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Preparation, Characterization and Magnetic Properties of some Rare-earth Zirconate

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Abstract

The Polycrystalline sample of $HoZrO_3$ & $ErZrO_3$ ceramics were synthesized by high temperature solid state reaction technique and characterised by XRD, differential thermal analysis (DTA), thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG). The structural characterisation by X-ray powder diffraction shows the orthorhombic structure of the sample at room temperature. The measurement of molar magnetic susceptibility of the powder sample has been reported in the temperature range 300-1100K at field 1.55×10^{-1} Tesla. In these samples magnetism arises from the rare-earth ions Ho^{3+} & Er^{3+}, while Zr is non magnetic. These samples show antiferromagnetic behaviour at low temperature and obey Curie-Weiss law.

Keywords: Magnetic susceptibility, XRD, DTA, TGA, DTG, $HoZrO_3$, $ErZrO_3$.

INTRODUCTION

Mixed rare-earth and transition metal oxides has been the subject of the study due to their interesting magnetic, dielectric, electrical properties and their application [1-3]. However, very few studies have been performed on 4d transition metal oxides. This seems to be due to the peculiar magnetic properties of the 4d transition metal ions. In general, since 4d electrons have a large spatial extent, very strong spin-orbit coupling and a large ligant-field effect are expected [4]. When the energy splitting caused by spin-orbit coupling is equivalent to that of the multiplets, a higher energy term offen mixes into the lowest lying term. For this reason, 4d transition metal ions offen have extremely small magnetic susceptibilities that caused be explained by hunds rule, which explained the magnetism of Iron-group ions. This seems to make the study on oxides with 4d transition metal ions difficult. However, since 4d transition metal oxides are very interesting candidates for use as metallic conductors, catalysts and materials of photoelectrolytes cells and superconductors. It seems important to investigate their magnetic properties in details.

In the present contribution we reports XRD, DTA, TGA, DTG and magnetic susceptibilities of $HoZrO_3$ and $ErZrO_3$.The literature survey showed that only limited studies are reported on these

compounds. These studies are related with their preparation and characterization [5], structural, magnetic and electrical properties [6-7] and thermal conductivity [8].

MATERIALS AND METHODS

The Polycrystalline specimens of $HoZrO_3$ & $ErZrO_3$ were prepared by the usual solid state reaction method. High purity raw materials Ho_2O_3, Er_2O_3 and ZrO_2 (99.99%, M/S Alfa Aesar, a Johnson Mathey chemicals India Pvt. LTD.) were mixed in an agate mortor so as to compose stiochiometric $HoZrO_3$ & $ErZrO_3$. The mixture was calcined in alumina crucible for 50h over one intermediate grinding. The process of mixing and caclination was repeated until homogeneous fine powder of samples was obtained. The prepared compounds undergo the following solid state reaction.

$$Ho_2O_3 + 2ZrO_2 \xrightarrow{1400K} 2HoZrO_3 + O$$
$$Er_2O_3 + 2ZrO_2 \xrightarrow{1400K} 2ErZrO_3 + O$$

The weight loss corresponding to oxygen on the right hand side of the reactions was observed in each case. The formation and quality of compound were checked by X-ray diffractogram technique. The X-ray diffraction pattern of calcined powder was recorded at room temperature using X-ray powder diffractometer (Thermoelectron- XRL EXTRA) with CuKα radiation (λ=0.15418nm) in a wide range of Bragg angle ($10^\circ \leq 2\theta \leq 90^\circ$).

The DTA, TGA and DTG studies of the compounds were carried out in nitrogen gas using a thermal analyser (PERKIN ELEMER PYRIS) at a heating rate of 10°/min and flow rate of 100ml/min from 50°C to 850°C.

The Magnetic measurements of powder sample were done at temperature between 300K to 1100K using Faraday´s method [9-10]. Gadolinium tungustate has been used for standardisation.

RESULT AND DISCUSSION

The X-ray powder diffraction profiles for specimens of $HoZrO_3$ & $ErZrO_3$ are shown in Figs (1-2). The sharp and single diffraction peak indicating better homogeneity and crystallization of the samples. The d_{hkl} values has been calculated by Bragg's equation.

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

From these values of d_{hkl}, structure of the studied compounds was resolved using usual procedure. All the peaks have been assigned and indexed with proper *hkl* values. Finally, orthorhombic unit cell was selected for which $\sum\Delta d = \sum(d_{obs} - d_{cal})$ was found to be minimum.

The good agreement between observed and calculated d-values support for correctness of selected crystal system and unit cell parameters. The unit cell parameters of the compounds are given in Table 1.

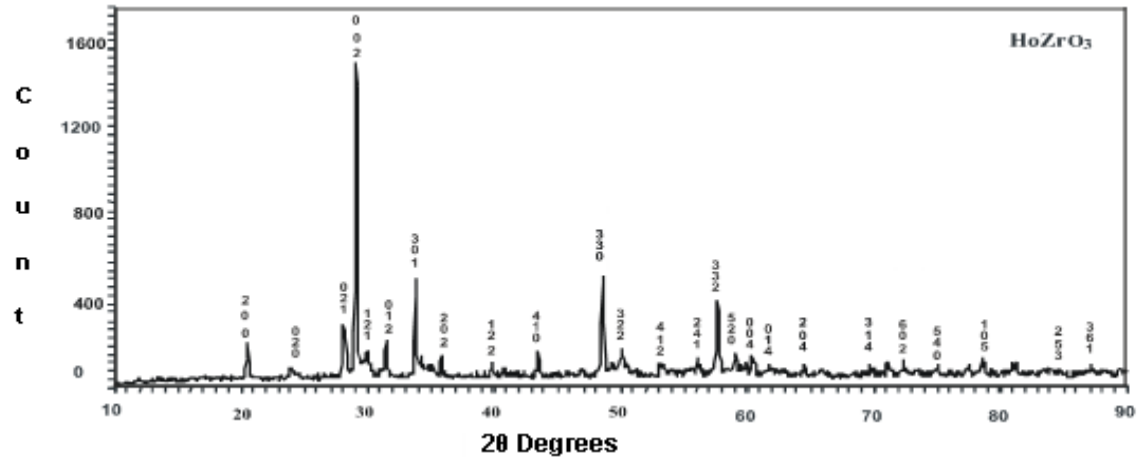

FIG.1 Room Temperature XRD of $HoZrO_3$

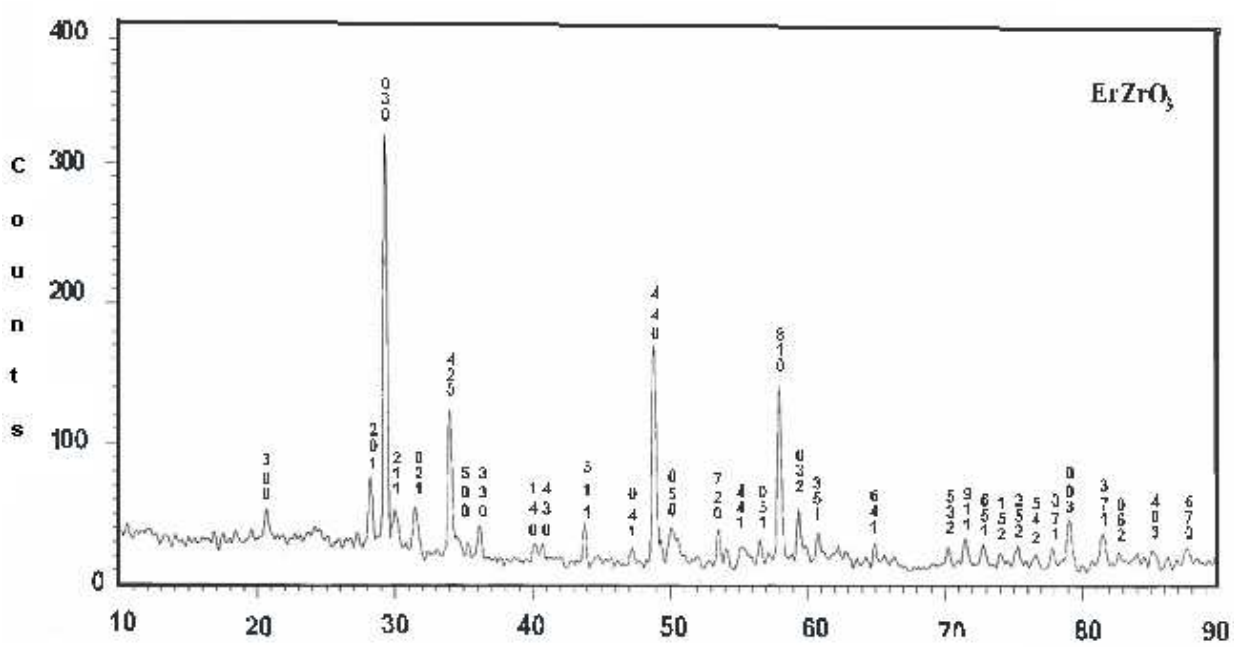

FIG.2 Room Temperature XRD of $ErZrO_3$

Table 1- Structural parameters of orthorhombic unit cell

Compounds	Unit Cell	a_0 (nm)	Lattice Parameters b_0 (nm)	c_0 (nm)
$HoZrO_3$	Orthorhombic	0.8676	0.7394	0.6132
$ErZrO_3$	Orthorhombic	1.2903	0.9123	0.3633

The DTA, TGA and DTG trace of $HoZrO_3$ and $ErZrO_3$ are shown in Figs.(3-4). The DTA trace of $HoZrO_3$ and its corresponding TGA trace show weight loss of 0.02% from 50°C to 275°C may be due primarily to the expulsion of absorbed water and other gaseous species. The DTG trace show maximum rate of mass change at 255°C. Above 275°C the compound is stable.

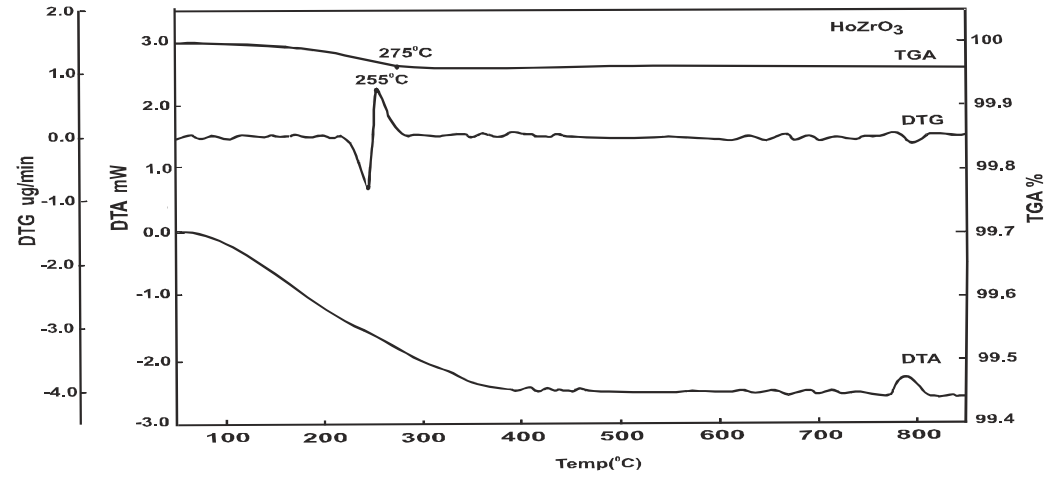

FIG. 3 DTA, TGA and DTG Curve of $HoZrO_3$

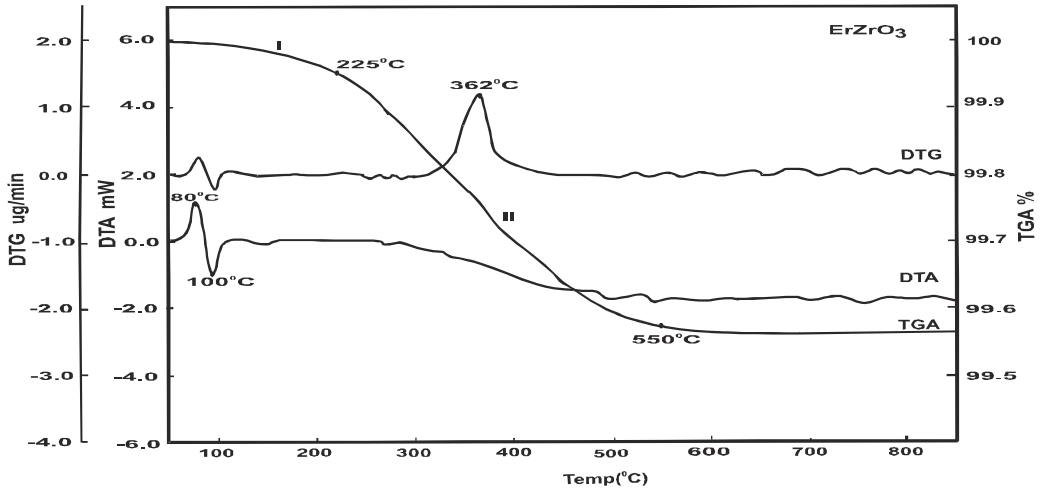

FIG. 4 DTA, TGA and DTG Curve of $ErZrO_3$

The DTA trace of $ErZrO_3$ show exothermic and endothermic peak at 80°C and 100°C respectively. The corresponding TGA trace show weight loss in two successive steps. The first step of weight loss 0.05% is from 50°C to 225°C may be due to presence of moisture and other gaseous species. The second step of weight loss 0.37% is from 225°C to 550°C due to thermal dehydration of the compound and above 550°C the compound is stable. The DTG trace show maximum rate of mass change at 362°C.

The molar magnetic susceptibility (χ_M) of the compound was measured in both heating and cooling cycle. No hysteresis was observed and χ_M values were found to be same in heating and cooling cycles. However, a small weight loss was noticed in heating cycle probably due to presence of moisture. The temperature dependence of reciprocal magnetic susceptibility χ_M^{-1} for specimens of $HoZrO_3$ & $ErZrO_3$ in an applied field 1.55×10^{-1} Tesla are shown in Figs.(5-6). It is seen from these figures that nature of all these plots are essentially similar. In general, χ_M^{-1} *vs T* plots are linear at higher temperature was fitted by the Curie weiss law and expressed by the relation

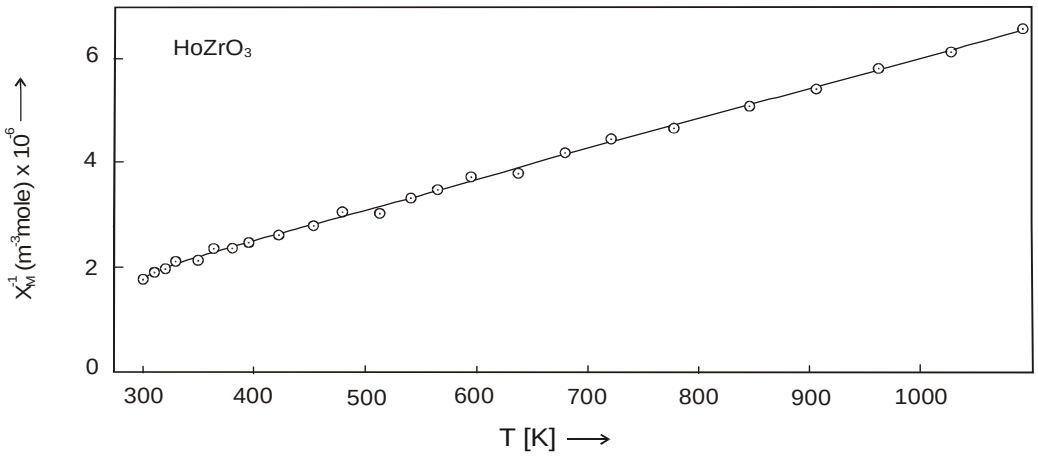

FIG.5 Variation of inverse of molar magnetic susceptibility (χ_M^{-1}) with absolute temperature of $HoZrO_3$

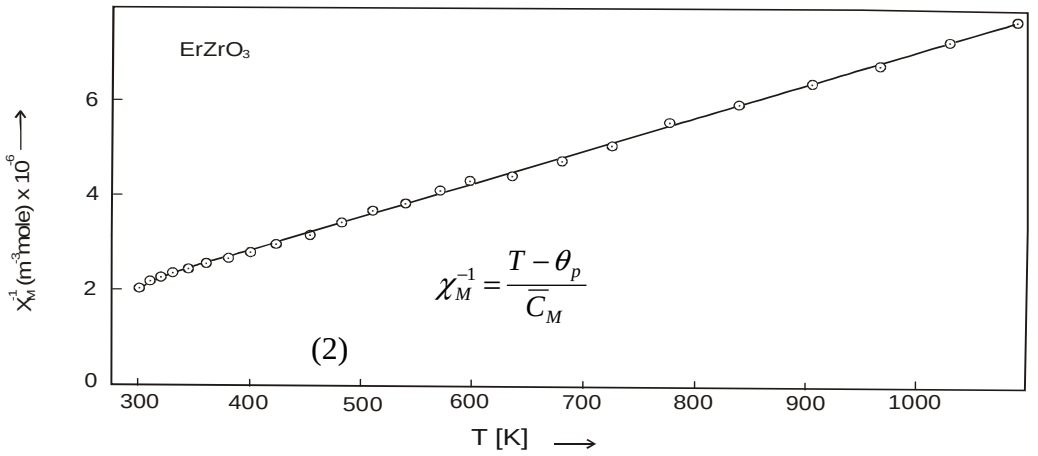

FIG.6 Variation of inverse of molar magnetic susceptibility (χ_M^{-1}) with absolute temperature of $ErZrO_3$

Where θ_p is paramagnetic Curie temperature and $\overline{C}_M$ is the molar curie constant

These two compounds $HoZrO_3$ & $ErZrO_3$ are magnetically simple because magnetism arises from the trivalent rare earth ions Ho^{3+} & Er^{3+} i.e. the magnetic interaction exists in these compounds due to rare earth ion. Thus at higher temperature the molar magnetic susceptibility of all these compounds can be approximated by the relation

$$\chi_M = \frac{N\mu_0\mu_B^2}{3k}\left[\frac{\overline{p}^2}{T-\theta_p}\right] \qquad (3)$$

Where N *i*s Avagadro number, μ_B is Bohr magneton, μ_0 is permeability constant, k is Boltzmann constant, $\overline{p}$ magneton numbers of magnetic ions and θ_p is the paramagnetic curie temperature.

We can write above equation as

$$\chi_M^{-1} = \frac{3k(T-\theta_p)}{N\mu_0\mu_B^2\overline{p}^2} \qquad (4)$$

Comparing eq^{n} (2) & (4) we have

$$\overline{C}_M = \frac{N\mu_0\mu_B^2\overline{p}^2}{3k}$$

This yields

$$\overline{p} = \left[\frac{3k\overline{C}_M}{N\mu_0\mu_B^2}\right]^{1/2} \quad (5)$$

The effective magneton number, which was deduced from $\overline{C}_M$ obtained from χ_M^{-1} *vs* T plot. The theoretical and experimental value of $\overline{p}$ with magnetic ions are listed in Table 2 and the values of θ_p and $\overline{C}_M$ are given in Table 3.

Table 2. Magnetic ion with theoretical and experimental value of Average magneton number ($\overline{p}$) of the studied compounds

Compounds	Magnetic ion	Theoretical value	Experimental value
$HoZrO_3$	Ho^{3+}	10.61	10.46
$ErZrO_3$	Er^{3+}	9.58	9.68

Table 3. Paramagnetic Curie temperature (θ_p) and molar Curie constant ($\overline{C}_M$) of the studied compounds

Compounds	θ_p (K)	$\overline{C}_M \times 10^5$ (m^3 K $mole^{-1}$)
$HoZrO_3$	-25	17.11
$ErZrO_3$	-10	14.11

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

The values of θ_p of all the specimens are negative, suggesting a possible antiferromagnetic 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

The $HoZrO_3$ & $ErZrO_3$ was prepared by solid state reactions and its crystallographic and magnetic properties were investigated. The XRD studies suggest that compounds has orthorhombic type structure at room temperature. The DTA, TGA and DTG studies show that the compounds are stable above certain temperature. The high temperature magnetic measurement shows that the magnetic ions contribute towards magnetic susceptibility as per their effective magneton number. All the studied compounds obey Curie Weiss law behaviour at higher temperature. They have negative value of paramagnetic Curie temperature indicating antiferromagnetic ordering at lower temperature.

Acknowledgements
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