Heat capacity, magnetic and lattice dynamic properties of TbMn$_{1-x}$Fe$_x$O$_3$

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Abstract. The effect of substitution of Fe$^{3+}$ ions by Mn$^{3+}$ ions on crystal structure, lattice dynamic, heat capacity and magnetic properties in TbMn$_{1-x}$Fe$_x$O$_3$ ceramics has been studied. X-ray powder diffraction and Raman spectroscopy revealed that lattice distortion can be mainly attributed to Jahn-Teller distortion and tilting of octahedrons for samples with $x < 0.4$; for higher Fe concentration, the distortions are dominated by the octahedra tilting with less contribution of the Jahn-Teller effect. The anomalies in heat capacity of parent compounds (TbMnO$_3$ and TbFeO$_3$), which are associated with magnetic transitions, are smeared out by ion substitution. Magnetization measurements indicate that magnetic ordering persists in whole concentration range. The butterfly-type magnetic hysteresis loops suggest that the magnetic ground state of the whole system is complex and thence interesting for next experimental and theoretical studies.

1. Introduction

Multiferroics, where spontaneous long-range magnetic and dipolar order coexist, represent a very attractive class of compounds combining rich and fascinating fundamental physics with potential for multifunctional applications. TbMnO$_3$ is a multiferroic compound which exhibits magnetic ordering of Mn ions with a longitudinal spin density wave propagating along the $a$-axis below $T_N = 41$ K [1]. This magnetic structure changes to the cycloidal phase with a component along the $b$-axis below $T_S = 28$ K [1] which is accompanied by the spontaneous electric polarization along the $b$-axis [2]. On further cooling, Tb spins order independently from the Mn sublattice at $T_i = 7$ K [1]. In the case of TbFeO$_3$, the Fe sublattice orders antiferromagnetically at $T_N = 681$ K and undergoes spin-reorientation phase transition at $T_S = 8$ K [3]. The ordering of Tb ions was also observed at $T_i = 3.1$ K [3]. No spontaneous electric polarization was reported for this compound.

Magnetoelectric coupling in the material is intrinsically very weak, however can induce a large effect in the frustrated materials [4]. In $RMnO_3$ ($R =$ Rare earth) perovskite manganites the magnetic frustration can be induced/tuned by modification of interactions among nearest and next nearest neighbour of Mn. In order to tune the balance between the competitive ferro and antiferromagnetic
interactions leading to frustration magnetic structures, we have performed the study of Fe$^{3+}$ substitution for Mn$^{3+}$ on selected physical properties of TbMn$_{1-x}$Fe$_x$O$_3$ system. In this work we report on the magnetic properties, crystal structure and local symmetry of TbMn$_{1-x}$Fe$_x$O$_3$ determined from heat capacity, magnetization, X-ray powder diffraction and Raman spectroscopy, respectively.

2. Sample preparation and experimental details

Samples of concentration $x = 0; 0.1; 0.3; 0.5; 0.7; 1$ were prepared by vertical floating zone (FZ) method in a 4-mirror optical furnace. As starting materials we have used oxides of MnO$_2$ (purity 3N) and Tb$_4$O$_7$ (purity 3N) provided by Alpha Aesar and Fe$_2$O$_3$ (purity 2N) provided by Sigma Aldrich. The starting materials were mixed in a stoichiometric ratio, cold isostatically pressed into rods and sintered at 1100 °C for 12 hours in air. As a next step the FZ experiment was performed with the parameters: pulling speed of 8 mm/h, feeding speed 7 mm/h, rotation of upper and lower shaft 15 rpm and flowing (2 l/min) air atmosphere.

Crystal structure of all studied samples was investigated by XRPD technique on two diffractometers, both X'Perto Pro PANalytical diffractometes, in the Bragg-Bentano geometry. The Cu K$_{\alpha 1,\alpha 2}$ doublet line was used as a source radiation. The diffractometer uses an X'Celerator detector, with a Ni filter to minimize the K$_{\beta}$ radiation, and a secondary monochromator. The spectra were measured, in the 10° to 70° in 2θ range, with a step of 0.017° and an acquisition time of 100 seconds per step. The calibration and alignment of the diffractometer were made by polycrystalline silica as external standard. Molar heat capacity ($C$) data were measured on bulk, highly textured samples directly cleaved from the grown ingot. For $C$ measurements we have used relaxation method incorporated in the PPMS (Quantum Design) apparatus. Magnetization ($M$) and susceptibility ($\chi$) measurements were performed using the SQUID magnetometer from Quantum Design and powder samples. The room temperature unpolarised Raman spectra were recorded on a LabRam spectrometer using a He-Ne laser at wavelength 633 nm. The laser power was kept below 5 mW on the sample surface to avoid sample heating. The spectra were fitted with a sum of independent damped oscillators on top of a polynomial baseline.

3. Results and Discussion

The ionic radius of both Mn$^{3+}$ and Fe$^{3+}$, for the 6th coordination and in the high spin configuration, is 0.645 pm. However, while Mn$^{3+}$ is Jahn-Teller active, Fe$^{3+}$ is not. The substitution of the Mn$^{3+}$ by the Fe$^{3+}$ ion changes the electronic and magnetic structure, which lead to distortions of the unit cell. For all compounds, a good profile matching accounting for all observed diffraction peaks was obtained with an orthorhombic cell with space group Pnma. The unit cell contains four formula units. The crystal structure consists of oxygen-shared Mn/FeO$_6$ octahedra, whose interstices are occupied by the Tb$^{3+}$ ions.
Figure 1(a) shows the x-dependence of the pseudocubic lattice parameters of the TbMn$_{1-x}$Fe$_x$O$_3$ system, with x ranging from 0 up to 1, defined as follows:

\[ a_{pc} = \frac{a}{\sqrt{2}}, \quad b_{pc} = \frac{b}{2}, \quad c_{pc} = \frac{c}{\sqrt{2}} \]

where \( a, b \) and \( c \) are the lattice parameters.

The x-dependence of the of the pseudocubic lattice parameters enable us to define two regimes. The first regime occurs for \( 0 \leq x < 0.4 \), where the relation \( a_{pc} > c_{pc} > b_{pc} \) found is typically for perovskites whose distortions are dominated by tilting of the octahedrons and Jahn-Teller distortion. The second regime is observed for \( 0.4 < x \leq 1 \), where the distortion is dominated by the octahedral tilting, as it is ascertain from the relation \( a_{pc} > b_{pc} > c_{pc} \).

The volume of the unit cell [figure 1(b)] decreases monotonously with increase of \( x \). The total decrease of the unit cell volume \( \sim 0.7\% \) of the value obtained for TbMnO$_3$. As the tolerance factor of the TbMn$_{1-x}$Fe$_x$O$_3$ system is independent on \( x \), the volume reduction evidences the decrease of the Jahn-Teller distortion, and its suppression for the compositions with \( x \approx 1 \).

Figure 2 shows the unpolarised Raman spectra, recorded at room temperature, in the spectral range 100 – 800 cm$^{-1}$, for several compositions.

Figure 2. Unpolarised Raman spectra, recorded at room temperature, in the spectral range 100 – 800 cm$^{-1}$, for several compositions.

Although the factor group of the aforementioned compound is the same, the differences between the Raman patterns of TbMnO$_3$ and TbFeO$_3$ arise from the different Wyckoff positions occupied by the different atoms in the unit cell. Factor group analysis provides the following decomposition corresponding to the 60 normal vibrations at the $\Gamma$-point of the Brillouin zone:
\begin{align*}
\Gamma_{\text{acoustic}} &= B_{1u} + B_{2u} + B_{3u} \\
\Gamma_{\text{optical}} &= (7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g}) \text{ Raman-active} + (9B_{1u} + 9B_{2u} + 9B_{3u}) \text{ IR-active} + (8A_u) \text{ silent}
\end{align*}

for TbMnO$_3$, while for TbFeO$_3$:

\begin{align*}
\Gamma_{\text{acoustic}} &= B_{1u} + B_{2u} + B_{3u} \\
\Gamma_{\text{optical}} &= (7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g}) \text{ Raman-active} + (7B_{1u} + 9B_{2u} + 9B_{3u}) \text{ IR-active} + (8A_u) \text{ silent}
\end{align*}

As the Fe-content increases, the Raman bands become broader and overlapped up to $x \approx 0.5$, due to the corresponding increase of both substitutional and distortion disorder. On further $x$ increase, the Raman pattern changes in such a way that the main features observed for $0 \leq x < 0.5$ are no longer detected in the Raman spectra of the compounds with $0.7 \leq x \leq 1$. The change of the Raman profile along with the crossing of the $b_{pc}$ and $c_{pc}$ lattice parameters around $x = 0.4$, point toward the probable switch between Jahn-Teller distorted dominated regime to non-distorted Jahn-Teller dominated regime. The change of Jahn-Teller distorted regime induces changes in the magnetic properties, as we will discuss later.

Specific heat measured at higher temperatures (see figure 3) exhibit phonon-like behaviour. We have modelled $C$ in this temperature region by 2 Debye contributions with multiplicity 2 (referred as $\Theta_{D1}$: describes heavy atoms) and 3 (referred as $\Theta_{D2}$: describes oscillations of oxygen atoms). The fitted parameters are summarized in table 1. At lower temperatures we have found peaks on the $C(T)$ data at $T = 41.1(3)$ K and $T = 25.8(3)$ K and broad bump with maximum around 6.5 K for $x = 0$; $T = 32.6(6)$ K for $x = 0.1$; $T = 10.9(2)$ K for $x = 0.9$ and $T \approx 2$ K for $x = 1$. The anomalies for $x = 0$ concentration coincide very well with the changes in the magnetic structure as reported before [1]. Extrapolating from the known changes of the magnetic structure of TbMnO$_3$ [1] we estimate that the peak observed at $T = 32.6(6)$ K for the $x = 0.1$ represents magnetic ordering of Mn/Fe sublattice. On the opposite site of the concentration interval the observed peaks for the concentration $x = 1$ are also completely in agreement with the magnetic phase changes as reported before [3]. In the intermediate region ($0.1 < x < 0.9$) we did not observed any peaks. The explanation might be that there are no phase transitions. This situation is very unlikely, since we have observed anomalies on the magnetization data (see next sections). More plausible explanation is that due to Mn-Fe disorder on the $4b$ crystallographic site the peaks connected with the phase transitions are smeared out.

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{specific_heat}
\caption{Specific heat of the TbMn$_{1-x}$Fe$_x$O$_3$ samples. The full lines represent the best fit as described in text; the dashed line in case of TbFeO$_3$ is guide for the eye.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{inverse_susceptibility}
\caption{Inverse susceptibility of TbMn$_{1-x}$Fe$_x$O$_3$ compounds measured in applied magnetic field $\mu_0 H = 0.1$ T. The lines represent the best fit due to Curie – Weiss law.}
\end{figure}
The inverse susceptibility for concentrations $0 \leq x \leq 0.5$ measured at sufficiently high temperatures exhibits a linear dependence on the temperature (see figure 4). For concentrations $x > 0.5$ the compounds are magnetically ordered already at room temperature and we were unable to measure data at sufficiently high temperatures. The results of the fitting of the experimental data to Curie-Weiss law are summarized in table 1. The fitted effective moments are somehow close to the theoretical moment of free Tb ion ($J = 6$; $\mu_{B} = 9.72 \mu_{B}$), but do not fit at all if one takes into account also the Mn$^{3+}$ and Fe$^{3+}$ magnetic ions (for Mn$^{3+}$ ion in high spin state: $J = S = 2$; $\mu_{B_{\text{Mn high}}} = 4.9 \mu_{B}$, for Mn$^{3+}$ ion in low spin state: $J = S = 1$; $\mu_{B_{\text{Mn low}}} = 2.83 \mu_{B}$; for Fe$^{3+}$ in low spin state: $J = S = 1/2$; $\mu_{B_{\text{Fe low}}} = 1.73 \mu_{B}$ and for Fe$^{3+}$ in high spin state: $J = S = 5/2$; $\mu_{B_{\text{Fe high}}} = 5.92 \mu_{B}$). Also the paramagnetic Curie temperatures ($\theta_{p}$) are uncorrelated from the ordering temperatures obtained experimentally. This raises a question, whether the Curie-Weiss description is correct for this type of compounds.

The inspection of Zero-field-cooled (ZFC) and Field-cooled (FC) magnetization curves (figure 5) revealed, that ZFC bifurcates from FC at $300.0(3)$ K; $91.4(4)$ K; $24.5(5)$ K for $x = 0.5$; 0.3; 0.1, respectively. Such a bifurcation is the indication of the vicinity of the magnetic ordering phase transition. We have defined the magnetic ordering temperature from the ZFC magnetization curves as $T_{N} = 681$ K for TbFeO$_{3}$ [3] and based on the ordering temperature of Mn/Fe sublattice we estimate that Mn$–$O$–$Fe magnetic interaction is weaker than Mn$–$O$–$Mn and Fe$–$O$–$Fe magnetic interaction. Apart from the splitting of the ZFC-FC curves we have observed additional anomalies at $T = 28.9(4)$ K for $x = 0.5$; $42(1)$ K for $x = 0.3$ and double bump at $T = 12.4(3)$ and $7.9(3)$ K for $x = 0.1$. We ascribe these anomalies either to some changes in the structure of already ordered magnetic sublattice (presumably Mn/Fe sublattice) or to ordering of additional magnetic ion (Tb). The fact that the ground state of all studied compounds is complex can be underlined by the non-trivial,
butterfly-type magnetic hysteresis loops (figure 6). For the parent compounds, TbMnO$_3$ and TbFeO$_3$, the magnetic structure was already solved with the help of the neutron diffraction experiments [1, 3]. For the intermediate concentrations ($0 < x < 1$) the differences in the bulk magnetization measurements from the bulk magnetization measurements of the parent compounds suggest that the magnetic structure might be different. That is why the neutron experiment for the concentrations $0 < x < 1$ is strongly required to reveal the magnetic structure.

4. Conclusions
Substitution of Mn BY Fe in TbMn$_{1-x}$Fe$_x$O$_3$ preserves the crystal structure in whole concentration range indicating very good solubility of Fe in TbMnO$_3$ indicating formation of solid solution. The change of the Raman profile along with the crossing of the $b_{pc}$ and $c_{pc}$ lattice parameters around $x = 0.4$ point toward the probable switch between Jahn-Teller distorted dominated regime to non-distorted Jahn-Teller dominated regime for higher concentration of Fe indicating reduction of electron phonon coupling. Only very small substitution of Fe for Mn in TbMnO$_3$ results in drastic changes in any characteristic temperatures of magnetically ordered state as it is indicating by $C(T)$ data which are showing shifts of characteristic peaks from $T = 41.1(3)$ K to $T = 25.8(3)$ K by changing concentration from $x = 0$ to $x = 0.1$. The same situation was observed for TbFeO$_3$ where peak at $T = 8.4(2)$ and $T \approx 2$ K was shifted to $T = 10.9(2)$ K, or is missing for $x = 0.9$. Inspection of paramagnetic state gives several arguments that the Curie Weiss law is valid only partially – the magneto-crystalline anisotropy in this system can be large. Magnetization measurements indicate that magnetic ordering persists in whole concentration range. The butterfly-type magnetic hysteresis loops suggest that the magnetic ground state of the whole system is complex and thence interesting for the future experimental and theoretical studies. Our study provides information concerning magnetic order, crystal structure and lattice dynamics in TbMn$_{1-x}$Fe$_x$O$_3$ and represents the first step in study of multiferroicity in this system. Incoming study of the dielectric properties, spontaneous electric polarisation and coupling between magnetic and electric order in this system will prove the effect of substitution on multiferroic properties of TbMnO$_3$.

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