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ABSTRACT

In this paper we investigated the structural and magnetic properties of the $Gd_{2-x}M_xRu_2O_7$ (M=Ho and Y, x=0.0, 0.1, 0.2, 1.0 and 2.0) pyrochlores. The samples were prepared by solid state reaction method, characterized structurally by X-ray diffraction with Rietveld refinement and magnetically by measuring the temperature dependence of the magnetization. X-ray diffractograms of all samples studied presented a cubic pyrochlore type crystal structure with lattice parameters varying linearly in accordance with Vegards law. It is shown that by substituting Gd by Ho one can tune the magnetic order of this system moving from antiferromagnetic (in the absence of Ho) to ferromagnetic (in the absence of Gd). On the other hand by replacing Gd for Y the antiferromagnetic order is decreased.© 2010 Elsevier Science. All rights reserved

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1. Introduction

Compounds with the pyrochlore structure, A₂B₂O₇, which crystallize in a face-centered-cubic structure (space group Fd-3m), have been extensively studied in recent years, due to its large variety of electrical and magnetic properties [1]. Depending on the elements occupying the A and B sites, pyrochlore oxides can exhibit an insulating like behavior as seen in Tb₂Mo₂O₇ [2], present semiconducting electrical properties (e.g. Y₂Mo₂O₇ [3]), or even show a superconducting (e.g. Cd₂Re₂O₇) [4]. Regarding the magnetic character, several behaviors have been reported, for examples: diamagnetism, paramagnetism, ferromagnetism and antiferromagnetism [5,6]. Special attention has been devoted to the pyrochlore system where occurs a spin-glass transition. This behavior is a consequence of the geometrical frustration inherent of this structure [7,8]. Although an ample variety of rare earth ruthenates have already been explored, a small number of studies involving the Gd₂Ru₂O₇ compound have been conducted until now. It is known that this compound has a magnetic transition to an antiferromagnetic state at T=35 K accompanied by a small difference between field-cooled and zero-field-cooled magnetic susceptibilities [9]. Gurgul and co-workers [9] had done low temperature Mossbauer studies of this material, examining both ruthenium and gadolinium sublattices. They concluded that there is an ordering of the Gd sublattice above 35 K, nevertheless, with tiny average magnetic moments and, at 4.2 K, both ruthenium and gadolinium sublattices are magnetically ordered. The

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focus of this work is to study the structural and magnetic properties of pure and Ho and Y doped $Gd_2Ru_2O_7$ samples.

2. Experimental procedures

Samples of $Gd_{2-x}M_{x}Ru_{2}O_{7}$, with x=0.0, 0.1, 0.2, 1.0, 2.0 and M=Ho and Y, were prepared by the solid state reaction method, where quantities of rare earth oxides Gd₂O₃ and Ho₂O₃, Y₂O₃ and ruthenium dioxide RuO₂ (all with purity > 99.9%) were weighed in stoichiometric proportions, mixed, homogenized in concentrated nitric acid [10]. The excess nitric acid was removed by gentle heating. The remaining powders were slowly heated to 673 K for 3 h and heated at 1123 K for 24 h. After cooling to room temperature, the samples were crushed into powders, reground, pressed into pellets, and then reheated at 1373 K for 24 h. The structural characterization of the samples was performed by X-rays diffraction, using a Siemens D-5000 diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å) at room temperature. The lattice parameters were refined by Rietveld analysis using the computer program GSAS with the interface EXPGUI. The magnetization as a function of temperature, M(T) were recorded using a Quantum Design MPMS-5S SQUID Magnetometer. The temperature dependence of the magnetic susceptibility was recorded under zero field-cooled condition (ZFC) with an applied dc magnetic field of 1000 Oe.

3. Results and discussions

Fig. 1 shows the powder X-ray diffractograms for $Gd_{2-x}M_xRu_2O_7$, with x = 0.0, 0.1, 0.2, 1.0, and M = Y and Ho, in the angle range $20-80^\circ$.





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Fig. 1. X-ray diffraction pattern for $Gd_{2-x}M_xRu_2O_7$ with x=0.0, 0.1, 0.2 and 1.0 to M=Y and Ho.



Fig. 2. Evolution of the lattice parameter with *x* for $Gd_{2-x}M_xRu_2O_7$ (M=Y and Ho). The (2 2 2) diffraction peak for the $Gd_{2-x}M_xRu_2O_7$ (M=Y and Ho) samples is plotted in the insets. The arrow indicates the direction of higher M concentration (*x*=0.0, 0.1, 0.2, 1.0 and 2.0).

The diffraction peaks of all the samples studied were indexed as a cubic pyrochlore type crystal structure (space group Fd-3m) and no traces of impurity phases were detected.

The lattice parameters calculated from Rietveld refinement to the pyrochlore-type unit cell are depicted in Fig. 2 a function of doping content. The low values of the *R*-factors ($R_p < 12\%$ and R_{wp} < 18%) and the *goodness of fit* ($1.4 < \chi^2 < 2.6$) indicate a good agreement between the calculated and experimental data. It can be seen that the lattice parameters decrease linearly with increasing Ho (or Y) content in agreement with Vegard's rule [11]. From these analyses we concluded that Ho³⁺ and Y³⁺ have completely occupied the site of Gd³⁺, and infinite solid solutions have been formed. The lattice parameters of both Gd₂Ru₂O₇ and Ho₂Ru₂O₂ are in excellent agreement with previously reported results [12]. The inset shows that the (2 2 2) plane peak reflection shifts to higher angles indicating a decrease in the lattice parameter with increasing dopant (Ho or Y) concentration.

Fig. 3 shows the temperature dependence *T* of magnetic susceptibility χ_{dc} measured at an applied magnetic field of $H_{app} = 1000$ Oe for both (a) Y and (b) Ho doped samples. It is



Fig. 3. Temperature dependence of the magnetic susceptibility. (a) $Gd_{2-x}Y_xRu_2O_7$ and (b) $Gd_{2-x}Ho_xRu_2O_7$ with x=0.0, 0.1, 0.2 and 1.0. In the inset is shown the inverse of susceptibility at low temperatures.

observed that the magnetic dilution with Y causes a decrease in magnetic moment of the compounds while the substitution of Ho in the Gd sites causes an increase in the magnetic moment. In both Gd-doped samples the χ_{dc} diminishes when the temperature increases and no kinks associated with the Ru-lattices magnetic transitions were observed between 2 K < *T* < 150 K. For the Y doped samples the inverse of magnetic susceptibility, shown in the inset of Fig. 3, presents a deviation from Curie–Weiss behavior down to 35 K. On the other hand the Ho doped samples present deviation from a Curie–Weiss behavior at temperatures ranging from 35 K to 13 K depending on the doping.

Table 1 presents Weiss temperature (Θ) and both the experimental (μ_{exp}) and theoretical (μ_{the}) magnetic moments obtained by fitting the measured susceptibility to a Curie–Weiss law $\chi(T) = C/(T-\Theta)$ for all samples except the Ho₂Ru₂O₇ sample in which it was necessary to include a small ($\alpha = 0.0023$ emu Oe⁻¹ mol⁻¹) temperature-independent Van Vleck paramagnetic contribution to the susceptibility [13]. It is observed that the magnetic dilution (doping with Y in site of Gd) causes a decrease in magnetic moment of the compounds while the substitution of Ho in the Gd sites causes an increase in the magnetic moment.

The negative value of Θ leads us to conclude that the deviation from the Curie–Weiss law is due to an antiferromagnetic order

Table 1

Fit parameters: Weiss constants Θ , magnetic moment experimental μ_{exp} and magnetic moment evaluated μ_{the} , for all samples studied.

| x | Θ (K) | μ_{exp} (µB) | $\mu_{the}~(\mu B)$ |
|---|--------------|------------------|---------------------|
| $Gd_{2-x}Y_{x}Ru_{2}O_{7}$ | | | |
| 0.0 | -11.77(7) | 11.74 | 11.92 |
| 0.1 | -11.06(8) | 11.50 | 11.65 |
| 0.2 | -11.1(1) | 11.17 | 11.37 |
| 1.0 | -8.46(5) | 8.52 | 8.89 |
| Gd _{2-x} Ho _x Ru ₂ C | 7 | | |
| 0.0 | -11.77(7) | 11.74 | 11.92 |
| 0.1 | -10.46(7) | 12.01 | 12.12 |
| 0.2 | -10.76(7) | 12.35 | 12.32 |
| 1.0 | -3.53(4) | 13.36 | 13.84 |
| 2.0 | 1.12(2) | 14.63 | 15.52 |

present in all samples except the sample Ho₂Ru₂O₇, in which the positive Θ shows evidence of ferromagnetic ordering. This is seen because by adding Ho one can tune the magnetic order of the sample by changing it from antiferromagnetic, in the absence of Ho, to ferromagnetic in the absence of Gd. Studies of specific heat at the samples $Gd_2Ru_2O_7$ and $Ho_2Ru_2O_7$ show anomalies in around 106 and 92 K, respectively [14], which are associated with long-range magnetic ordering of ions Ru⁴⁺. In our study of the magnetic of the $Y_2Ru_2O_7$ sample, we observe a characteristic peak followed by irreversibility in ZFC and FC measures at the temperature of 80 K, which agrees with the results of specific heat studied by Ito et al. [14]. Comparing the magnetic response of the $Y_2Ru_2O_7$ with the $Gd_2Ru_2O_7$, we saw that the last one has the value of magnetic susceptibility 11 times bigger than Y₂Ru₂O₇. Thus it is likely that, in the doped samples, the magnetic response of the site Ru^{4+} is masked by the high response of Gd^{4+} ions. We stress that in order to obtain a good agreement between the experimental and theoretical magnetic moment values it is necessary to include the contribution of both the Gd and Ru magnetic sites. Thus μ_{the} was evaluated considering the orbital and spin contributions to the total magnetic moment $2(J(J+1))^{1/2}$ for Gd³⁺ and Ho³⁺ ions, whereas for Ru⁴⁺ ions we considered only the spin contribution $2(S(S+1))^{1/2}$ in a low spin state with S=1 [9]. The concordance between the values of μ_{exp} and μ_{the} indicates that the magnetic response of the studied samples arises from the contribution of both magnetic sites.

It has been observed in previous studies that $\Theta = -1250$ K for Y₂Ru₂O₇ [9], showing that this is a highly frustrated system, and not that it is strongly antiferromagnetic. As seen in Table 1, our study shows a decrease of the values for the Gd_{2-x}Y_xRu₂O₇ compound, with

a decreasing Gd content, indicating an inhibition of AFM interactions. We conclude that the antiferromagnetic order in the $Gd_{2-x}Y_xRu_2O_7$ systems is mainly due to Gd^{3+} ions.

4. Conclusions

In this study, we focus our attention on the study of the structural and magnetic properties of rare earth ruthenates pyrochlores, $Gd_{2-x}M_xRu_2O_7$, with x=0.0, 0.1, 0.2, 1.0, and M=Y and Ho. Structural analysis indicates that the samples crystallize in a cubic pyrochlore type crystal structure, with space group Fd-3m. The lattice parameters decrease linearly with increasing Ho (or Y) content in agreement with Vegard's rule. We conclude that by adding Ho one can tune the magnetic ordering of the sample by changing it from antiferromagnetic, in the absence of Ho, to ferromagnetic in the absence of Gd. On the other hand the Y doped samples preserver the magnetic order of the compound. It presents an antiferromagnetic order for all the dopant concentration studied.

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References

- [1] J.S. Gardner, M.J.P. Gingras, J.E. Greedan, Rev. Mod. Phys. 82 (2010) 53.
- [2] M. Sawada, A. Kimura, K. Miyoshi, J. Takeuchi, M. Arita, K. Shimada, H. Namatame, M. Taniguchi, T. Ishikawa, K. Tamasaku, Y. Nishino, D. Miwa, Y. Takata, S. Shin, K. Kobayashi, E. Ikenaga, M. Yabashi, M. Awaji, A. Takeuchi, Physica B 383 (2006) 152.
- [3] J.E. Greedan, M. Sato, N. Ali, W.R. Datars, J. Solid State Chem. 68 (1987) 300.
 [4] R. Jin, J. He, S. McCall, C.S. Alexander, F. Drymiotis, D. Mandrus, Phys. Rev. B 64 (2001) 180503.
- [5] B.P. Mandal, A. Banerji, V. Sathe, S.K. Deb, A.K. Tyagi, J. Solid State Chem. 180 (2007) 2643
- [6] A.V. Korolev, G.V. Bazuev, Phys. Solid State 46 (2004) 294.
- [7] J.E. Greedan, J. Mater. Chem. 11 (2001) 37.
- [8] J.E. Greedan, J. Alloys Compds. 408 (2006) 444.
- [9] J. Gurgul, M. Rams, Z. Swiatkowska, R. Kmiec, K. Tomala, Phys. Rev. B 75 (2007) 064426.
- [10] N. Taira, M. Wakeshima, Y. Hinatsu, J. Mater. Chem. 12 (2002) 1475.
- [11] L. Vegard, Z. Phys. 5 (1921) 17.
- [12] N. Taira, M. Wakeshima, Y. Hinatsu, J. Phys. Condens. Matter 11 (1999) 6983.
- [13] J.H. Van Vleck, Theory of Electric and Magnetic Susceptibilities, Clarendon,

Oxford, 1932.

[14] M. Ito, Y. Yasui, M. Kanada, H. Harashina, S. Yoshii, K. Murata, M. Sato, H. Okumura, K. Kakurai, J. Phys. Chem. Solids 62 (2001) 337.