Weak ferromagnetism in Tb(Fe₀.₂Mn₀.₂Co₀.₂Cr₀.₂Ni₀.₂)O₃ high-entropy oxide perovskite thin films

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We have studied the structural and magnetic properties of Tb(Fe₀.₂Mn₀.₂Co₀.₂Cr₀.₂Ni₀.₂)O₃ (T5BO) high-entropy oxide perovskite (HEOP) thin films. Using synchrotron-based x-ray absorption spectroscopy, employing x-ray magnetic circular dichroism, we performed an element-sensitive study of epitaxial T5BO thin films. The measurements reveal a magnetic multiphase with variable ferromagnetic ordering of all transition metal elements, providing a promising route towards designer ferroic properties in Tb-based HEOP thin films.

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Rare-earth transition metal oxide perovskites with the general formula ABO₃ (A: rare-earth ion; B: 3d transition metal ions) have been the focal point of intense research efforts in recent decades due to a wide range of ferroic properties and functionalities [1,2]. The magnetic interaction between the rare-earth ions and the 3d transition metal ions has been found to be a key ingredient in determining a variety of properties such as magnetocaloric, magnetoelastic, and multiferroic behavior [3–5]. Within this group, Tb-based transition metal perovskites represent an interesting collection of compounds with diverse properties. In this particular series, TbMnO₃ exhibits low-temperature tunable magnetoelastic multiferroic behavior [6,7]. TbFeO₃ exhibits a commensurate spin order driven by Tb-Tb and Tb-Fe interactions [8] and has been reported to be a potentially promising dielectric material [9], along with TbCrO₃, showing similar properties [5]. Far less is known about TbCoO₃ and TbNiO₃, except for the existence of a low-temperature Tb-driven noncollinear magnetic order below 3.3 K in TbCoO₃ [10] and theoretically predicted magnetic ground states in TbNiO₃ [11].

The recent introduction of high-entropy oxide perovskites (HEOPs), both in the bulk [12–14] and thin film form [15,16], provides a new route towards the creation of novel designer ferroics. In high-entropy oxides or alloys, five or more elements are combined in equiatomic fashion to occupy the same lattice sites, resulting in high-quality single crystals [17,18]. The diversity of material designs based on entropy-driven phase stabilization enables the engineering of novel complex oxides with interesting properties, including enhanced wear-resistant coatings, thermoelectric properties, thermal insulation, catalysis, water splitting, and energy storage [17,18]. With respect to HEOPs, La(Fe₀.₂Mn₀.₂Co₀.₂Cr₀.₂Ni₀.₂)O₃ (LSBO) and its various stoichiometric variations have been the main focus of recent research [12,15,19,20]. Based on initial findings, LSBO features predominantly G-type antiferromagnetic order interspersed with ferromagnetic clusters [12,15]. This order competition is believed to be driven by Mn⁴⁺, as B-O-B superexchange bonds containing Mn support ferromagnetic ordering, while most other bond combinations favor antiferromagnetic order [20].

In this Letter, we investigate how replacing La at the rare-earth sites with Tb affects the overall magnetic response and functional properties of HEOP thin films. We demonstrate the stabilization of HEOP Tb(Fe₀.₂Mn₀.₂Co₀.₂Cr₀.₂Ni₀.₂)O₃ (T5BO) single-crystal thin films. In addition to structural characterization, we performed element-sensitive measurements of emerging magnetism in T5BO using x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) spectroscopy at the L₂,₃ absorption edges of all Tb, Mn, Co, Cr, and Ni absorption edges of all Tb, Mn, Co, Cr, and Ni.

Using pulsed laser deposition (PLD), we grew T5BO thin films on atomically flat TiO₂-terminated SrTiO₃ (STO) substrates with a (001) orientation. Thin film growth via PLD offers a variety of single-crystal stabilization mechanisms that go beyond the simple entropy-driven stabilization concept. These include substrate-induced stabilization mechanisms and growth parameters such as substrate temperature, pressure, and laser fluence. A KrF excimer laser (λ = 248 nm) operating at 5 Hz was used for target ablation, with a laser fluence of 1.4 J/cm² and a-target-substrate distance of 5.5 cm. Optimal growth conditions were achieved when the substrate was held at a temperature of 840 °C, with an oxygen partial pressure of 0.12 mbar. A relatively slow growth rate was observed with 20 000 laser pulses resulting in 10-nm-thick films. Following the growth, the films were cooled down to 260 °C with a cooling rate of 4 °C/min under an oxygen pressure of 100 mbar.
FIG. 1. (a) XRD scan of a 10-nm-thick T5BO film grown on a (001)-oriented STO substrate. (b) AFM image of the same film revealing a smooth surface with an average roughness of 0.523 nm. The terraces of the underlying TiO\textsubscript{2}-terminated STO substrate are still visible. The yellow scale bar represents a length of 400 nm. (c) High-resolution STEM image of the same film taken along the [100] direction. (d) Element-sensitive EDX analysis showing a random and homogeneous distribution of transition metal elements throughout the T5BO thin film. The noisy EDX measurement points for some transition metal elements within the substrate area can be attributed to partial overlaps of absorption edges of these transition metals with Ti.

As determined by the x-ray diffraction (XRD) scan shown in Fig. 1(a), the T5BO thin films are single crystalline with an out-of-plane lattice parameter $c = 3.761$ Å. Growth of T5BO onto STO (001) substrates ($a = 3.905$ Å) thus induces tensile film strain. Atomic force microscopy (AFM) was performed to determine the surface morphology [Fig. 1(b)]. The surface of the T5BO films is smooth with an average roughness of 0.523 nm and the terraces of the STO substrates are still visible. Scanning transmission electron microscopy (STEM) measurements demonstrate coherent epitaxial growth of T5BO films on STO (001) with an abrupt interface and a low density of structural defects [Fig. 1(c)]. We performed energy dispersive x-ray (EDX) spectroscopy [see Fig. 1(d)], revealing that the transition metal elements (Cr, Fe, Co, Ni, and Mn) are homogeneously distributed across the T5BO film and no signs of clustering of elements across the investigated region are measured.

Following this structural and chemical analysis, we now turn our focus to the magnetic properties of T5BO. Using a superconducting quantum interference device (SQUID) magnetometer from Quantum Design, we recorded magnetic hysteresis loops, with the magnetic field applied both parallel (in-plane) and vertically (out-of-plane) with respect to the film surface (see Fig. 2). Looking at the in-plane measurements as a function of temperature [Fig. 2(a)], we observe negligible magnetic hysteresis of the magnetization with a small opening and large saturation fields beyond 5 T. The out-of-plane magnetization curves [Fig. 2(b)] are shaped differently, with the measurement at 2 K showing a wasp-waisted hysteresis typical of complex multiphase ordering, similar to previous reports on L5BO bulk crystals and thin films [12,15]. The shape of the out-of-plane hysteresis curves changes with increasing temperature, resembling that of a soft magnet with small coercivity at 60 K [Fig. 2(b)]. The SQUID magnetometry data indicate ferromagnetic ordering with a significant strain-induced perpendicular magnetic anisotropy. This persistent soft magnetic response to out-of-plane applied fields stands in contrast to comparable L5BO thin films grown on (001) STO, where a significant hardening of the magnetization reversal is reported with increasing temperature [15]. A comparison of zero-field-cooled and field-cooled magnetization measurements (see SM 2 in the Supplemental Material [23]) indicates a transition temperature around 75 K.

Although SQUID measurements provide a macroscopic view of the overall magnetic response of the T5BO thin films, synchrotron-based XAS, employing x-ray magnetic circular dichroism (XMCD) [21], can pick the magnetic contributions apart on an element-by-element basis. This is done by recording x-ray absorption spectra around the L\textsubscript{2} and L\textsubscript{3} absorption edges of all five transition metal elements within the 5B\textsubscript{block} using both circular right ($c^+$) and circular left ($c^-$)
pure presence of octahedral Ni\textsuperscript{2+} spectra for Ni [shown in Fig.3(a)] indicate a dominant if not experimental broadening and the simulation is shifted by a Lorentzian [25]. To correctly fit the experimental data, a broadening of each edge, associated to lifetime effects, is simulated by the reduction of the Slater integrals. The intrinsic the spin orbit coupling and the screening and mixing effects, field splitting, used to account for the octahedral component, by tuning the parameters, which are related to the crystal out by selecting the electric configuration of the element and ligand field theory (red lines). The computations are carried out by selecting the electric configuration of the element and by tuning the parameters, which are related to the crystal field splitting, used to account for the octahedral component, the spin orbit coupling and the screening and mixing effects, simulated by the reduction of the Slater integrals. The intrinsic broadening of each edge, associated to lifetime effects, is simulated by convoluting the calculated natural spectra with a Lorentzian [25]. To correctly fit the experimental data, a Gaussian broadening of 0.2 eV is used to account for the experimental broadening and the simulation is shifted by −2.1 eV in the photon energy. From the analysis of these spectra, the following picture emerges: The XAS and XMCD spectra for Ni [shown in Fig. 3(a)] indicate a dominant if not pure presence of octahedral Ni\textsuperscript{2+} [28,29], with a large magnetic moment. The Fe L\textsubscript{2,3} spectra [Fig. 3(b)] are consistent with a dominant presence of octahedral Fe\textsuperscript{3+} (O\textsubscript{h}) and the absence of tetrahedral Fe\textsuperscript{3+} [26]. The Co XAS and XMCD spectra [see Fig. 3(c)], in contrast, reveal a mixture of high-spin Co\textsuperscript{2+} and low-spin Co\textsuperscript{3+}. For this element, the XMCD signal arises from the estimated 23\% of octahedral Co\textsuperscript{2+} (O\textsubscript{h}) [27], whereas the 77\% low-spin Co\textsuperscript{3+} does not contribute to the XMCD signal. From the XAS and XMCD spectra of Mn [Fig. 3(d)], we derive a dominance of Mn\textsuperscript{4+} [30,31]. Similarly, the Cr spectra (see the Supplemental Material [23]) show a pure presence of octahedral Cr\textsuperscript{3+} [32]. From this mixture of valencies, we can already conclude ferromagnetism to emerge from X-O-Y superexchange interactions involving Mn\textsuperscript{4+}, for example Mn\textsuperscript{4+} − O − Co\textsuperscript{2+}, Mn\textsuperscript{4+} − O − Ni\textsuperscript{2+}, while most combinations involving Fe or Cr are expected to support antiferromagnetism [19].

The orbital (m\textsubscript{l}), spin (m\textsubscript{s}) and total magnetic moment (m\textsubscript{t} = m\textsubscript{l} + m\textsubscript{s}) per average transition metal ion can be estimated by applying XMCD sum rules [33–35] to the recorded XAS and XMCD spectra. For L\textsubscript{2,3} XMCD spectra, the signal is directly proportional to the atomic magnetic moment of the excited transition metal ion. Using an approach where spin-quadrupole contributions are neglected [36], we extracted the orbital (m\textsubscript{l}) and spin (m\textsubscript{s}) moments, in addition to the ratio (m\textsubscript{l}/m\textsubscript{s}). It should be noted that sum rules require a good separation between the L\textsubscript{2} and L\textsubscript{3} absorption edges, which for Ni, Co, and Fe is far better than for early transition metal elements such as Cr and Mn. For the latter elements, significant correction factors are needed [37]. Leaving Cr out for the aforementioned reasons, the results of these calculations are summarized in Table I. The most glaring results from this sum rule analysis are the large spin magnetic moment obtained for Mn (m\textsubscript{s} = −1.6 \(\mu\textsubscript{B}\)), which is more than three times the spin magnetic moment of Fe (m\textsubscript{s} = −0.46 \(\mu\textsubscript{B}\)). Furthermore, the ratio m\textsubscript{l}/m\textsubscript{s} = 0.63 for Co is significantly larger than for all the other elements, which can be attributed to distortions resulting from the tensile strain in the T5BO thin film [38].

To distinguish how the five transition metal elements contribute to the magnetization reversal process in the T5BO films, we recorded XMCD hysteresis loops [39] for all transition metal elements. In an out-of-plane geometry, we recorded XMCD hysteresis loops for magnetic fields between −6 T and +6 T with a step size of 0.1 T per measurement. The measurements were conducted at 2.5 and 50 K (Fig. 4). Interestingly, it is Ni that shows the largest opening in its hysteresis curve, which closes around 50 K. Mn, Co, and Fe show similar XMCD hysteresis loops, but with decreasing XMCD signal upon saturation. Finally, Cr features only a very weak hysteresis, which disappears around 50 K. These element-sensitive XMCD hysteresis loops, with their clear openings, differ from the macroscopic hysteresis loops shown in Fig. 2. This can be attributed to the fact that we probe a limited spot size (around...
160 × 160 (μm²) and depth of 4–6 nm with XMCD, while SQUID magnetometry measures the whole volume of film and substrate, including the interface between them.

In summary, we demonstrated the growth of high-quality single-crystal entropy-stabilized T5BO thin films, which feature a complex magnetic multiphase as a result of a large range of possible superexchange interactions between the transition metal elements within the 5B block. Combinations involving Mn⁴⁺ and high-spin Co²⁺ are likely drivers of the observed ferromagnetism in T5BO, which is embedded in an antiferromagnetic matrix. This type of multiphase ordering appears to be a common feature in HEOPs. Our element-sensitive study provides a route for further studies on how rare-earth ion choices and stoichiometric variations within the transition metal block affect the ionic configuration and interactions, with direct consequences on the overall ferroic properties. As an example, it remains an interesting open question on how the portion of high-spin Co²⁺ can be tuned by either rare-earth ion selection or strain-induced effects by growing T5BO thin films on various substrates.

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**TABLE I.** XMCD sum rule analysis for four transition metal ions in T5BO. Due to the large overlap of the L₂ and L₃ absorption edges in Cr and the inaccuracies that come with it, Cr was left out of the sum rule analysis.

<table>
<thead>
<tr>
<th>Element (corr. factor)</th>
<th>No. holes</th>
<th>$m_S$ (μB)</th>
<th>$m_L$ (μB)</th>
<th>$m_L/m_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (0.9)</td>
<td>2</td>
<td>−0.36(3)</td>
<td>−0.086(8)</td>
<td>0.23</td>
</tr>
<tr>
<td>Mn (0.59)</td>
<td>7</td>
<td>−1.61(1)</td>
<td>0.014(1)</td>
<td>−0.009</td>
</tr>
<tr>
<td>Co (0.89)</td>
<td>3</td>
<td>−0.13(1)</td>
<td>−0.082(8)</td>
<td>0.63</td>
</tr>
<tr>
<td>Fe (0.68)</td>
<td>5</td>
<td>−0.46(4)</td>
<td>−0.038(3)</td>
<td>0.08</td>
</tr>
</tbody>
</table>

FIG. 4. XMCD hysteresis loops recorded at the L₃ edge of all five transition elements (Ni, Mn, Co, Fe, and Cr) involved in T5BO thin films. All measurements were performed with an out-of-plane magnetic field.