Synthesis, Electrical, Dielectric and Magnetic Properties of $\text{Ce}_2\text{Zr}_2\text{O}_7$ Compound

POOJA RAGHUVANSHI, A.N. THAKUR*, PRIYANKA RANI and AJAY KUMAR

Department of Physics, Tilak Dhari Post Graduate College, Jaunpur-222 002, India

*Corresponding author: E-mail: ant_tdc@yahoo.com

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The synthesis, characterization, electrical, dielectric and magnetic properties of $\text{Ce}_2\text{Zr}_2\text{O}_7$ compound have been studied. The compound was prepared by solid state reaction technique and characterized by XRD, differential thermal analysis, thermogravimetric analysis and derivative thermogravimetry. The XRD shows the formation of single phase orthorhombic structure at room temperature. The electrical conductivity (σ), dielectric constant (ϵ'), dielectric loss (ϵ'') and quality factor (Q) of $\text{Ce}_2\text{Zr}_2\text{O}_7$ was measured in the temperature range 300-1125 K at an internal frequency of 1 kHz. The $\log \sigma$ vs. $10^3/T$ plot yield two different slopes separated by break temperature (T_1). The activation energy below and above T_1 have been estimated as 0.10 eV and 2.7 eV respectively. Hence the electrical conductivity 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. The dielectric constant of $\text{Ce}_2\text{Zr}_2\text{O}_7$ show rapid increase above 670 K. The dielectric loss show similar behaviour as dielectric constant. The magnetic susceptibility of the compound was measured in the temperature range 300-1100 K at field 1.55×10^{-1} Tesla. The magnetism in this compound arises from the rare-earth ions, while Zr is non magnetic. This compound show antiferromagnetic behaviour at low temperature and obey Curie-Weiss law.

Key Words: XRD, Differential thermal analysis, Thermogravimetric analysis, Derivative thermogravimetry, $\text{Ce}_2\text{Zr}_2\text{O}_7$.

INTRODUCTION

Pyrochlore $\text{R}_2\text{Zr}_2\text{O}_7$ (R = rare earth element) compounds have been studied for their optical, electrical and catalysis properties because these materials have possible applications as hosts of fluorescence centre^{1,2} and oxidation catalysis³. 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}. Due to their excellent properties such as low thermal conductivity and high thermal expansion coefficient⁶, the complexes are widely used in gas turbines and diesel engines^{7,8}. In this paper, we discussed the synthesis, characterization, electrical and magnetic properties of $\text{Ce}_2\text{Zr}_2\text{O}_7$. The literature survey showed that only limited studies are reported on this compound. These studies are related with heat capacity, thermal expansion and crystal structure of $\text{Ce}_2\text{Zr}_2\text{O}_7$ ⁹⁻¹¹.

EXPERIMENTAL

Sample preparation and characterization: The polycrystalline sample of $\text{Ce}_2\text{Zr}_2\text{O}_7$ was obtained by solid state reaction using stoichiometric amounts of CeO_2 (99.99 % Alfa Aesar) and ZrO_2 (99.7 % Alfa Aesar), which were ground in an agate mortar for 3 h in wet medium and then dried by slow evaporation. The air dried powder of the compound was heated

in an alumina crucible at 1300 K for 50 h with one intermediate grinding and final product was cool down slowly. The formation of the compound was checked by X-ray diffraction (Thermo-electron -XRL EXTRA) at room temperature using $\text{CuK}\alpha$ line ($\lambda = 0.15418$ nm) in a wide range of Bragg angle ($10^\circ \leq 2\theta \leq 90^\circ$) as shown in Fig.1. From XRD pattern d_{hkl} values have been evaluated using relation¹².

$$d_{hkl} = \frac{0.15418}{2 \sin \theta} \quad (1)$$

Fig. 1. Room temperature XRD pattern of $\text{Ce}_2\text{Zr}_2\text{O}_7$

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 parameter are $a_0 = 3.2172$ nm, $b_0 = 1.780$ nm and $c_0 = 0.680$ nm.

The DTA, TGA and DTG studies of $\text{Ce}_2\text{Zr}_2\text{O}_7$ was carried out in N_2 gas using a thermal analyser (Perkin Elemer Pyris) at a heating rate of 283 K/min and flow rate of 100 mL/min as shown in Fig. 2. The DTA trace shows endothermic peak at 373 K. The corresponding TGA trace show weight loss of 0.36 % from 338K to 423K may be due to removal of absorbed water and gaseous species. Above 423 K the compound is stable. The DTG trace show maximum rate of weight loss at 423 K.

Fig. 2. DTA, TGA and DTG curves of $\text{Ce}_2\text{Zr}_2\text{O}_7$

Electrical and dielectric measurement: The electrical conductivity (σ), dielectric constant (ϵ') and dielectric loss (ϵ'') of the sample was measured by measuring the resistance and capacitance of the sample on pressed pellet by two electrode method using auto compute LCR-Q meter (Model 928, Systronics India). From powder of $\text{Ce}_2\text{Zr}_2\text{O}_7$ pellet (area - $0.95 \times 10^{-4} \text{ m}^2$ and thickness - $0.30 \times 10^{-2} \text{ m}$) was prepared by isostatic pressure of $7.19 \times 10^8 \text{ Nm}^{-2}$ using a hydraulic press. The pellet was then sintered at 1500 K in air atmosphere for 30 h. Both the faces of the sintered sample were coated with high purity air drying silver paste after making both surface flat and parallel and then inserted between two silver electrodes.

Magnetic measurement: Magnetic susceptibility measurements were done on powdered sample using Faraday's method^{13,14}. $\text{Gd}_2(\text{WO}_4)_3$ has been used for standardization.

RESULTS AND DISCUSSION

Electrical properties: Values of σ have been measured in the temperature range 300-1125 K at frequency 1 kHz. The variation of $\log \sigma$ vs. $10^3/T$ is shown in Fig. 3. The curve follows the well known exponential relation for semiconductor $\sigma = \sigma_0 \exp(-E_a/kT)$ but with two different slopes. A kink occurs at 670 K termed as break temperature. The pre-exponential constant (σ_0) and activation energy (E_a) have been calculated from the slopes. The values of pre exponential constant, activation energy and break temperature have been presented in Table-1.

The electrical conductivity of $\text{Ce}_2\text{Zr}_2\text{O}_7$ at room temperature is $\sigma = 10^{-4} \Omega^{-1}\text{m}^{-1}$, which indicate that the compound is insulator. However with increasing temperature their conductivity rapidly increases and becomes conductor.

Fig. 3. Plots of logarithms of electrical conductivity ($\log \sigma$) against inverse of absolute temperature (T^{-1}) for $\text{Ce}_2\text{Zr}_2\text{O}_7$

TABLE-1
ELECTRICAL TRANSPORT PARAMETER
OF $\text{Ce}_2\text{Zr}_2\text{O}_7$ COMPOUND

Compound	Break temp. T_1	For $T < T_1$		For $T > T_1$	
		σ_0	E_a	σ_0	E_a
$\text{Ce}_2\text{Zr}_2\text{O}_7$	670	17.78×10^{-7}	0.10	8.59×10^{10}	2.7

The activation energies below and above break temperature are nearly 0.10 eV and 2.7 eV 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 activation energy. The contribution of defects or impurities towards conduction in solid can be explained in terms of donors or acceptors and is represented by the following expression¹⁵.

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

where, E_i is ionization energy of donors or acceptors and usually E_i ca. 0.10 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 ca. 2.7 eV estimated in the higher temperature range $T > T_1$ seems to be an intrinsic because σ_0 is in the correct range for intrinsic conductivity. Thus the change in the nature of the $\log \sigma$ 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.

Dielectric properties: Values of ϵ' and ϵ'' have been measured in the temperature range 300-1125 K at frequency 1 kHz. Plots of ϵ' , ϵ'' and quality factor (Q) vs. temperature T are shown in Fig. 4. The values of ϵ' and ϵ'' at 400 K, 600 K, 800 K and 1000 K at frequency 1 kHz are given in Tables 2 and 3 respectively. These plots indicate that the values of ϵ' increase slow at lower temperature. This shows that there is

no chance for the existence of thermally generated charge carriers at lower side of temperature. This rules out the possibility of strong space charge polarizability. Well made electrode rules out the chance of interfacial polarization. Therefore the slow increase seems to be combined effects of lattice and electronic polarizabilities of individual ions. The increase of these polarizabilities seems to compensate the slight decrease of polarizability due to decrease in the number of ions per unit volume following the expansion of temperature. However it must be noticed that the increase of ϵ' with T is very slow in comparison to variation one expects for ionic solids. This indicates that either thermal expansion of this material is very small or they have some other kind of polarization mechanism.

Fig. 4. Plots of dielectric constant ($\log \epsilon'$) dielectric loss ($\log \epsilon''$) and quality factor (Q) against absolute temperature (T) for $\text{Ce}_2\text{Zr}_2\text{O}_7$

TABLE-2
DIELECTRIC CONSTANT (ϵ') for $\text{Ce}_2\text{Zr}_2\text{O}_7$
AT DIFFERENT TEMPERATURE

Compound	400 K	600 K	800 K	1000 K
$\text{Ce}_2\text{Zr}_2\text{O}_7$	27	32	63	335

TABLE-3
DIELECTRIC LOSS (ϵ'') for $\text{Ce}_2\text{Zr}_2\text{O}_7$ AT
DIFFERENT TEMPERATURE

Compound	400 K	600 K	800 K	1000 K
$\text{Ce}_2\text{Zr}_2\text{O}_7$	2.82	4.46	56.23	1.41×10^3

As the temperature rises, the values of ϵ' increase comparatively rapidly above certain critical temperature ($T_k = 620$ K). The dielectric loss (ϵ'') shows similar behaviour above T_k . The rapid increase in dielectric constant above T_k is due to space charge polarization^{12,16}. The pressed sample develops a considerable amount of space charge polarization arising out from the defects or impurities present in the bulk or at the surface of the material.

Magnetic properties: The magnetic susceptibility measurement of $\text{Ce}_2\text{Zr}_2\text{O}_7$ was done in heating and cooling cycles. No hysteresis was observed and χ_M values were found

to be same in heating and cooling cycles, although a small loss of weight is detected in heating cycle may be due to presence of moisture. The results are shown in Fig. 5 as χ_M^{-1} vs. T plots. At higher temperature the χ_M^{-1} vs. T plots are linear and obey Curie-Weiss law¹⁷.

$$\chi_M^{-1} = \frac{T - \theta_p}{\bar{C}_M} \quad (3)$$

where, θ_p is paramagnetic Curie temperature and $\bar{C}_M$ is the molar Curie constant.

Fig. 5. Variation of inverse of molar magnetic susceptibility (χ_M^{-1}) with absolute temperature of $\text{Ce}_2\text{Zr}_2\text{O}_7$

$\text{Ce}_2\text{Zr}_2\text{O}_7$ is magnetically simple because magnetism arises from the trivalent rare earth ions *i.e.* the magnetic interaction exists in $\text{Ce}_2\text{Zr}_2\text{O}_7$ is $R^{3+}-R^{3+}$ (R -rare-earth ions). Thus at temperature much higher than ordering temperature the molar magnetic susceptibility of $\text{Ce}_2\text{Zr}_2\text{O}_7$ can be approximated by the relation¹⁴.

$$\chi_M = \frac{N\mu_0\mu_B^2}{3k} \left[\frac{\bar{P}^2}{T - \theta_p} \right] \quad (4)$$

where, N is Avagadro number, μ_B is Bohr magneton, μ_0 is permeability constant, k is Boltzmann constant, $\bar{P}$ magneton numbers of magnetic ions R^{3+} and θ_p is the paramagnetic Curie temperature. The eqn. (4) can also be written as:

$$\chi_M^{-1} = \frac{3k(T - \theta_p)}{N\mu_0\mu_B^2\bar{P}^2} \quad (5)$$

Comparing eqn. (3) and (5) we have:

$$\bar{C}_M = \frac{N\mu_0\mu_B^2\bar{P}^2}{3k}$$

$$\text{or } \bar{P} = \left[\frac{3k\bar{C}_M}{N\mu_0\mu_B^2} \right]^{1/2} \quad (6)$$

The experimental value of $\bar{P}$ can be evaluated from the value of $\bar{C}_M$ obtained from χ_M^{-1} vs. T plot. The theoretical value of $\bar{P}$ has been already known. The theoretical and experimental values of $\bar{P}$ with magnetic ions are given in Table-4 and the values of θ_p and $\bar{C}_M$ are given in Table-5.

TABLE-4
MAGNETIC ION WITH THEORETICAL AND EXPERIMENTAL
VALUE OF AVERAGE MAGNETON NUMBER $\bar{P}$
OF THE STUDIED COMPOUND

Compounds	Magnetic ion	Theoretical value	Experimental value
$\text{Ce}_2\text{Zr}_2\text{O}_7$	Ce^{3+}	2.54	2.49

TABLE-5
PARAMAGNETIC CURIE TEMPERATURE (θ_p) AND MOLAR
CURIE CONSTANT ($\bar{C}_M$) OF THE STUDIED COMPOUNDS

Compounds	θ_p (K)	$\bar{C}_M \times 10^5$ ($\text{m}^3 \text{K mol}^{-1}$)
$\text{Ce}_2\text{Zr}_2\text{O}_7$	-38	0.97

It is seen from the table that there is a good agreement between theoretical and experimental values of $\bar{p}$, which shows that ionic moment involved in the magnetization process concern the tripositive rare earth ions.

The value of θ_p is negative for studied compounds suggesting a possible antiferromagnetic ordering of this compound at lower temperature. However, such small values of θ_p can also be due purely to the crystal field effect with a little contribution from simple dipole-dipole interaction between the magnetic ions.

Conclusion

XRD confirms the pyrochlore structure of $\text{Ce}_2\text{Zr}_2\text{O}_7$. DTA, TGA and DTG studies show that the compound is stable above certain temperature. $\text{Ce}_2\text{Zr}_2\text{O}_7$ is insulator at room temperature but becomes conductor at higher temperature. The dielectric constant (ϵ') and dielectric loss (ϵ'') have very slow increase upto T_k , but above T_k this increase becomes much faster. The reason for faster increase above T_k is due to space charge polarization. The magnetic measurement shows that the magnetic ions contribute towards magnetic susceptibility as per their effective magneton number. $\text{Ce}_2\text{Zr}_2\text{O}_7$ obey Curie-Weiss law behaviour at higher temperature. They have negative value of paramagnetic Curie temperature indicating antiferromagnetic ordering at lower temperature.

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