Effects of substituting Mn with Ga in the multiferroic properties of $TbMnO_3$.

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Abstract. We here report the characterization of the crystal structure, magnetic properties and specific heat of $TbMn_{1-x}Ga_xO_3$ samples ($x \leq 0.4$). Metamagnetic transition was observed at low temperature for all compounds. Heat capacity was used to test the effect of Ga on the different phase transitions. The substitution of Ga for Mn is detrimental for the antiferromagnetic ordering of Mn^{3+} showing a continuous decrease of T_N with increasing the Ga content. This substitution also decreases the entropy content of the transition due to the ordering of Tb^{3+} moments. The anomaly ascribed to the ferroelectric transition is absent at zero field in Ga-based samples but it reappears at high magnetic fields in compounds with low Ga content. This result suggests that an external magnetic field induces ferroelectricity in the doped compounds.

1. Introduction.

$TbMnO_3$ has recently attracted enormous interest because of the coexistence of ferroelectricity and antiferromagnetic orderings [1]. Detailed studies indicate a strong coupling between the magnetic and polarization order parameters [2,3] which opens the opportunity for new types of magnetoelectronic devices.

This compound shows an incommensurate sinusoidal spin ordering of Mn^{3+} atoms (q_{Mn}~0.295) below T_N~41 K [4]. The incommensurability decreases as temperature is lowered but it is locked at q_{Mn} =0.27 below T_{lock}~30 K. At this temperature, spontaneous polarization P parallel to the c axis ($P \parallel c$) occurs. The application of a magnetic field (H) flops the electric polarization from $P \parallel c$ to $P \parallel a$. The critical field to achieve it depends on the relative orientation (~4.5 T if $H \parallel b$).

Substitution of Tb^{3+} with other heavy rare earth atoms has been widely explored observing important changes in both electric and magnetic properties [5]. However, the effects of substituting a non-magnetic trivalent cation for Mn^{3+} in $TbMnO_3$ have not been reported so far. This type of substitution enhances the ferrielectric transition temperature in hexagonal manganites [6]. Ga also has strong effects on related orthomanganites such as $LaMnO_3$ because it induces the disappearing of the cooperative Jahn-Teller effect of Mn^{3+} leading to the appearing of a ferromagnetic ground state for $LaMn_{1/2}Ga_{1/2}O_3$ [7].

This work is devoted to the study of the changes produced in the physical properties of $TbMnO_3$ after replacing Mn^{3+} by Ga^{3+}. We have determined the crystal structure and both magnetic and heat capacity measurements have been carried out with the aim of gaining insights into the multiferroic properties of $TbMnO_3$.

2. Experimental section.

The samples were prepared by means of solid state methods but the specific synthetic route depends on the chemical composition of each sample. For $x \leq 0.3$, stoichiometric amounts of $MnCO_3$, Ga_2O_3 and Tb_4O_7 were mixed and heated at 1000º C in air overnight. The resulting powders were ground, pressed into pellets and sintered at 1200º C for 1 d. The pellets were ground, repressed and sintered at 1400º C for 2 d in a current flow of Ar. This procedure does not work for $x \geq 0.4$ samples where competitive phases, such as $Tb_3Ga_2O_8$ (garnet) and Tb_3GaO_6, are also formed. The perovskite phase can be favored by fast quenching from the melt into water. Following this method, we were successful in preparing the x=0.4 sample with only traces of impurities.

The samples were characterized by x-ray powder diffraction using a Rigaku DMAX 2000 diffractometer. A fixed graphite monochromator was used to select Cu K_α radiation. Step-scanned patterns were measured between 18º and 130º in steps of 0.03º at room temperature and the crystal structures were refined by the Rietveld method.

Magnetic measurements were carried out using a commercial Quantum Design SQUID magnetometer. Temperature scans of the dc magnetization at 0.1 T were performed between 2 and 295 K whereas hysteresis loops were collected at selected temperature between -5 and 5 T. Heat capacity was measured in commercial PPMS system (Quantum Design) using a relaxation technique. The temperature range was between 2 and 60 K using external magnetic fields ranging between -5 and 5 T.

3. Results and discussion.

The crystal structure of $TbMn_{1-x}Ga_xO_3$ compounds was studied for x=0, 0.05, 0.1, 0.2, 0.3 and 0.4. The unit cell of these samples is orthorhombic, space group *Pbnm*, as was reported for $TbMnO_3$ [4]. Table 1 shows the unit cell parameters for these samples at room temperature. These data reveal a volume decrease for the unit cell with decreasing Mn. Similar result was found in the $LaMn_{1-x}Ga_xO_3$ system where it was also found the weakening of the cooperative Jahn-Teller effect in the Mn-sublattice due to the dilution with Ga^{3+} cations [7].

Table 1. Refined lattice parameters and unit cell volume for $TbMn_{1-x}Ga_xO_3$ at room temperature. Data for x=0 has been taken from ref. 4. Numbers in parentheses refers to standard deviations.

	x=0	x=0.05	x=0.1	x=0.2	x=0.3	x=0.4
a (Å)	5.3019(1)	5.3002(1)	5.2992(1)	5.2985(1)	5.2974(1)	5.2976(1)
b (Å)	5.8557(1)	5.8404(1)	5.8242(1)	5.7921(1)	5.7575(2)	5.7577(2)
c (Å)	7.4009(1)	7.4084(2)	7.4179(3)	7.4376(2)	7.4572(2)	7.4575(3)
Vol(Å^3)	229.77(1)	229.33(1)	228.94(1)	228.26(1)	227.44(1)	227.46(1)

Fig. 1 shows the zero-field-cooled dependence of the dc susceptibility (M/H) for $TbMn_{1-x}Ga_xO_3$ samples in a field of 100 Oe. All curves show a peak at low temperature (~ 7 K) as was reported for the parent compound, $TbMnO_3$ [4]. Taking into account these results, the peak at ~7 K is attributed to the magnetic ordering of the Tb^{3+} moments (T_{Tb}). At high temperature, M/H seems to follow a Curie-Weiss law. This fact is confirmed in the inset of Fig. 1 where the temperature dependence of the magnetic susceptibility is plotted for $TbMn_{0.9}Ga_{0.1}O_3$. A linear behavior characteristic of a Curie law is observed in a wide temperature range. The separation between the experimental data and the linear fit occurs below 50 K where it is expected the long range antiferromagnetic ordering of Mn^{3+} moments in $TbMnO_3$ [1,4]. Similar behavior was found for the rest of studied compounds. The effective paramagnetic moments obtained from the linear fits range between ~11 and ~10.25 μ_B fu^{-1}, obtained for x=0 and x=0.4, respectively. These values reasonably agree with the theoretical ones. The slight decrease with increasing x is ascribed to the replacement of paramagnetic Mn^{3+} by diamagnetic Ga^{3+}.

Fig. 2 shows the magnetization loops at 5 K for the whole set of samples. The loops confirm the presence of metamagnetic transitions for all compounds and the value of the magnetic moment at 5 T

decreases with the increasing of diamagnetic Ga^{3+} in the chemical composition. It reaches ~7 and ~5 $\mu_B fu^{-1}$ for $TbMnO_3$ and $TbMn_{0.6}Ga_{0.4}O_3$, respectively. A step-like increase of the magnetization occurs between H=1 and 2 T in the $TbMnO_3$ loop. The magnetic behavior of $TbMnO_3$ is very anisotropic and it strongly depends on the relative orientation between the external field and the crystallographic axes [1,2]. As we are measuring a polycrystalline sample, we would expect to find an average behavior of the three crystal directions, ie H ‖ a, H ‖ b and H ‖ c. However the hysteresis cycle from Fig. 2 strongly resembles the results obtained from crystals with the H ‖ a orientation. In this way, the step-like feature is ascribed to the reported metamagnetic transition [5]. Such a feature is fading out as the Ga content is increased between x=0 and x=0.4. However, the changes in the loops with the chemical composition are not continuous and the curves are almost equal for $0.05 \leq x \leq 0.3$ samples.

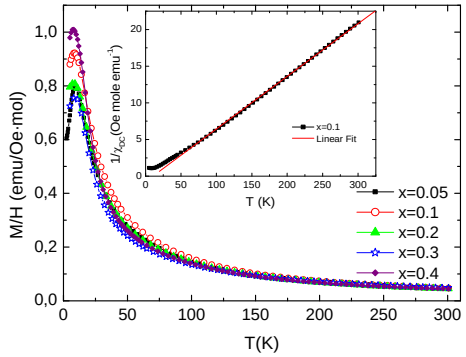

Figure 1. Temperature dependence of the dc magnetization for the indicated samples. Inset: Inverse of susceptibility vs. temperature for $TbMn_{0.9}Ga_{0.1}O_3$. The line is a linear fit.

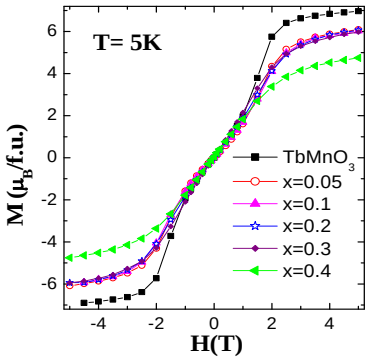

Figure 2. Magnetization loops at 5 K for $TbMn_{1-x}Ga_xO_3$ compounds.

The specific heat divided by temperature is shown in Fig. 3 for all compounds. The curve of $TbMnO_3$ exhibits three anomalies as reported elsewhere [1]. The peaks at 6.5 and at 41 K are attributed to T_{Tb} and T_N, respectively. The intermediate anomaly at 26 K is ascribed to T_{lock} where the ferroelectric transition is coupled to the commensurate-incommensurate transition of the Mn^{3+} moments. The substitution of Mn with Ga gives rises to three significant changes in the specific heat. First of all, the intensity of T_{Tb} peak decreases with increasing the Ga content, indicating a decrease in the entropy content of this transition. for the samples with Ga. Secondly, the T_{lock} peak vanishes since the lowest amount of Ga^{3+} introduced into the $TbMnO_3$ lattice. Finally, the peak attributed to the Mn ordering at T_N is shifted towards lower temperatures as Ga content increases. The later change is produced by the dilution effect with the diamagnetic Ga^{3+} which weakens the Mn^{3+}-O-Mn^{3+} interaction. Moreover, the entropy content of the transition diminishes with increasing the Ga content.

The application of a magnetic field also affects the specific heat of these samples, especially for compounds with low content of Ga. Fig. 4 shows the data collected for $TbMn_{0.9}Ga_{0.1}O_3$ at three values of H. The intensity of the T_{Tb} peak is strongly reduced by applying H and it is vanished at H=9 T. This result reveals the coupling between H and the magnetic arrangement of the Tb-sublattice. The suppression of the antiferromagnetic ordering is in agreement with the ferromagnetic alignment of the Tb moments for H≥ 2 T reported in ref. [3].

The magnetic field does not affect the position of the peak at T_N but this anomaly is more rounded at high H. Moreover, it is asymmetric with an additional shoulder at the high-temperature side. This result indicates two separate transitions at high H in the temperature range where the Mn moments are ordered.

The most striking point in these measurements is the appearing of a new anomaly indicated by an asterisk in Fig. 4. The temperature for this anomaly depends on the strength of H in a way that resembles the behavior of the spin flop in $TbMnO_3$. Accordingly, it seems that low amounts of Ga are detrimental for the occurrence of the T_{lock} and therefore the ferroelectric P ‖ c phase is not established. However, the presence of ferromagnetic ordering in the Tb-lattice induced by H allows the formation of the ferroelectric P ‖ a phase. Nevertheless, both neutron diffraction and electric measurements are necessary to shed light on this subject.

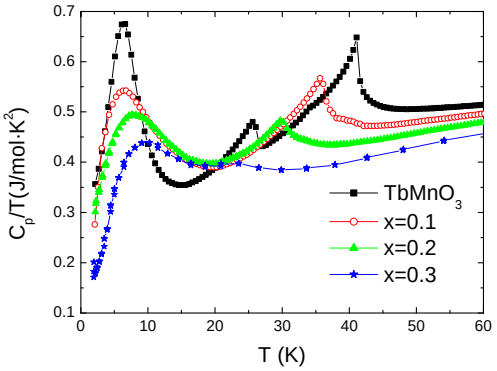

Figure 3. Specific heat divided by temperature vs. temperature for $TbMn_{1-x}Ga_xO_3$ compounds at zero field.

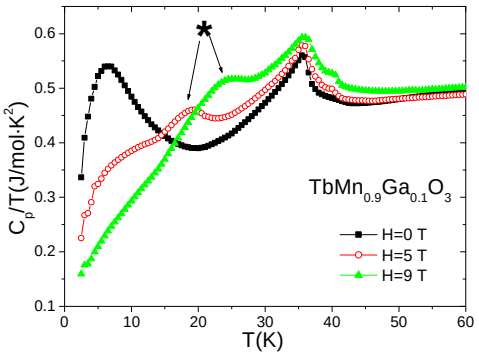

Figure 4. Comparison of the specific heat measured at the magnetic fields indicated in the figure.

4. Conclusions.

We were successful in preparing $TbMn_{1-x}Ga_xO_3$ samples by solid state methods up to x=0.4. They are isostructural to the $TbMnO_3$ and the magnetic susceptibility showed the characteristic features of the antiferromagnetic ordering of Mn and Tb moments. The samples follow a Curie-Weiss law above T_N with the expected effective paramagnetic moments. T_N of Mn ordering decreases as the Ga content is increased in agreement with the expected dilution effect by the solid solution. Another effect of this substitution is the decrease in the entropy content of the phase transition at T_{Tb}. Nevertheless, the most striking point is the suppression of the ferroelectric transition at zero field for sample with low Ga content (x=0.1). This result reveals that Ga inhibits the lock transition in the Mn sublattice. However, the application of an external field induces the ferromagnetism in the Tb-sublattice and a new anomaly is observed in the C_p/T curves suggesting the formation of the ferroelectric phase with P ‖ a at high H.

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