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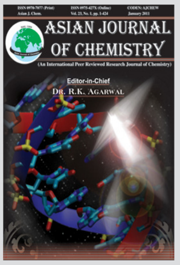

Magnetic Properties of $Ln_2Zr_2O_7$ (Ln = Ho and Er) Compound

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The heavy rare earth zirconate compound $Ln_2Zr_2O_7$ (where Ln = Ho, Er) were prepared by solid state reaction method. The prepared compounds have been characterized by XRD, DT, TG and DTG. XRD studies suggest the formation of single phase orthorhombic structure at room temperature. We describe magnetic susceptibility measurements of the compounds at high temperature. In these compounds magnetism arises from the rare-earth ions, while Zr is non magnetic. All the compounds show antiferromagnetic behaviour at low temperature and obey Curie-Weiss law.

Key Words: Magnetic susceptibility, XRD, Thermal properties, $Ho_2Zr_2O_7$, $Er_2Zr_2O_7$.

INTRODUCTION

The compounds with general formula $A_2B_2O_7$, where A is trivalent rare earth and B is tetravalent transition element, have attracted a lot of attention in recent years[1-3]. However, very few studies have been performed on 4*d* transition metal oxides. This seems to be due to the peculiar magnetic properties of the 4*d* transition metal ions. In general, since 4*d* electrons have a large spatial extent, very strong spin-orbit coupling and a large ligand-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, 4*d* 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 4*d* transition metal ions difficult. However, since 4*d* transition metal oxides are very interesting candidates for use as metallic conductors, catalysts and materials of photoelectrolytic cells and superconductors. It seems important to investigate their magnetic properties in details.

Several such compounds have been investigated in the past[5-11]. In this paper, we present the preparation, characterization and magnetic susceptibilities of $Ho_2Zr_2O_7$ and $Er_2Zr_2O_7$.

EXPERIMENTAL

The starting material for the preparation of $Ln_2Zr_2O_7$ (where Ln = Ho and Er) compounds were Ho_2O_3 (≈ 99.9 % purity, Alfa Aesar), Er_2O_3 (≈ 99.99 % purity, Alfa Aesar) and ZrO_2 (≈ 99.7 % purity, Alfa Aesar). The stoichiometric amount of these oxides were mixed and heated in an alumina crucible for 50 h at a temperature of 1300 K followed by one intermediate grinding and final product was cool down slowly. The cooled material was powdered and the formation of the prepared material was checked by X-ray diffraction technique at room temperature.

The X-ray diffraction of the compounds was studied using X-ray diffractometer (Thermoelectron-ARL EXTRA) at room temperature by using CuK_α radiation with $\lambda = 0.15418$ nm in a wide range of Bragg angle ($10° \leq 2\theta \leq 80°$). The DT, TG and DTG studies of the compounds were carried out in nitrogen gas using a thermal analyzer (Perkin-Elmer Pyris) at a heating rate of 283 K/min and flow rate of 100 mL/min from 323 to 1123 K. Magnetic susceptibility measurements were done on powdered samples using Faraday's method[12,13]. $Gd_2(WO_4)_3$ has been used for standardization.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of the compound was taken at room temperature using CuK_α line ($\lambda = 0.15418$ nm) as shown in Figs. 1 and 2. From XRD pattern, d_{hkl} values have been evaluated using relation[14].

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

From these values of d_{hkl}, structures of the studied compounds were 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 Table-1.

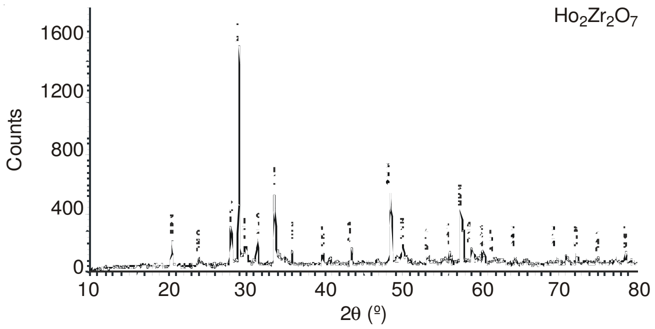

Fig. 1. Room temperature XRD pattern of $Ho_2Zr_2O_7$

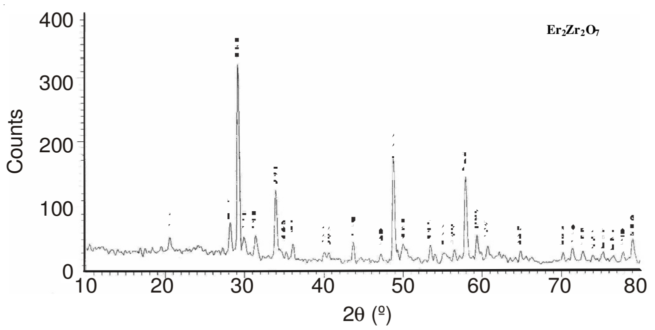

Fig. 2. Room temperature XRD pattern of $Er_2Zr_2O_7$

TABLE-1
STRUCTURAL PARAMETERS OF $Ln_2Zr_2O_7$
HAVING ORTHORHOMBIC UNIT CELL

Compound	Lattice parameters		
	a_0 (nm)	b_0 (nm)	c_0 (nm)
$Ho_2Zr_2O_7$	0.8676	0.7394	0.6132
$Er_2Zr_2O_7$	1.2903	0.9123	0.3633

The differential thermal (DT), thermogravimetric (TG) and derivative thermogravimetry (DTG) thermogram of $Ln_2Zr_2O_7$ compounds are shown in Figs. 3 and 4. The DT thermogram of $Er_2Zr_2O_7$ show exothermic and endothermic peaks at 353 and 373 K, respectively.

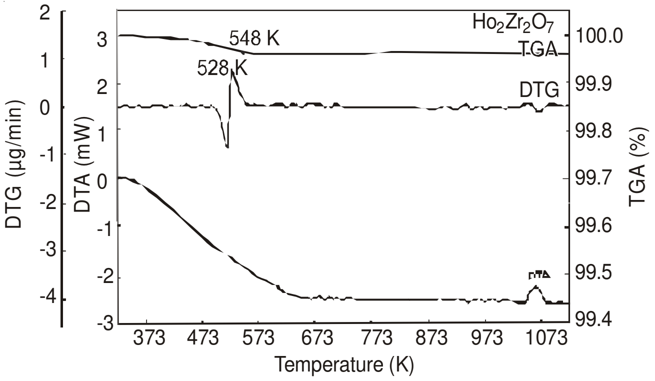

Fig. 3. DT, TG and DTG thermogram of $Ho_2Zr_2O_7$

In TG thermogram, the compound losses mass in successive steps. The mass loss and temperature region is shown in Table-2 for $Ho_2Zr_2O_7$ and $Er_2Zr_2O_7$.

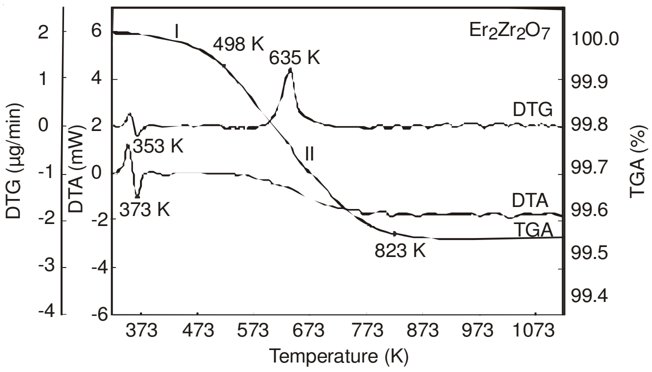

Fig. 4. DT, TG and DTG thermogram of $Er_2Zr_2O_7$

TABLE-2
MASS LOSS (%) CALCULATED FROM TG THERMOGRAM

Compound	Mass loss (%) in the			
	1st step		2nd step	
	Temp. region (K)	Mass loss (%)	Temp. region (K)	Mass loss (%)
$Ho_2Zr_2O_7$	323-548	0.02	–	–
$Er_2Zr_2O_7$	323-498	0.05	498-823	0.37

The first step of mass loss may be due to removal of absorbed water and other gaseous species and the second step of mass loss could be responsible for major thermal dehydration of the compound. DTG thermogram of $Ho_2Zr_2O_7$ and $Er_2Zr_2O_7$ show maximum rate of mass change at 528 and 635 K, respectively.

The magnetic susceptibility measurement of all the studied compound was done in heating and cooling cycle. 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 for all the compounds in heating cycle may be due to presence of moisture. The variation χ_M^{-1} *vs.* T of compounds in the temperature range 300-1100 K at field of 1.55×10^{-1} Tesla are shown in Figs. 5 and 6. It is seen from these plots that at higher temperature the χ_M^{-1} *vs.* T plots are linear and obey Curie-Weiss law and expressed by the relation[15].

$$\chi_M^{-1} = \frac{T - \theta_p}{\overline{C}_M} \qquad (2)$$

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

All the studied compounds are magnetically simple because magnetism arises from the trivalent rare earth ions *i.e.* the magnetic interaction exists in these compounds is Ln^{3+}- Ln^{3+}. Thus at temperature much higher than ordering temperature the molar magnetic susceptibility of all these compounds can be approximated by the relation[16].

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

where N is Avagadro number, μ_B is Bohr magneton, μ_0 is permeability constant, k is Boltzmann constant, $\overline{p}$ magneton numbers of magnetic ions Ln^{3+} and θ_p is the paramagnetic Curie temperature.

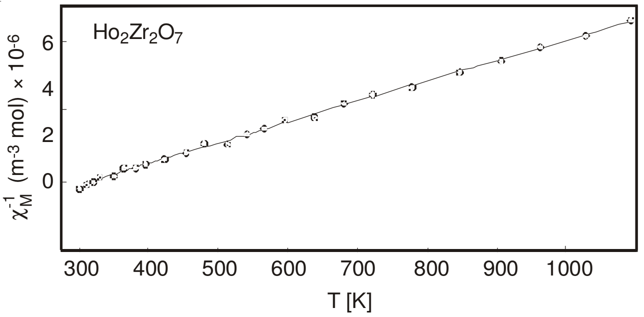

Fig. 5. Variation of inverse of molar magnetic susceptibility (χ_M^{-1}) with absolute temperature of $Ho_2Zr_2O_7$

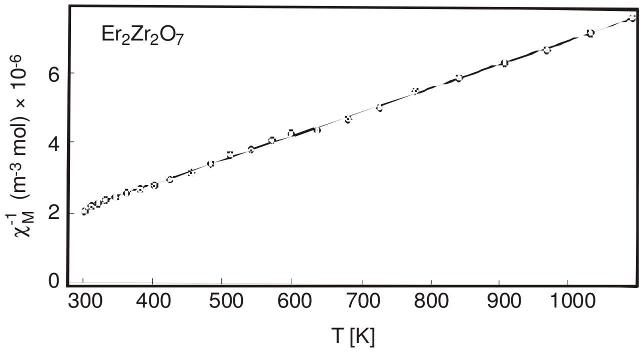

Fig. 6. Variation of inverse of molar magnetic susceptibility (χ_M^{-1}) with absolute temperature of $Er_2Zr_2O_7$

We can write above equation as:

$$\chi_M^{-1} = \frac{3k\left(T - \theta_p\right)}{N\mu_0\mu_\beta^2\bar{p}^2} \tag{4}$$

Comparing eqns. 2 and 4 we have

$$\bar{C}_M = \frac{N\mu_0\mu_\beta^2\bar{p}^2}{3k}$$

This yield

$$\bar{p} = \left[\frac{3k\bar{C}_M}{N\mu_0\mu_\beta^2}\right]^{1/2} \tag{5}$$

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-3 and the values of θ_p and $\bar{C}_M$ are given in Table-4.

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.

TABLE-3
MAGNETIC ION WITH THEORETICAL AND EXPERIMENTAL VALUE OF AVERAGE MAGNETON NUMBER ($\bar{p}$) OF THE $Ln_2Zr_2O_7$

Compounds	Magnetic ion	Theoretical value	Experimental value
$Ho_2Zr_2O_7$	Ho^{3+}	10.61	10.46
$Er_2Zr_2O_7$	Er^{3+}	9.58	9.50

TABLE-4
PARAMAGNETIC CURIE TEMPERATURE (θ_p) AND MOLAR CURIE CONSTANT ($\bar{C}_M$) OF $Ln_2Zr_2O_7$

Compounds	θ_p (K)	$\bar{C}_M \times 10^5$ (m^3 K mol^{-1})
$Ho_2Zr_2O_7$	-25	17.11
$Er_2Zr_2O_7$	-10	14.11

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

Conclusion

From XRD studies, it is confirmed that the studied compounds have single phase orthorhombic structure at room temperature. DT, TG and DTG studies show that the compounds are stable above certain temperature. The high temperature magnetic measurement shows 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.

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