7], electrical properties [8-10] and thermal conductivity [11-13].

MATERIALS AND METHODS

2. Material preparation and experimental procedure

The starting materials for the preparation of $Tb_2Zr_2O_7$ compound were Tb_4O_7 and ZrO_2 (≈99.99% purity, procured from Alfa Aesar, a Johnson Mathey chemicals India Pvt. Ltd.). The stoichiometric amount of these oxides were mixed and heated in an alumina crucible for 50h at a temperature of 1300K followed by one intermediate grinding and final product was cool down slowly. The formation of the prepared material was checked by X-ray diffraction technique at room temperature.

The X-ray diffraction pattern of the compound was taken at room temperature using CuKα line (λ = 0.15418nm) as shown in Fig. 1. From XRD pattern, d_{hkl} values have been evaluated using relation [14].

$$d_{hkl} = \frac{0.15418}{2Sin\theta} \qquad (1)$$

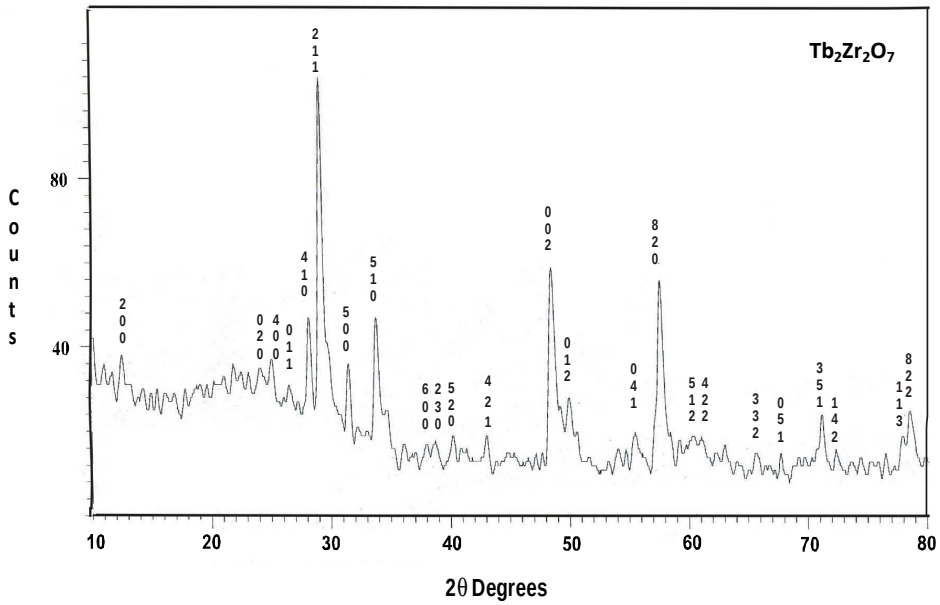

FIG. 1 Room Temperature XRD pattern of $Tb_2Zr_2O_7$

From these values of d_{hkl}, structures of the studied compound were resolved using usual procedure. All the peaks have been assigned with proper *hkl* planes. This confirms that prepared compound has single phase and no unreacted part of the starting material was left. The unit cell is orthorhombic and lattice parameters are a_0=1.4162 nm, b_0=0.7400 nm and c_0=0.3748 nm.

DTA, TGA and DTG studies of the powder of $Tb_2Zr_2O_7$ were carried out in nitrogen gas using a thermal analyzer (PERKIN ELEMER PYRIS) at a heating rate of 283K/min and flow rate of 100ml/min from 323K to 1123K.

The DTA, TGA and DTG traces of $Tb_2Zr_2O_7$ are shown in Fig. 2. The DTA trace of $Tb_2Zr_2O_7$ shows endothermic peaks at 363K and 673K. The corresponding TGA trace shows weight loss in two successive steps. The first step of weight losses 0.075% is from 323K to 593K may be due to removal of absorbed water and other gaseous species. The second step of weight loss

0.27% is from 593K to 773K and above 773K the compound is stable. The DTG trace shows maximum rate of mass change at 673K.

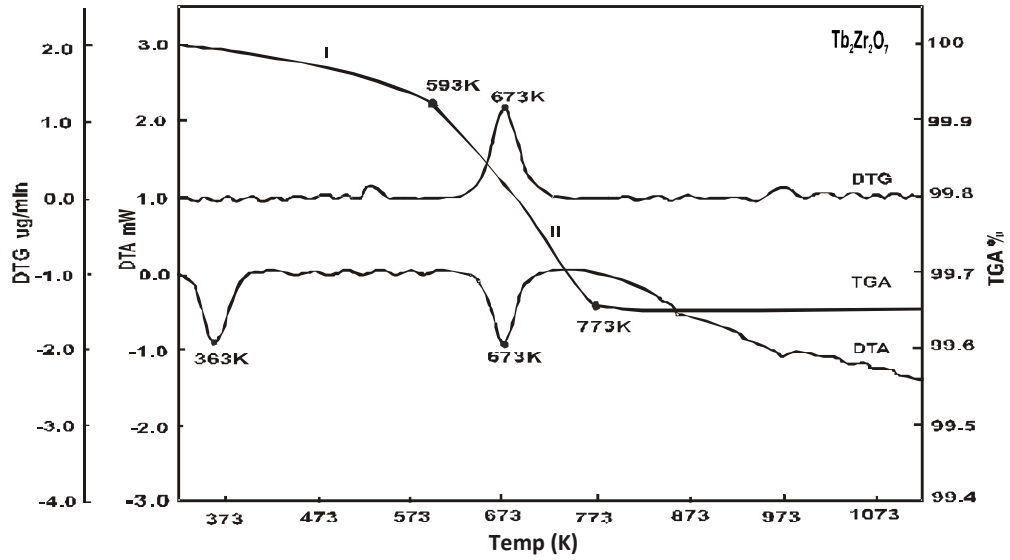

FIG. 2 DTA, TGA and DTG traces of $Tb_2Zr_2O_7$.

3. Electrical conductivity measurement

The electrical conductivity of sample was measured by finding out the resistance of the sample on pressed pellet by two electrode method. From homogenous powder of $Tb_2Zr_2O_7$ compounds, pellet (Area ~ 0.90×10^{-4} m^2 and thickness ~0.30×10^{-2} m) were prepared by isostatic pressure at 7.16×10^8 Nm^{-2} using a hydraulic press. The pellet were then sintered at 1500K in air atmosphere for 30h. Both the faces of the sintered sample were coated with high purity air drying silver paste after making both surface flat and parallel and were inserted between the two silver electrodes. The silver foils were electrically insulated from the sample holders by mica sheets. The electrical conductivity was measured by an autocompute LCR-Q meter (Model 928, Systronics India).

RESULTS AND DISCUSSION

We have measure the ac electrical conductivity of $Tb_2Zr_2O_7$ compound in 300-1125K temperature range using silver foil electrodes. The variation of Logσ *vs* $10^3/T$ is shown in Fig. 3.

The curve follows the well known exponential relation for semiconductors $\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right)$, but with two different slopes. A kink occur at T_1 (T_1= 633K) for $Tb_2Zr_2O_7$ termed as Break temperature are presented in Table.1 for studied zirconate. The value of pre exponential constant (σ_0) and activation energies (E_a) have been calculated from the slopes. The electrical transport parameter, activation energy and pre exponential constant in the two temperature region have been presented in Table 1.

Table1. Electrical transport parameter of heavy rare earth zirconate

Compound	Break temperature T_1	For T< T_1		For T>T_1	
		σ_0	E_a	σ_0	E_a
$Tb_2Zr_2O_7$	633	7.76×10^{-3}	0.13	1.96×10^{19}	3.4

An investigation of electrical conductivity of $Tb_2Zr_2O_7$ compound shows that this compound is insulator at room temperature ($\sigma = 10^{-4}\ \Omega^{-1}m^{-1}$). However with increasing temperature their conductivity rapidly increases and becomes conductor.

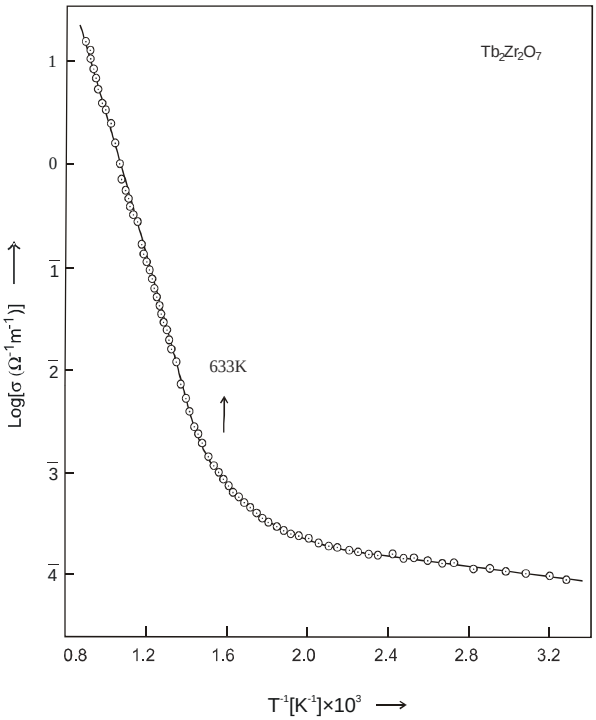

FIG.3 Plots of logarithm of electrical conductivity (Log σ) against inverse of absolute temperature (T^{-1}) for $Tb_2Zr_2O_7$

The activation energies below and above break temperature are nearly 0.13eV and 3.4eV respectively. In semiconducting materials, the electrical conduction at low temperature is always associated with impurities, defects and interstitials which generally provide states in forbidden energy gap of the material and lower value of activations energy. The contribution of defects or impurities towards conduction in solid can be explained in terms of donors or acceptors and is represented by expression [14].

$$\sigma_d = A exp\left(\frac{-E_i}{KT}\right) \qquad (2)$$

Where E_i is ionization energy of donors or acceptors and usually $E_i \sim 0.13$eV for semiconducting material. The activation energy below break temperature is found approximately comparable to the ionization energy E_i and therefore the conclusion that electrical conduction is certainly due to impurities, point defects, or interstitials seems to be reasonable.

The activation energy ~ 3.4eV estimated in the higher temperature range $T>T_1$ seems to be an intrinsic activation energy because σ_0 is in the correct range for intrinsic conductivity. Thus the change in the nature of the logσ *vs.* $10^3/T$ curve at T_1 is due to the change in the conduction mechanism i.e. transition from extrinsic to intrinsic conduction.

CONCLUSION

XRD studies confirm that $Tb_2Zr_2O_7$ compound has single phase orthorhombic structure at room temperature. DTA, TGA and DTG studies show that the compound is stable above certain temperature (≈ 773K). The electrical conductivity of $Tb_2Zr_2O_7$ compound shows that the compound is insulator at room temperature. However with increasing temperature their electrical conductivity rapidly increases and becomes conductors.

Acknowledgements
The authors are thankful to UGC for financial assistance. The authors are also thankful to Prof. K. Das and Mr. N.K. Das, central research facility, IIT Kharagpur for providing DTA, TGA, DTG facility and Mr. U.S. Singh, IIT Kanpur for providing XRD facility.

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