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Magnetic Study of Cerium-Iron-Transition Metal Mixed Compounds

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The compounds of cerium-iron-transition element mixed oxides of the type $CeFeTO_4$ have been prepared by a solid-state reaction technique and characterized by XRD pattern. The molar magnetic susceptibility (χ_M) of the powdered sample has been reported in a wide temperature range (300 to 1100 K). All the materials show a typical ferrimagnetic nature. The slope of asymptotic line yields an average magneton number, which indicates that all the materials are perfectly ionic. The transition ions are Ce^{3+}, Fe^{2+} and Fe^{3+} in $CeFe_2O_4$; Ce^{3+}, Cr^{3+} and Fe^{2+} in $CeFeCrO_4$; Ce^{3+}, Mn^{3+} and Fe^{2+} in $CeFeMnO_4$ and Ce^{3+}, Fe^{3+} and Co^{2+} in $CeFeCoO_4$.

Key Words: Magnetic susceptibility, Cerium-iron-transition elements, Mixed oxides.

INTRODUCTION

Mixed rare-earth and transition metal oxides have been the subject of detailed studies due to their interesting magnetic, dielectric, electrical transport properties and applications[1–3]. Earlier, a series of rare-earth and transition metal mixed compounds with a general formula $RTT'O_4$, where R stands for rare-earth, T and T′ for transition metals, was reported. The electrical transport properties of $GdFeTO_4$ and $YFeTO_4$ where T = Fe, Cr, Mn, Co and Ni[4, 5] and magnetic behaviour of $GdFeTO_4$ and $YFeTO_4$[6, 7] has also been reported. This paper reports results of the study on the magnetic behaviour of the compounds with a general formula $CeFeTO_4$ (where T = Fe, Cr, Mn and Co).

EXPERIMENTAL

The meterials for the preparation of these compounds were Ce_2O_3, Fe_2O_3, Cr_2O_3, MnO_2 and CoO of 99.99% purity. The stoichiometric amounts of these oxides were mixed and heated in a silica crucible for 50 h at 1400 K. The mixture was subjected to one intermediate grinding and the final product was cooled down slowly. The prepared compounds underwent the following solid state reactions:

$$2Ce_2O_3 + 4Fe_2O_3 \xrightarrow[\text{Air}]{1400\ K} 4CeFe_2O_4 + O_2$$

$$2Ce_2O_3 + 2Fe_2O_3 + 2Cr_2O_3 \xrightarrow[\text{Air}]{1400\text{ K}} 4CeFeCrO_4 + O_2$$

$$Ce_2O_3 + Fe_2O_3 + 2MnO_2 \xrightarrow[\text{Air}]{1400\text{ K}} 2CeFeMnO_4 + O_2$$

$$Ce_2O_3 + Fe_2O_3 + 2CoO \xrightarrow[\text{Air}]{1400\text{ K}} 2CeFeCoO_4$$

The weight loss corresponding to loss of oxygen on the right hand side of the reactions was observed in all cases except in $CeFeMnO_4$. In this case, the observed loss was slightly less than expected. The details are described elsewhere[8].

To get confirmation on the complete formation of the compounds, X-ray diffraction study were carried out at room temperature using CuK_α radiation ($\lambda = 0.15418$ nm). From X-ray diffraction pattern, d_{hkl} of each reflection was evaluated using the relation

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

From d_{hkl} values, structures of the compounds were resolved by the usual procedure. All the peaks were assigned with hkl values. This confirms that the compounds are in single phase. All the compounds were found orthorhombic unit cell with cells parameters a, b and c as given in Table-1.

TABLE-1
UNIT CELL PARAMETERS (nm) AND CALCULATED DENSITY (ρ) OF THE $CeFeTO_4$ COMPOUNDS

Compounds	Unit cell parameters (nm)			ρ ($kg\ m^{-3} \times 10^{-3}$)
	a	b	c	
$CeFe_2O_4$	0.6138	0.7416	0.8750	4.70
$CeFeCrO_4$	0.6138	0.7280	0.8660	4.61
$CeFeMnO_4$	0.6158	0.7286	0.8725	4.45
$CeFeCoO_4$	0.6151	0.7410	0.8440	4.40

Measurement of magnetic susceptibility

Magnetic susceptibility measurement was done using Faraday method. $Gd_2(WO_4)_3$ with molar magnetic susceptibility value of 6.85×10^{-7} mol m^{-3} at 300 K was used as standard substance.

The standard material and the sample were suspended from the hook provided in the pan of the balance in constant $H\left(\frac{dH}{dZ}\right)$ region in the pyrex tube and weight was measured in both cases, with and without applied magnetic field. The molar magnetic susceptibility of the sample was obtained from the relation

$$\chi_M = \left(\frac{\Delta m}{\Delta m_s}\right)\left(\frac{m_s}{m}\right)\chi_s \quad (2)$$

Δm and Δm_s are changes in the weights of the sample and standard substance, m and m_s are their masses and χ_s is the molar magnetic susceptibility of the standard substance. Due to relative method most of the errors are automatically eliminated except the errors in the measurement of mass m and weight change Δm. The maximum probable error in these measurements has been about 2% at lower temperatrue (T < 500 K), but increasese with increase of temperature and becomes as high as 5% around 1000 K, because hot air movement disturbs the sample holder in spite of the closed end of the furnace[8, 9].

RESULTS AND DISCUSSION

The molar magnetic susceptibility (χ_M) of all the compounds was measured in both heating and cooling cycles. No hysteresis was observed in χ_M and values were found to be almost same in both heating and cooling cycles. However, a small weight loss was observed in the heating cycle probably due to the presence of moisture. The results are shown in Fig. 1 (χ_M^{-1} *vs.* T plots). It is seen from the figure that the nature of all the plots is similar. In geneal, χ_M^{-1} *vs.* T plot is linear at higher temperature. However, there is systematic trend of experimental points towards temperature axis at lower side of temperature. The curves are similar to a standard ferrimagnetic material and systematic downward trend is due to onset

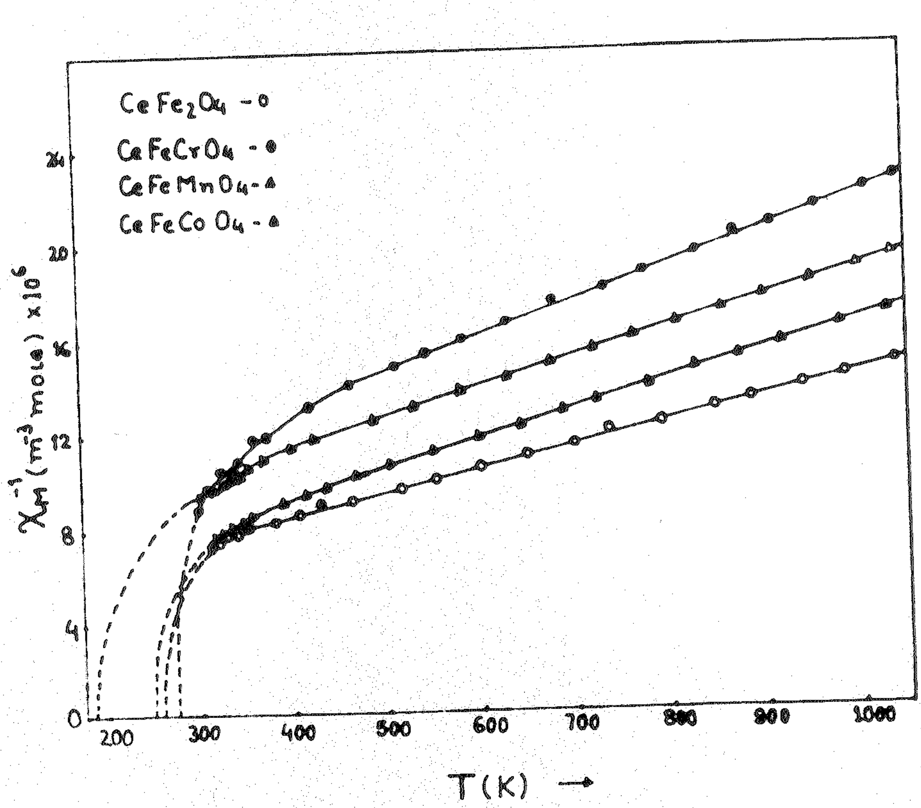

Fig. 1. Plots of inverse of magnetic susceptibility against absolute temperature for $CeFe_2O_4$, $CeFeCrO_4$, $CeFeMnO_4$ and $CeFeCoO_4$

of short range magnetic interaction at lower temperature. We have tried to fit the experimental data to the standard equation of ferrimagnetism[8] as given below:

$$\frac{1}{\chi_M} = \frac{T-\theta_a}{\overline{C}_M} - \frac{\theta_b^2}{\overline{C}_M\,(T-\theta)} \quad (3)$$

where $\overline{C}_M$ is the average value of Curie constant, θ_a is the asymptotic Curie temperature, θ_b and θ are parametric temperatures. These curves using eqn. (3) are drawn by full line in the respective χ_M^{-1} *vs.* T plots. The experimental points can be well fitted by eqn. (3) over a wide temperatrue range. The values of $\overline{C}_M$, θ_a, θ_b and θ are given in Table-2. The ferrimagnetic Curie (or Neel) temperature has been evaluated using the condition $T \longrightarrow T_c$, $\chi_M^{-1} \longrightarrow 0$. This gives

$$(T_c-\theta_a)(T_c-\theta) = \theta_b^2 \quad (4)$$

The real and positive values of T_c are meaningful and have been calculated using the above relation (Table-2).

TABLE-2
MAGNETIC PARAMETERS OF THE FOLLOWING COMPOUNDS

Compounds	θ_a (K)	θ (K)	θ_b (K)	T_c (K)	$\overline{C}_M$ ($mol^{-1} m^3$ K) · 10^4
$CeFe_2O_4$	–517	255	61	259	1.033
$CeFeCrO_4$	–570	245	155	273	0.689
$CeFeMnO_4$	–599	166	124	186	0.833
$CeFeCoO_4$	–477	237	100	250	0.880

The compound $CeFeTO_4$ contains three types of magnetic ions Ce^{3+}, Fe^{3+} or Fe^{2+} and T^{3+} or T^{2+}. Hence at temperature much higher than T_c, the molar magnetic susceptibility of these compounds can be expressed by the relation

$$\chi_M = \frac{N\mu_\beta^2\mu_0}{3k}\left[\frac{p_1^2}{T-\theta_{a_1}} + \frac{p_2^2}{T-\theta_{a_2}} + \frac{p_3^2}{T-\theta_{a_3}}\right] \quad (5)$$

where N is Avogadro number, μ_β is Bohr's magneton, μ_0 is the permeability constant, k is Boltzman constant, p_1, p_2 and p_3 are the magneton numbers of three types of magnetic ions, respectively and θ_{a_1}, θ_{a_2} and θ_{a_3} are paramagnetic Curie temperatures which takes into account the effect of various interactions. Assuming $\theta_{a_1} = \theta_{a_2} = \theta_{a_3}$, then the above equation can be written as

$$\chi_M^{-1} = \frac{k(T-\theta_a)}{N\mu_\beta^2\mu_0\,\overline{p}^2} \quad (6)$$

where $\overline{p}^2 = (p_1^2 + p_2^2 + p_3^2)/3$ is the effective magneton per ion. Comparing this equation with asymptotic equation of the curve given by eqn. 3, one gets (3),

$$\theta = \theta_a \quad \text{and} \quad \overline{C}_M = \frac{N\mu_\beta^2\overline{P}^2}{k}$$

or

$$\overline{P} = [k\overline{C}_m/N\mu_\beta^2\mu_0]^{1/2} \quad (7)$$

The experimental value of $\bar{P}$ can be calculated from the evaluated value of $\bar{C}_M$. The theoretical values of p_1, p_2 and p_3 are known, so one can obtain the theoretical values of $\bar{P}$. The experimetnal and theoretical values of $\bar{P}$ are given in Table-3 with magnetic ions used to obtained theoretical values of $\bar{P}$.

TABLE-3
MAGNETIC IONS AND AVERAGE EFFECTIVE MAGNETON NUMBER PER ION ($\bar{P}$)

Compounds	Magnetic ion	Values of $\bar{P}$	
		Expt.	Theo.
$CeFe_2O_4$	Ce^{3+}, Fe^{3+}, Fe^{2+}	4.69	4.68
$CeFeCrO_4$	Ce^{3+}, Cr^{3+}, Fe^{2+}	3.83	3.90
$CeFeMnO_4$	Ce^{3+}, Mn^{3+}, Fe^{2+}	4.21	4.27
$CeFeCoO_4$	Ce^{3+}, Fe^{3+}, Co^{2+}	4.33	4.38

One can notice that there is a good agreement between theoretical and experimental values of $\bar{P}$. This shows that all the studied compounds are essentially ionic and magnetic states of the ions are as indicated in Table-3. It can also be seen that in $CeFeCrO_4$, $CeFeMnO_4$ and $CeFeCoO_4$ compounds, there exist Ce^{3+}, Mn^{3+} and Co^{2+} ions, which replace Fe^{3+}, Fe^{3+} and Fe^{2+} ions respectively. This is quite reasonable in view of natural valency of these elements.

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