STRUCTURAL AND DIELECTRIC STUDY OF HEAVY RARE-EARTH ZIRCONATE

PRIYANKA RANI[a], S.V. SINGH[b], U.P. SINGH[c1] AND S.K. YADAV[d]

[abcd]**Department of Physics, Tilak Dhari Post Graduate College Jaunpur, U.P. India**

ABSTRACT

The synthesis, characterization and dielectric properties of $R_2Zr_2O_7$, where R = Ho and Er have been studied. All the 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 dielectric constant (ε'), dielectric loss (ε'') and quality factor (Q) of the compounds have been measured at 1kHz in the temperature range 300 to 1125K. The dielectric constant of $Ho_2Zr_2O_7$ and $Er_2Zr_2O_7$ show rapid increase above 670K and 710K respectively. The dielectric loss shows similar behaviour as dielectric constant.

KEYWORDS: dielectric constant; dielectric loss; XRD; DTA; TGA; DTG; $Ho_2Zr_2O_7$; $Er_2Zr_2O_7$

Rare-earth zirconate ($R_2Zr_2O_7$, R = rare earth) have attracted a lot of attention due to their interesting physical properties and their potential for technological application (Zhang, A.Y. *et al*., 2006; Li, J.Y. *et al*., 2006; Subramanian, M.A. *et al*., 1983; Weller, M.T., *et al*., 2004 and Wilde, P.J. & Catlow, C.R., 1998). The electrical properties of these materials make them promising candidates for fuel-cell applications where high ionic conductivity and low activation energy are desired (Moreno, K.J. *et al*., 2006 and Moreno, K.J. *et al*., 2006). Also, due to their low thermal conductivity and high thermal expansion coefficient (Vassen, R., *et al*., 2000) they were widely applied in gas turbines and diesel engines (Saruhan, B., *et al*., 2004). Dielectric studies are informative in the study of ferroelectricity and phase transition (Gady, W.G., 1964). However to the best of our knowledge, there have been no reports in the literature on the dielectric studies. In this paper, we present the preparation, characterization, dielectric constant, dielectric loss and quality factor study of $Ho_2Zr_2O_7$ and $Er_2Zr_2O_7$.

EXPERIMENTAL DETAILS

Sample preparation

Polycrystalline samples of $R_2Zr_2O_7$ compounds were synthesized by the solid state reaction technique using high purity Ho_2O_3, Er_2O_3 and ZrO_2 ($\approx$ 99.99% purity, procured from Alfa Aesar, a Johnson Mathey chemical India Pvt. Ltd.). The stoichiometric mixture of these oxides were thoroughly mixed in an agate mortar for 3h in wet medium and then dried and calcined in an alumina crucible at 1300K for 50h in air atmosphere followed by one intermediate grinding. The final product was cool down slowly and checked by X-ray diffraction technique at room temperature.

XRD, DTA, TGA and DTG measurement

The X-ray diffraction of the compounds was studied using X-ray diffractometer (Thermoelectron-ARL EXTRA) at room temperature by using CuKα radiation with λ=0.15418nm in a wide range of Bragg's angle ($10° \leq 2\theta \leq 80°$).

DTA, TGA and DTG studies of the compounds 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.

Dielectric measurement

For dielectric studies the compounds were pressed at pressure of 7.16×10^{-8} Nm^{-2} to form pellets of circular cross section (Area ~ 0.90×10^{-4} m^2 and thickness ~ 0.30×10^{-2} m). The pellets were then sintered in air for 30 h at 1500K. The pellet covered with film of silver paint on the opposite surfaces to obtain a good contact was inserted between the two silver electrodes. A LCR-Q meter (Model 928, Systronics India) was used to measure the capacitance (C) and quality factor (Q) of the sample at different temperature and at a frequency of 1kHz. The dielectric constant (ε') and dielectric loss (ε'') of the sample was calculated by using the following relations (Cusack, M., 1967 & Suchet, J.P., 1975).

[1]**Corresponding Author**

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \tag{1}$$

$$\varepsilon'' = \frac{\varepsilon'}{Q} \tag{2}$$

Where C = the capacitance of the capacitor in Farad, d = the thickness, A = face area of the pellet, ε_0 = the permittivity of free space and Q = quality factor respectively.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of $Ho_2Zr_2O_7$ and $Er_2Zr_2O_7$ are shown in Figs. (1,2). From XRD pattern, d_{hkl} planes have been evaluated using relation (Kittel, C., 1996).

$$d_{hkl} = \frac{0.15418}{2 Sin\theta} \tag{3}$$
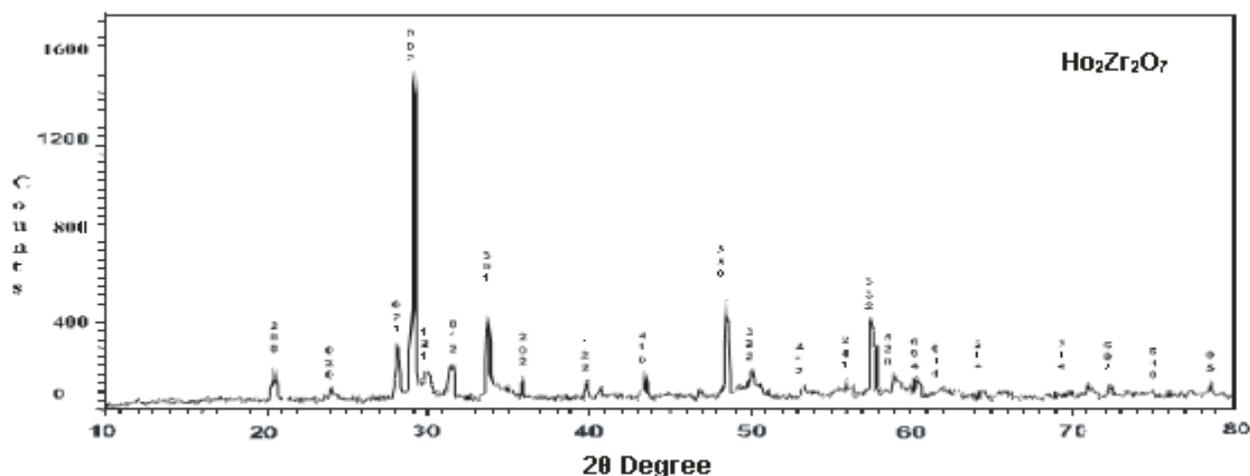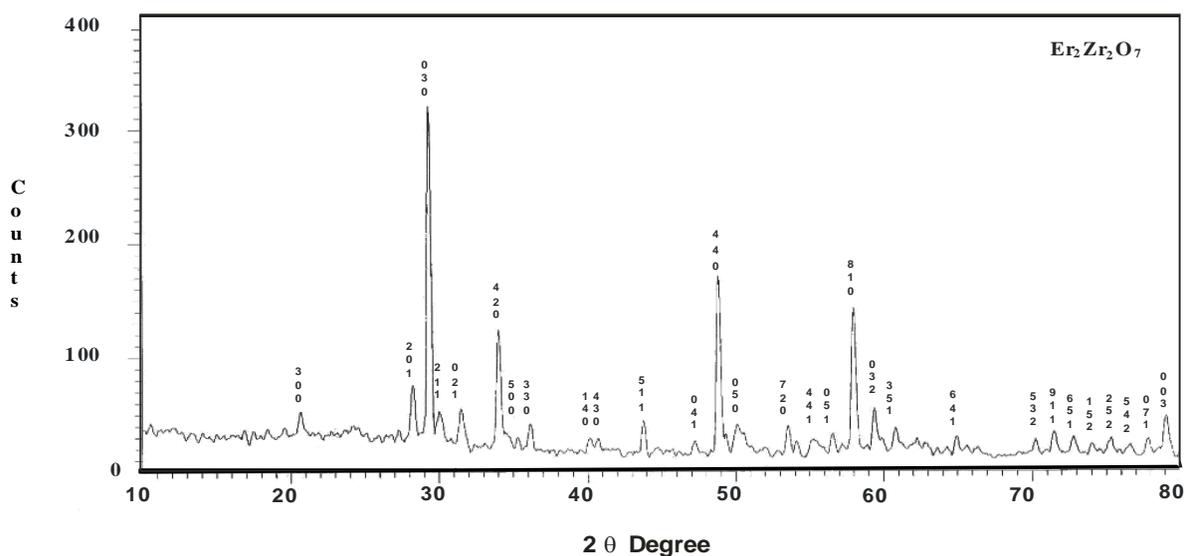
Figure 1: Room Temperature XRD pattern of $Ho_2Zr_2O_7$.

Figure 2: Room Temperature XRD pattern of $Er_2Zr_2O_7$.

From these d_{hkl} planes, structure of the studied compounds was resolved using usual procedure. All the peaks have been assigned with proper hkl planes. This confirms that prepared compounds has single phase and no unreacted

part of the starting material was left. The unit cell parameters are given in Table1.

Table 1-:Structural parameters of orthorhombic unit cell, calculated density (d_0), density of pressed pellets (d_p) and values of pore fraction (f_p)							
Compound	Unit Cell	Lattice Parameters			Pellet Density		Pore - fraction
		a_0 (nm)	b_0 (nm)	c_0 (nm)	d_0 kgm$^{-3}\times10^{-3}$	d_p kgm$^{-3}\times10^{-3}$	f_p
$Ho_2Zr_2O_7$ $Er_2Zr_2O_7$	OrthorhombicO rthorhombic	0.8676 1.2903	0.7394 0.9123	0.6132 0.3633	5.14 4.76	5.08 4.68	0.012 0.017

The DTA, TGA and DTG trace of $Ho_2Zr_2O_7$ and $Er_2Zr_2O_7$ are shown in Figs.(3,4). The DTA trace of $Ho_2Zr_2O_7$ and its corresponding TGA trace show weight loss of 0.02% from 323K to 548K may be due to removal of absorbed water and other gaseous species. The DTG trace shows maximum rate of mass change at 528K. Above 548K the compound is stable.
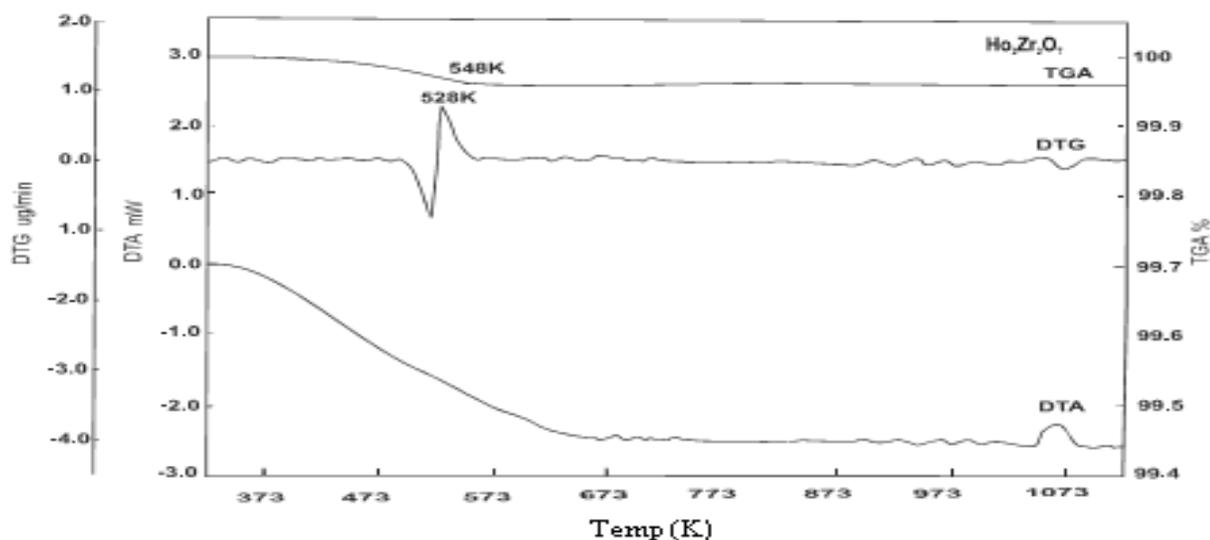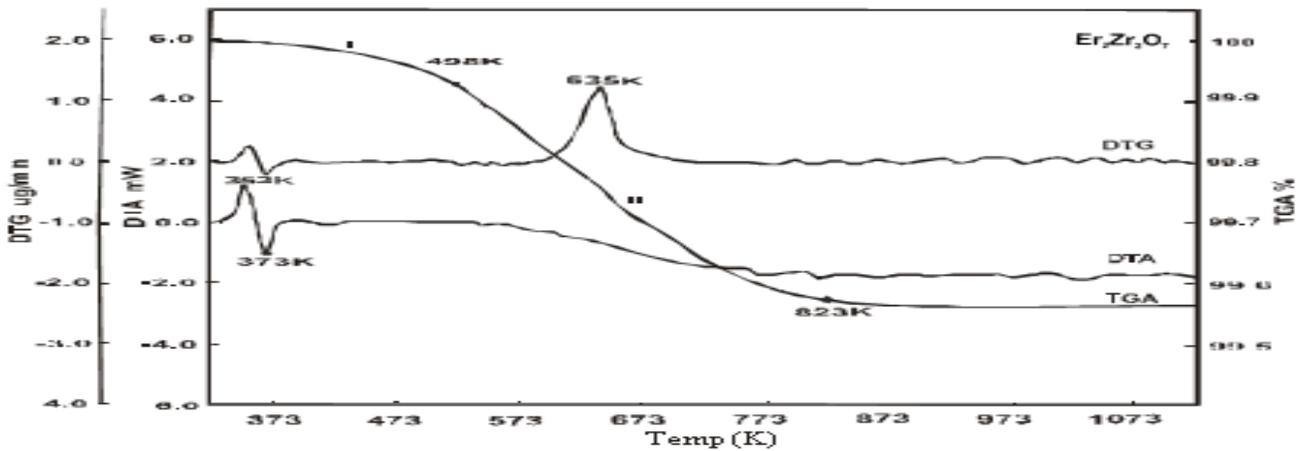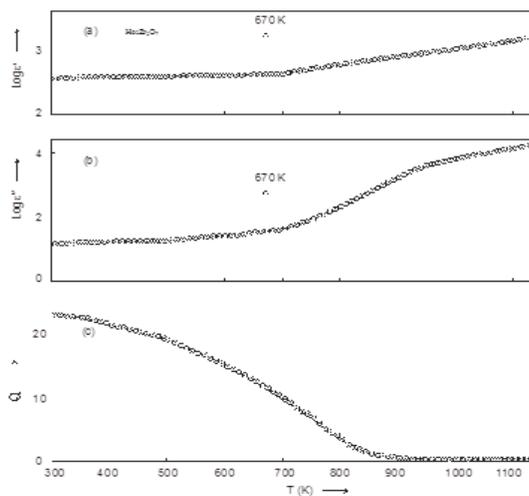
Figure 3: DTA, TGA and DTG trace of $Ho_2Zr_2O_7$.

Figure 4: DTA, TGA and DTG trace of Er$_2$Zr$_2$O$_7$.

The DTA trace of Er$_2$Zr$_2$O$_7$ show exothermic and endothermic peaks at 353K and 373K respectively. The corresponding TGA trace shows weight loss in two successive steps. The first step of weight loss 0.05% is from 323K to 498K may be due to presence of moisture and other gaseous species. The second step of weight loss 0.37% is from 498K to 823K due to thermal dehydration of the compound and above 823K the compound is stable. The DTG trace shows maximum rate of mass change at 635K.

The variation of dielectric constant (ε'), dielectric loss (ε'') and quality factor (Q) with temperature at 1kHz is shown in Figs. (5,6). It is seen that these compounds have dielectric constant 380 and 550 for Ho$_2$Zr$_2$O$_7$ and Er$_2$Zr$_2$O$_7$ respectively at 400K. Since dielectric constant (ε') seems to have almost temperature independent, so these values may be taken as the room temperature values of the material. The value of ε' has been calculated using the capacitance of the pressed pellets. The density of these pellets remains less than the theoretical density of these materials. This means pellets contain air pores. Therefore a correction for pore fraction (f_p) is essential to obtain the bulk value of the dielectric constant (ε'_b) and is given by (Thakur, A.N., 1996)

Figure 6: Plots of dielectric constant (ε'), dielectric loss (ε'') and quality factor (Q) against absolute temperature (T) for Er$_2$Zr$_2$O$_7$.

Figure 5: Plots of dielectric constant (ε'), dielectric loss (ε'') and quality factor (Q) against absolute temperature (T) for Ho$_2$Zr$_2$O$_7$
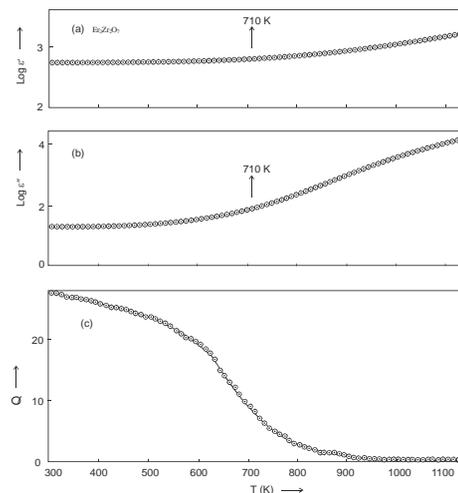
$$f_p = \frac{d_0 - d_p}{d_0} \qquad (4)$$

For low conducting solid ε'_b, ε' and f_p are related by the relation (Srivastava, V.P., 1998).

$$\varepsilon'_b = \frac{(\varepsilon'^{1/3} - f_p)^3}{1 - f_p} \qquad (5)$$

The evaluated values of ε'_b are given in Table 2.

Table 2: The bulk value of dielectric constant (ε'_b) of the studied zirconates

Compound	ε'_b at 400K
$Ho_2Zr_2O_7$	383
$Er_2Zr_2O_7$	556

The values of ε' of all these compounds become large as temperature is increased and validity of eq^n (5) becomes doubtful. Further this formula affects only the magnitude but not the nature of temperature variation of ε'. Therefore we have not used this correction at higher temperatures. The values of dielectric constant (ε') and dielectric loss (ε'') of all the studied compounds at temperature 400K, 600K, 800K and 1000K at frequency 1kHz are given in Tables 3 and 4 respectively.

The dielectric constant has very slow increase at lower temperature. This shows that there is no chance for the existence of thermally generated charge carriers at lower side of temperature. Well made electrode rules out the chance of interfacial polarization. Therefore this slow increase seems to be the combined effect of lattice and electronic polarizability 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 lattice expansion with temperature. However, it must be noticed that the increase of ε' with T is very slow in comparison to the variation one expects for ionic solids. This indicates that either thermal expansion of these materials is very small or they have some other kind of polarization mechanism.

The dielectric constants (ε') of these materials have much faster increase above certain critical temperature (T_K). The dielectric loss (ε'') shows similar behavior above critical temperature (T_K). The critical temperature (T_K) observed in ε' and ε'' are given Table 5.

The faster increase in dielectric constant above T_K is due to space charge polarization (Nanda, M. L., *et al*., 1999 & Singh, N.K., *et al*., 2000). 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.

Table 3-:Dielectric constant (ε') for studied zirconates at different temperature

Compound	Dielectric constant			
	400 K	600 K	800 K	1000 K
$Ho_2Zr_2O_7$	3.80×10^2	4.02×10^2	5.75×10^2	1.00×10^4
$Er_2Zr_2O_7$	5.50×10^2	6.03×10^2	6.91×10^2	1.10×10^3

Table 4- Dielectric loss (ε'') for studied zirconates at different temperature				
Compound	Dielectric loss			
	400 K	600 K	800 K	1000 K
$Ho_2Zr_2O_7$	18	25	2.09×10^2	6.31×10^3
$Er_2Zr_2O_7$	21	30	2.51×10^2	3.98×10^3

Table 5- Critical temperature (T_K) obtained from ε' and ε'' of the studied zirconates.	
Compound	Critical temperature(T_K)
$Ho_2Zr_2O_7$	670
$Er_2Zr_2O_7$	710

CONCLUSIONS

XRD studies confirm that the studied compounds have single phase orthorhombic structure at room temperature. DTA, TGA and DTG studies show that the compounds are stable above certain temperature. The dielectric constant (ε') and dielectric loss (ε'') have very slow increase upto T_K. Above T_K, this increase becomes much faster. The value of T_K is different for different compounds. The reason for faster increase of ε' and ε'' above T_K is due to space charge polarization.

ACKNOWLEDGEMENTS

REFERENCES

Cusack M., 1967. The electrical and magnetic properties of solids (London: Longmans).

Gady W G., 1964. Piezoelectricity (Newyork: Dover).

Kittel C., 1996. Introduction to solid state physics 7th edition (Newyork: Wiley).

Li J Y, Dai H, Li Q, et al., 2006. Mater Sci Eng, B **133** : 209.

Moreno K J, Guevara-Liceaga M A, Fuentes A F, et al., 2006. J Solid State Chem, **179** : 928.

Moreno K J, Fuentesa A F, Garcia-Barriocanal J, et al, 2006. J Solid State Chem, **179** : 323.

Nanda M L Goswami, Choudhary R N P and Mahapatra P K, 1999. Ind J Phys, **73A(4)** 445.

Saruhan B, Francois P, Fristscher K, et al, 2004. Surf Coat Technol, **182** : 175.

Singh N K, Sharma Seema and Choudhary R N P, 2000. Ind J Phys, **74A(1)** : 63.

Srivastava V P, PhD thesis, 1998. Gorakhpur University, India.

Subramanian M A, Aravamudan G and SubbaRao G V., 1983. A review Prog Solid State Chem, **15** : 55.

Suchet J P., 1975. Electrical conduction in solids materials (London: Pergamon).

Thakur A N, Gaur K and Lal H B., 1996. Ind J Phys **70A(2)** : 225.

Vassen R, Cao X Q, Tietz F, et al., 2000. J Ame Ceram Soc, **8** : 2023.

Weller M T, Hughes R W, Rouke J, et al., 2004. Dalton Trans, 3032.

Wilde P J and Catlow C R A., 1998. Solid State Ionics, **112** : 173.

Zhang A Y, Lü M K, Zhou G J et al.., 2006.   J Phys ChemSolids,**67**:243