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STRUCTURAL AND MAGNETIC PROPERTIES OF SOME RARE-EARTH ZIRCONATE

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ABSTRACT

The polycrystalline rare earth zirconate $R_2Zr_2O_7$, (where R = Gd, Tb and Dy) was synthesized by solid state reaction technique at 1300K. The synthesized compounds have been characterized by XRD, differential thermal analysis (DTA), thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG). The XRD characterization suggests the formation of single phase orthorhombic structure at room temperature. We describe magnetic susceptibility measurements of the compounds in the temperature range 300-1100K at field 1.55×10^{-1} Tesla. 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.

KEYWORDS : Magnetic susceptibility, XRD, DTA, TGA, DTG, $Gd_2Zr_2O_7$, $Tb_2Zr_2O_7$, $Dy_2Zr_2O_7$

The mixed rare-earth and transition metal oxides have received considerable attention in recent years (Standley K. J., 1972; Wohlforth E. P., 1980) due to their excellent properties, such as metal-insulator transitions, ferroelectric properties, fluorescent and phosphorescent properties (Wohlforth E. P., 1980). 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 ligand-field effect are expected (Van Vleck J.H., 1980). 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 photoelectrolytic cells and superconductors. It seems important to investigate their magnetic properties in details.

Several such materials have been investigated in the past (Bramwell S.T. et al., 2000; Durand A. M. et al., 2000; Qiang X. et al., 2005; Tong Y. P. et al., 2008; Tong Y. P. et al., 2008; Yamamura H., et al., 2003). The magnetic properties such as susceptibilities, coercivity and Curie temperature of the compounds help in understanding the nature of remanent magnetism and chemical composition. In this paper we presented the preparation, characterization and magnetic susceptibilities of $Gd_2Zr_2O_7$, $Tb_2Zr_2O_7$ and $Dy_2Zr_2O_7$.

EXPERIMENTAL DETAILS

Sample Preparation

The Polycrystalline compounds of $Gd_2Zr_2O_7$, $Tb_2Zr_2O_7$ and $Dy_2Zr_2O_7$ were prepared by the standard solid state reaction technique by heating them at temperature 1300K for 50h with one intermediate grinding. The starting materials Gd_2O_3, Tb_2O_3, Dy_2O_3 and ZrO_2 (99.99% pure) are procured from M/S Alfa Aesar, a Johnson Mathey chemicals India Pvt. Ltd. The stiochiometry mixture of these oxides were thoroughly mixed in an agate mortar for 3h in wet medium and then dried by slow evaporation. The air dried powders of the compounds are calcined in an alumina crucible followed by one intermediate grinding. The cooled material was powdered and the formation of the prepared material was 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 angle ($10^\circ \leq 2\theta \leq 80^\circ$).

The 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.

Magnetic measurement

Magnetic susceptibility measurements were done on

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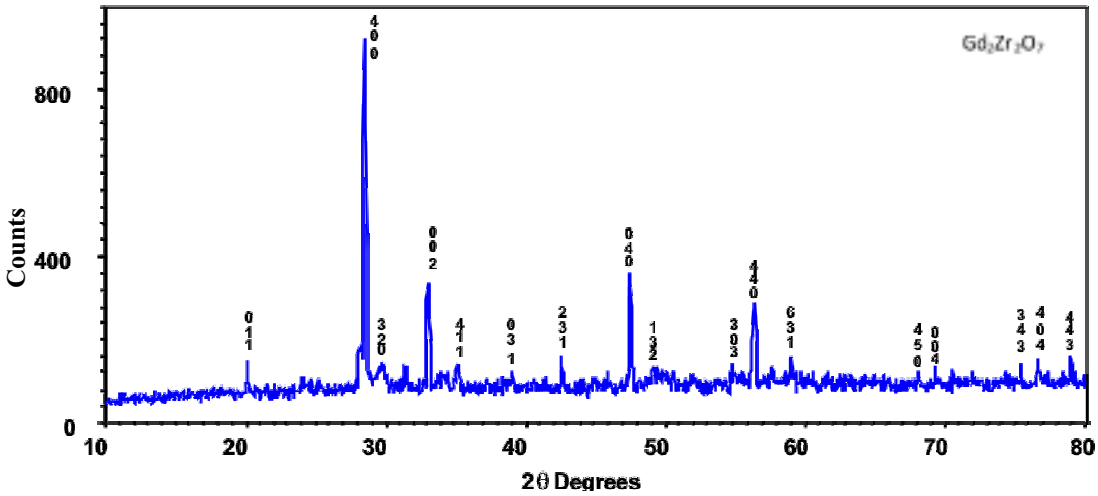

Figure 1 : Room Temperature XRD Pattern of $Gd_2Zr_2O_7$.

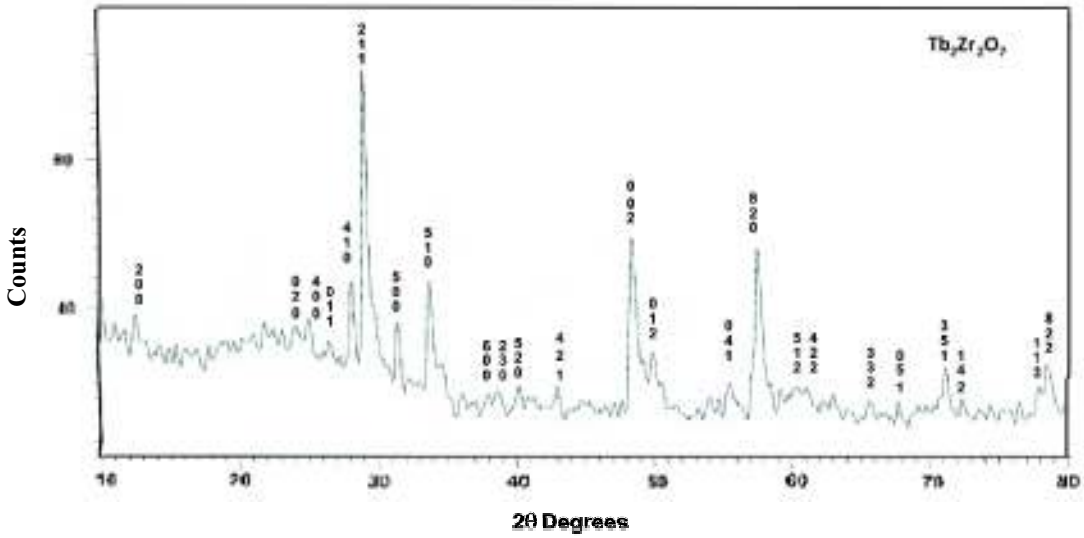

Figure 2 : Room Temperature XRD pattern of $Tb_2Zr_2O_7$.

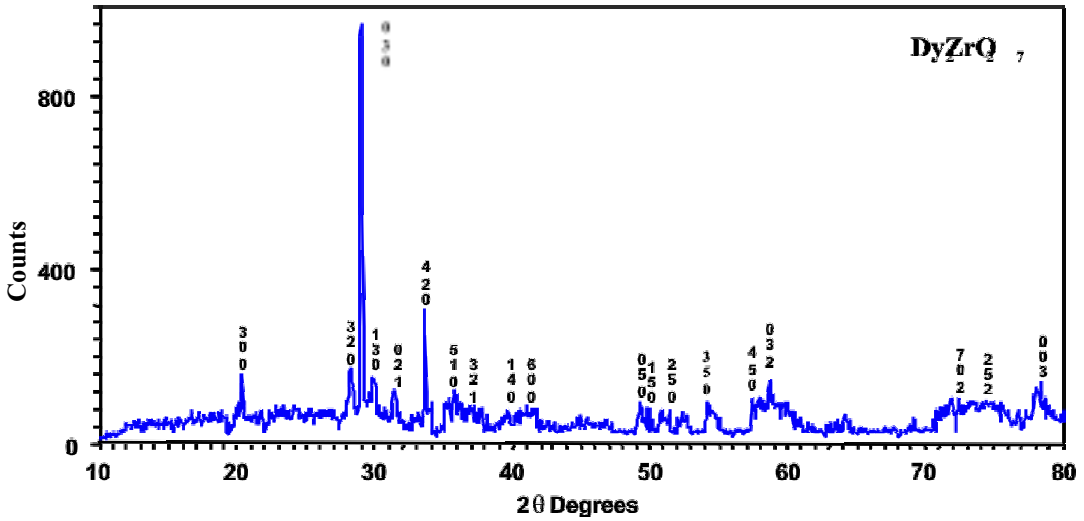

Figure 3 : Room Temperature XRD pattern of $Dy_2Zr_2O_7$.

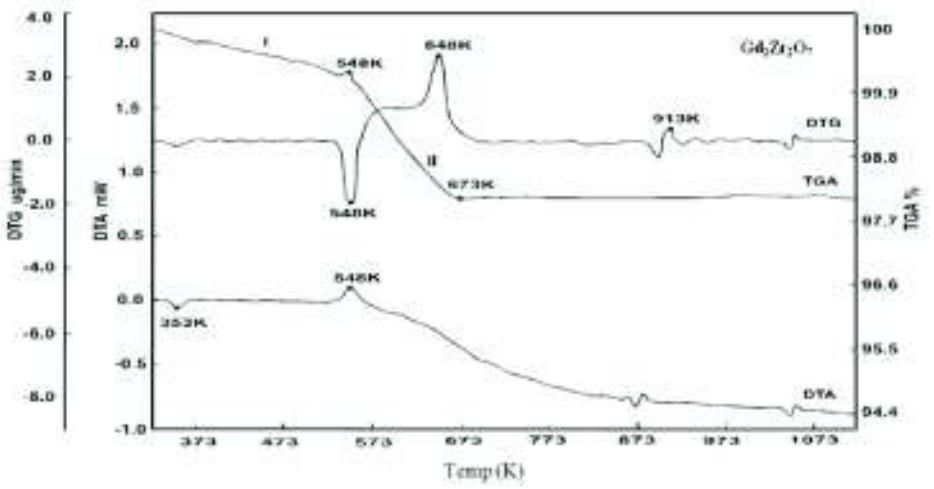

Figure 4 : DTA, TGA and DTG curves of $Gd_2Zr_2O_7$.

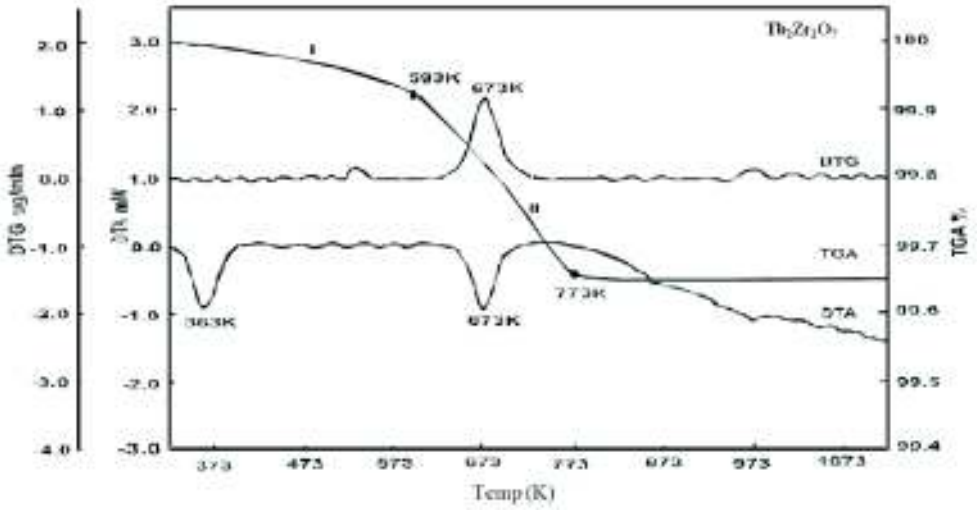

Figure 5 : DTA, TGA and DTG curves of $Tb_2Zr_2O_7$.

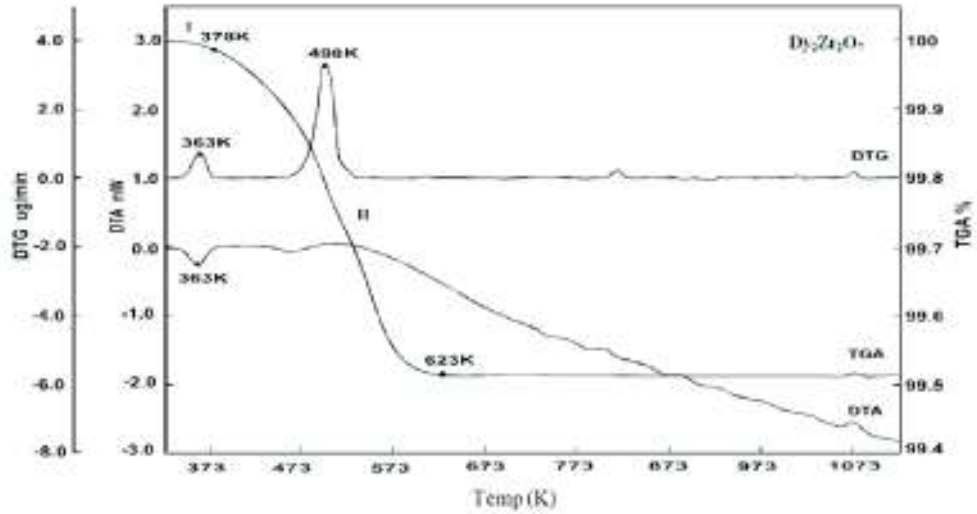

Figure 6 : DTA, TGA and DTG curves of $Dy_2Zr_2O_7$.

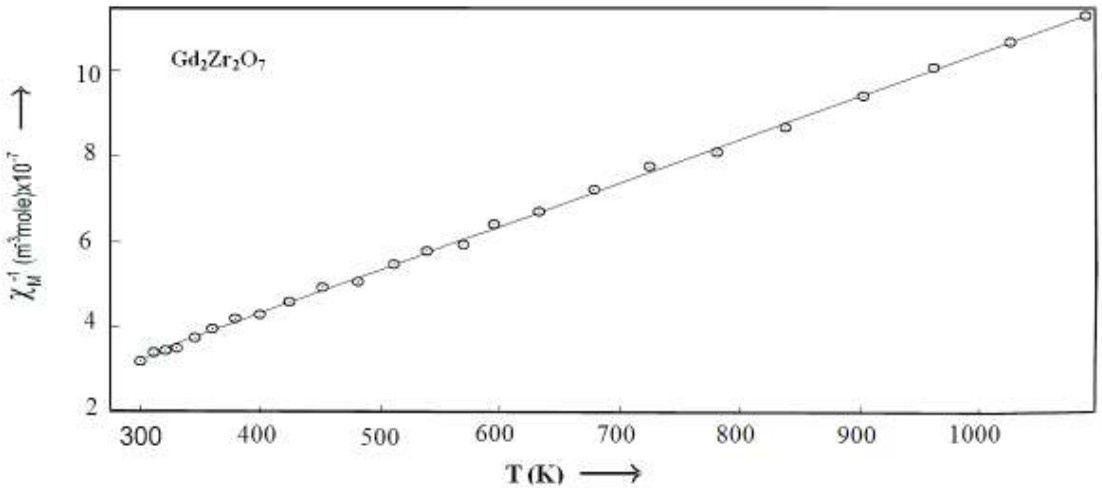

Figure 7 : Variation of Inverse of Molar Magnetic Susceptibility (χ_M^{-1}) With Absolute Temperature of $Gd_2Zr_2O_7$.

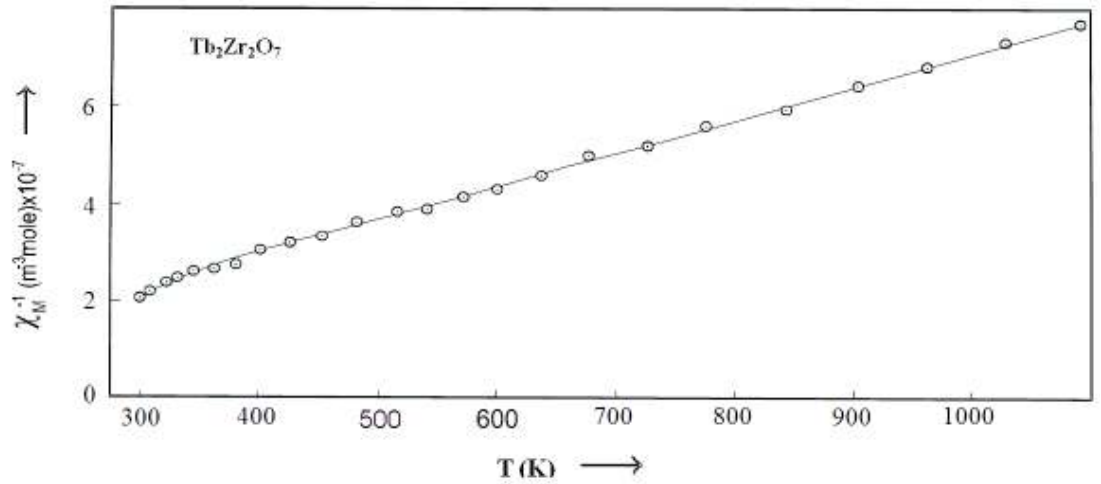

Figure 8 : Variation of Inverse of Molar Magnetic Susceptibility (χ_M^{-1}) With Absolute Temperature of $Tb_2Zr_2O_7$.

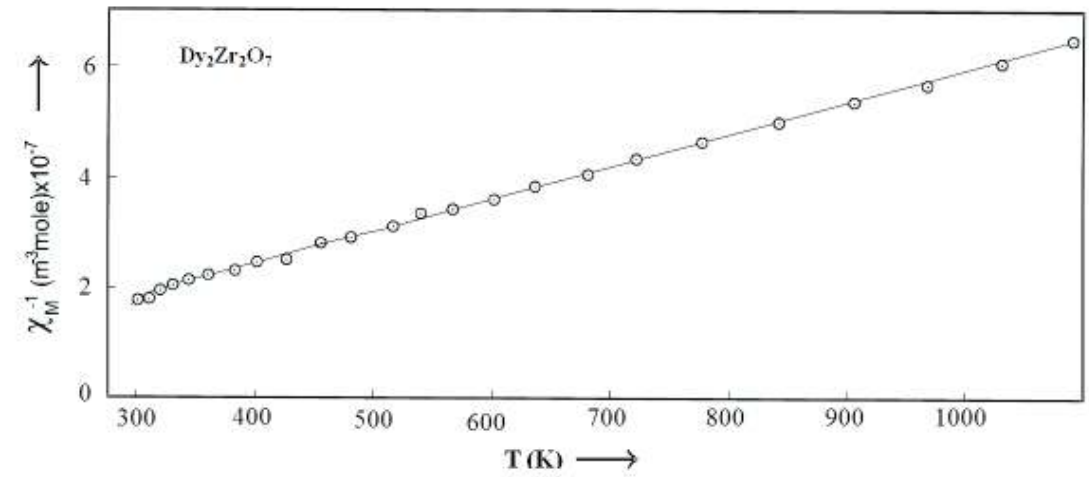

Figure 9 : Variation of Inverse of Molar Magnetic Susceptibility (χ_M^{-1}) With Absolute Temperature of $Dy_2Zr_2O_7$.

Table 1: Structural Parameters of Orthorhombic Unit Cell

Compounds	Unit Cell	Lattice Parameters		
		a_0 (nm)	b_0 (nm)	c_0 (nm)
$Gd_2Zr_2O_7$	Orthorhombic	1.2496	0.7652	0.5416
$Tb_2Zr_2O_7$	Orthorhombic	1.4162	0.7400	0.3748
$DyZr_2O_7$	Orthorhombic	1.3077	0.9228	0.3663

powdered samples using Faraday´s method (Bates L. F., 1951; Thakur A. N. et al., 1997). $Gd_2(WO_4)_3$ has been used for standardization.

RESULTS AND DISCUSSION

The room temperature XRD patterns of the calcined sample are shown in Figures. (1-3). The sharp and single diffraction peaks of the sample suggest the formation of a single phase compound. The d_{hkl} value has been calculated by using relation [4].

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

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

The DTA, TGA and DTG trace of $R_2Zr_2O_7$ compounds are shown in Figs. (4-6). The DTA trace of $Gd_2Zr_2O_7$ show endothermic peak at 353K and exothermic peak at 548K. The corresponding TGA trace show weight loss in two successive steps. The first step of weight losses 0.07% is from 323K to 548K may be due to removal of absorbed water and other gaseous species. The second step of weight loss 0.195% is from 548K to 673K and above 673K the compound is stable. The DTG trace show maximum rate of mass change at 548K and 648K.

The DTA trace of $Tb_2Zr_2O_7$ show endothermic peak at 363K and 673K. The corresponding TGA trace shows weight loss in two successive steps. The amount of weight loss in the two steps are 0.07% and 0.27% respectively and above 773K the compound is stable. The DTG trace show maximum rate of mass change at 673K.

The DTA trace of $Dy_2Zr_2O_7$ show endothermic at 363K. The corresponding TGA trace show weight loss in two successive steps. The amount of weight loss in two steps are 0.015% and 0.475% respectively and above 623K the compound is stable. The DTG trace show maximum rate of mass change at 498K.

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 results are shown in Figures. (7-9) as χ_M^{-1} vs T plots. It is seen from these figures that at higher temperature the χ_M^{-1} vs. T plots are linear and obey Curie-Weiss law and expressed by the relation [4].

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

Where θp is paramagnetic Curie temperature and 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 R^{+3}- R^{+3} (R-rare-earth). Thus at temperature much higher than ordering temperature the molar magnetic susceptibility of all these compounds can be approximated by the relation (Thakur Y. P. et al., 1997).

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

Where N is Avagadro number, μB is Bohr magneton, μ_0 is permeability constant, k is Boltzmann constant, $\bar{p}$ magneton numbers of magnetic ions R^{+3} ions and θp is the paramagnetic Curie temperature.

We can write above equation as

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

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

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

This yield

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

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 has been already known. The theoretical and experimental values of with magnetic ions are given in Table 2 and the values of θp and are given in Table 3.

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

The values of θp are negative for studied compounds suggesting a possible antiferromagnetic ordering of these compounds at lower temperature. However, such small values of θp 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 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 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.

Table 2 : Magnetic Ion With Theoretical and Experimental Value of Average Magneton Number ($\bar{p}$) of the Studied Compounds.

Compounds	Magnetic ion	Theoretical value	Experimental value
$Gd_2Zr_2O_7$	Gd^{3+}	7.94	7.91
$Tb_2Zr_2O_7$	Tb^{3+}	9.72	9.68
$Dy_2Zr_2O_7$	Dy^{3+}	10.65	10.42

Table 3 : Paramagnetic Curie Temperature (θp) and Molar Curie Constant ($\bar{C}_M$) of the Studied Compounds.

Compounds	θ_p (K)	$\bar{C}_M \times 10^5$ (m^3 K $mole^{-1}$)
$Gd_2Zr_2O_7$	-23	9.80
$Tb_2Zr_2O_7$	-37	14.63
$Dy_2Zr_2O_7$	-12	17.73

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