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Dy_3TaO_7, A stoichiometric spin glass and the effect of disorder via chemical substitution in the $Dy_{3-x}Y_xTaO_7$ $(0 \le x \le 3)$ solid solution

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ABSTRACT

In this work, we present both structural and magnetic (DC magnetization and AC susceptibility) studies of the $Dy_{3-x}Y_xTaO_7$ solid solution. The structural characterization of samples was performed by Rietveld refinements of the X-ray diffraction data. All compounds crystallized in a weberite-related structure in the orthorhombic *C222₁* space group (No. 20); the variations of the lattice parameters obey the Vegard´s law in the whole range of composition. DC magnetic measurements of the $Dy_{3-x}Y_xTaO_7$ system showed a Curie-Weiss paramagnetic behaviour, with antiferromagnetic interactions at T > 150 K. Below 3 K a spin glass behaviour in the $0 \le x \le 1$ range of the solid solution was observed. The stoichiometric Dy_3TaO_7 compound showed spin glass behaviour although there is no evidence of structural disorder. For some Y^{3+} doped compounds (x = 0.33, 0.66 and 1.0), chemical disorder reduced the freezing temperature (T_g) values with a $x^{1/3}$ dependence. Cole-Cole analysis of the AC magnetic field response showed similar phenomenological parameters for the stoichiometric (x = 0) and the Y^{3+} doped compounds with spin glassiness, suggesting an analogous mechanism for these compounds. For the $Dy_{3-x}Y_xTaO_7$ system, in which the spin glass behaviour seems to exhibit a critical concentration, a magnetic phase diagram is proposed.

1. Introduction

Tantalum oxide-based compounds attract great attention because they display remarkable properties as dielectric [1,2] and magnetic systems [3–9]. In Ln_3MO_7 systems, when M = Ta, a possible application as electrolyte for solid oxide full cell has been suggested [10], as well as a photocatalyst in water splitting for hydrogen generation [11,12]. When Ln = Dy, Y or Gd and M = Ta or Nb, the compounds crystallize in a weberite-related (WR) structure. In this case the Ln^{3+} ions lie on a sublattice formed of corner-sharing tetrahedral, that also share a common edge between them. This arrangement is closely related to the Kagomé lattice displayed in the pyrochlore structure [13]. On the basis of the structural analogy, it is expected that WR compounds with nominal formula Ln_3MO_7 display non-conventional magnetism when Ln is a magnetic ion [13]. On the other hand, Ln_3MO_7 (Ln = rare earth element) compounds crystallizing in the WR structure have been reported exhibiting long-range magnetic order with antiferromagnetic coupling [5,7,9,13], while no ferromagnetic order has been found, and, to the best of our knowledge, none of them has been identified as a magnetically frustrated system. Additionally, Dy_3TaO_7, crystallizing in the WR structure, has been previously reported exhibiting spin glass (SG) behaviour [14] but, an exhaustive analysis about how the SG behaviour takes place has not been performed yet.

On the other hand, random quenching of magnetic moments in SG systems has been one of the most challenging topics in condensed matter studies for the last decades. It is widely accepted that both, frustration and disorder, are essential in all spin glasses [15]. However, there is a reduced number of geometrically frustrated stoichiometric compounds in which, the absence of apparent disorder is not consistent with the requirement to create a randomly frustrated system leading to the SG state. These stoichiometric compounds include several pyrochlores such as $Tb_2Mo_2O_7$, $Y_2Mn_2O_7$, $Tb_2Sn_2O_7$, $Y_2Mo_2O_7$ [16–19], among others [20]; $SrCr_8Ga_4O_{19}$ magnetoplumbite [21] and $Gd_3Ga_5O_{12}$ garnet [22].

In addition to Dy_3TaO_7, four compounds of the $Dy_{3-x}Y_xTaO_7$ system with WR structure exhibit SG behaviour [14]. In the $Dy_{3-x}Y_xTaO_7$ solid solution, the x = 0 case corresponds to the stoichiometric compound in which the only possible disorder occurs when Dy^{3+} occupies the Ta^{5+} sites. This randomness in the crystallographic site occupation is unlike,

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given the large difference in ionic radii, bond valence and coordination number [23] (cubic coordination for Dy and octahedral for Ta). Under such considerations there is no possibility of structural disorder in this compound, which is essential to display a SG behaviour according to the mean field theories [24–26]. In the case of those compounds in which Y^{3+} substitutes Dy^{3+}, and considering the significant differences between the ionic radii of Ta^{5+}, Y^{3+} and Dy^{3+} (0.64, 0.96 and 0.97 Å, respectively [27]), it is reasonable to assume that such substitution occurs only at the Dy^{3+} crystallographic positions. In this scenario, in the $Dy_{3-x}Y_xTaO_7$ system the tetrahedral magnetic sublattice is being diluted because of the Y^{3+} substitutions on the Dy^{3+}sites.

The aim of this work is to provide an alternative methodology to study the SG transition, via the AC magnetic susceptibility data on the basis of the Cole-Cole formalism [28,29], in order to correlate chemical composition with the SG behaviour in the $Dy_{3-x}Y_xTaO_7$ system. This methodology yields information about the relaxation times and its temperature dependence in both SG and PM states for each compound. Additionally, this methodology allows us to correlate the relaxation times behaviour with chemical composition in a solid solution. On the other hand, when the compounds displayed a non-Debye response [28], a relaxation times distribution function could be obtained [30] and a qualitative analysis of the number of thermally available states, for the system, could be correlated with the SG behaviour.

2. Experimental

All samples were synthesized by the solid state reaction method. Stoichiometric amounts of Dy_2O_3, Y_2O_3 and Ta_2O_5 (all supplied by Aldrich at 99.99% purity) were weighted, according to Eq. (1), for x = 0.0, 0.33, 0.66, 1.0, 1.33, 1.66, 2.0, 2.33, 2.66 and 3.0. Further details on synthesis and X-ray experimental setup can be found in previous work [14].

$$\frac{3-x}{2}Dy_2O_3+\frac{x}{2}Y_2O_3+\frac{1}{2}Ta_2O_5\xrightarrow[1400^\circ C,48h]{}Dy_{3-x}Y_xTaO_7 \qquad (1)$$

The GSAS [31] code with the graphical tool EXPGUI [32] was used to refine the experimental Cu-k_α X-ray patterns. The DC magnetic measurements were performed at 100 Oe with temperature ranging from 2 to 300 K in zero-field-cooling mode (ZFC) using a MPMS 3 (Quantum Design). For the AC magnetization measurements, a quantum interference device (SQUID) magnetometer (MPMS) coupled with an AC device was used, at 1 Oe with temperature ranging from 2 to 20 K, with a frequency ranging from 50 to 1000 Hz.

3. Results and discussion

3.1. Structural characterization

All samples of the $Dy_{3-x}Y_xTaO_7$ system showed a single crystalline phase in the $0 \le x \le 3$ range. The limit cases, x = 0 and x = 3 (Y_3TaO_7 [33] and Dy_3TaO_7 [34]), have been previously reported as weberite-type structures [35]. As can be observed in Fig. 1, the intermediate compositions displayed similar reflections which appeared between the Y_3TaO_7 and Dy_3TaO_7 characteristic reflections. No secondary crystal phases were detected and no additional reflections related with cation ordering were observed, suggesting that Y^{3+} ions were randomly distributed in the Dy^{3+} sites.

In this way, the Dy^{3+} and Y^{3+} ions were randomly distributed along the lattice which yielded a kind of disorder on magnetic Dy^{3+} ions, we associated this characteristic of the system with chemical disorder. Since the Dy^{3+} and Y^{3+} ions have the same charge, no extra defects were generated for charge compensation and the stoichiometry of the system depends only on two factors: a) the intrinsic defects, which can be minimized, considering the low volatility and because of the high refractory properties of the reagents, and b) the chemical composition, which was fixed according to Eq. (1).

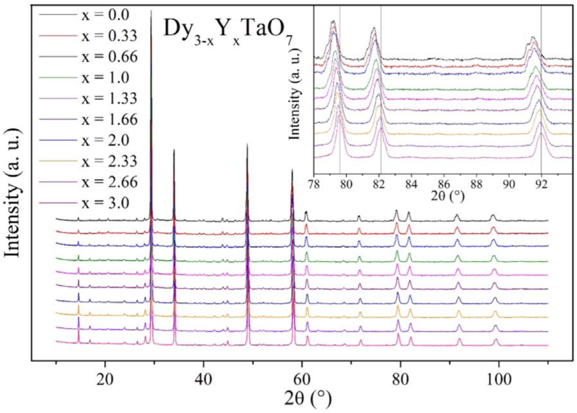

Fig. 1. X-ray patterns of all studied compositions of the $Dy_{3-x}Y_xTaO_7$ solid solution. The reflections shift progressively from Y_3TaO_7 to Dy_3TaO_7 as Y^{3+} content is modified.

Rietveld refinements were performed using the crystallographic data proposed by Wakeshima et al. [7] as initial model. All compositions were refined in the orthorhombic *C222₁* space group (No. 20), the refinement plots are shown in Fig. 2. Fig. 3 displays the lattice parameters as a function of the yttrium content. The linear behaviour in Fig. 3 agrees with Vegard law [36] and confirms the formation of a solid solution in the whole composition range studied. The refined atomic positions as well as the lattice parameters and the goodness-of-fit criteria of each refinement are presented in the Supplementary information section, which only shows data for x = 3.0, 2.66, 2.33, 2.0, 1.66 and 1.33; crystallographic data for x = 1.0, 0.66, 0.33 and 0.0 have previously been reported [14]. The site occupation factors (SOFs) were not refined once no preferential ordering between Y^{3+} and Dy^{3+} cations is assumed, and the SOFs correspond to the chemical composition. The low values of the goodness-of-fit indicate the reliability of the Rietveld refinements.

From the crystallographic data obtained from Rietveld refinement (see Supplementary information section), a structural representation of the $Dy_{3-x}Y_xTaO_7$ compounds can be built, this is shown in Fig. 4. Here, it is possible to observe the corner-sharing chains of distorted TaO_6 octahedra along *c* axis (green polyhedra), the distorted LnO_8 cubic polyhedra which form edge-linked chains along *c* axis (orange polyhedra); the octahedra and cubic chains are linked by edges and form an alternated layer of chains along *b* direction. The blue polyhedra in Fig. 3 represents the LnO_7 coordination polyhedra which are linked by edges along *c* axis and by corners along *b* axis, forming a layer of LnO_7 polyhedra; along *a* axis the layer of LnO_7 polyhedra alternates with the octahedra and cubic layer. This atomic arrangement is distinctive of the weberite-related structures [35].

3.2. DC and AC magnetic characterization

The temperature dependence of magnetic susceptibility for all the studied compounds is shown in Fig. 5, the temperature range studied was 2–300 K (Compounds with x = 0.0 0.33, 0.66 and 1.00 had been previously reported [14]). As can be observed in inset A, all compositions behave according to the Curie-Weiss (CW) law. Fittings of the susceptibility data to the CW law were performed in the 150–300 K temperature range and the results are listed in Table 1. Here, the negative Θ values suggest antiferromagnetic (AF) interactions; besides, the effective magnetic moment ($\mu_{eff.}$) calculated from the *C* values are close to those of the Dy^{3+} free-ion in the $^6H_{15/2}$ state which is 10.66 Bohr magnetons (μ_B). In this way, the magnetization of samples in the entire range of Dy composition shows only the Dy^{3+} ion magnetic contribution. The $\mu_{eff.}$ was calculated according to Eq. (2), where k_B is the Boltzmann constant, N_A is the Avogadro's number and *n* is the moles of magnetic ions in the chemical formula $Dy_{3-x}Y_xTaO_7$.