Measuring room-temperature intrinsic multiferroic properties by excluding the secondary magnetic inclusion contribution

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The assertion that a new material could become a potential single-phase and room-temperature functioning multiferroic material may be confounded by the presence of minor amount of secondary magnetic inclusions, especially in the Aurivillius-type material system. In this study, we demonstrated that the derivative thermo-magneto-gravimetry (DTMG) technique can be a sensitive tool to identify and quantify the magnetic secondary phases in the $\text{Bi}_7\text{Fe}_{2.25}\text{Co}_{0.75}\text{Ti}_3\text{O}_{21}$ ceramic, which shows the potential to become a single-phase multiferroic material. The accuracy of this DTMG measurement experimentally reaches to ~0.5 wt.%, far below the detection limit of the traditional X-ray diffraction. The impurity identified in the specimen is the ferrimagnetic CoFe_2O_4 spinel phase with an amount of ~3.6 wt.%. Significantly, the room-temperature intrinsic magnetism of the ceramic was measured, which is solely from the main phase.

INTRODUCTION

Seeking a single-phase and room-temperature functional multiferroic material has been a long-standing challenge, although it is of great importance to understand fundamental physics and to explore the potential application [1–3]. As candidates with the potential to become a single-phase multiferroic material exhibiting simultaneous coexistence of ferroelectric (FE) and ferromagnetic (FM) orders, layer-structured oxides with a general formula of $\text{Bi}_{n+1}\text{Fe}_{n-3}\text{Ti}_3\text{O}_{3n+3}$ (n denotes an integer corresponding to the number of the sandwiched perovskite layers) have attracted increasing attention in recent years [4–6]. Recently, numerous studies regarding to the realization of a remarkable coexistence of FE and FM properties at room temperature (RT) from these layered oxides by chemical modifications, e.g., various A- or B-site doping, have been reported [7–11]. However, the question whether the multiferroic responses in these materials are intrinsic from the

main phase or from the secondary phase formed during the sample preparation is still under debate [12,13]. Therefore, some new methods or sensible techniques have to be developed to identify intrinsic multiferroic responses in studying such complicated layered oxides.

Normally, the X-ray diffraction (XRD) method provides a direct way to detect a secondary phase in powders, thin films or bulk ceramics, but this method cannot deal with the case that the weight ratio of the impurity is below a certain critical level (~5 wt.%, for example). Scanning electron microscopy (SEM) and/or electron backscatter (EBS) coupled with an energy dispersive X-ray spectroscopy (EDX/EDS) [14] can also offer useful information to detect the possible existence of secondary phase, but they are limited to very small sample volumes [12]. Interestingly, the derivative thermo-magneto-gravimetry (DTMG) technique [15], using the principle that magnetic transition affects weight, is very promising for tracing various subtle changes of the magnetic property vs. temperature, especially the magnetic contributions.

In this study, we applied the DTMG technique to quantitatively discern the content and the magnetic contribution of the possible ferromagnetic/ferrimagnetic inclusions in a $\text{Bi}_7\text{Fe}_{2.25}\text{Co}_{0.75}\text{Ti}_3\text{O}_{21}$ (BFCT) layered oxide ceramic, which is chosen because of its relatively stronger FE and FM properties observed at RT [16]. The impurity identified in BFCT ceramic is CoFe_2O_4 with a weight ratio of ~3.6% and its magnetic contribution to weight loss is ~15%. Significantly, it was testified that this layered oxide has good magnetic response at RT, which is intrinsic. Our experimental results also suggested that the measurement accuracy of DTMG method can reach to ~0.5 wt.%, far below the detection limit of XRD. In short, this DTMG method is

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powerful and effective to detect and quantify the ferromagnetic/ferrimagnetic response, which can be easily applied to other magnetic materials and be of great help to explore new magnetic materials.

EXPERIMENTAL SECTION

Materials synthesis

Polycrystalline BFCT was prepared by a modified Pechini method. Detailed synthesis process was as follows: $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ according to the stoichiometric ratio of the BFCT were dissolved into HNO_3 as precursors. $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ and ethylene diamine tetraacetic acid (EDTA) were added to the solution as the coordinating agents. Then $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added dropwise into the solution to adjust the pH value to 6–7, and the precursors formed a stable transparent solution. Then, the precursor sol was heated until combustion inside the crucible. Afterwards, the product was calcined at 1025 K for 2 h to remove organic residues. The obtained powders were pressed into pellets and then were sintered in a hot-pressed furnace at 1153 K for 3 h, under the atmosphere of mixed Ar/O_2 gas and a pressure of 10 MPa (Materials Research Furnaces Inc., Suncook, NH). The powders of $\text{BiFe}_{0.75}\text{Co}_{0.25}\text{O}_3$ and CoFe_2O_4 , the possible impurity phases, were also synthesised by the same method. Co_3O_4 (analytic pure) and Fe_3O_4 (analytic pure) powders were used as reference samples.

Characterization and measurements

XRD patterns of the samples were obtained by using a TTR-III X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). Rietveld refinements of the XRD pattern were made using GSAS software. Magnetic properties were characterized by vibrating sample magnetometer (VSM) option of the Quantum Design physical property measurement system (PPMS, USA). Thermo-magneto-gravimetry (TMG) measurements were realized using Thermo-gravimetric Analysis (TGA Q5000IR, USA) to measure the weight of a sample as a function of testing temperatures at an applied magnetic field. The TMG measurements were performed in nitrogen atmosphere at a heating rate of 20 K or 5 K min^{-1} with or without a 0.02 T applied magnetic field. DTMG gave the derivative weight of a sample with respect to temperatures. For the ferroelectric measurements, the pellets were polished to a thickness of $\sim 0.3 \text{ mm}$ and then Ag was evaporated on both sides as electrodes. The ferroelectric measurements were conducted using a Precision LC ferroelectric analyzer (Radiant Technology, USA) at an applied frequency of 10 Hz.

RESULTS AND DISCUSSION

Fig. 1a shows the XRD patterns of the BFCT powder and some reference samples, such as $\text{BiFe}_{0.75}\text{Co}_{0.25}\text{O}_3$, CoFe_2O_4 , Fe_3O_4 and Co_3O_4 . The Rietveld refinement of BFCT XRD pattern was performed using GSAS software, as shown in Fig. 1a. The pattern was refined with the orthorhombic lattice space group of $A2_1am$ and the observed peaks are all in good accordance with the standard powder diffraction data for the four-layer $\text{Bi}_5\text{FeTi}_3\text{O}_{15}$ (JCPDS, No.82-0063). The lattice parameters turn out to be $a = 5.462 \text{ \AA}$, $b = 5.434 \text{ \AA}$, $c = 41.115 \text{ \AA}$ ($R_p = 12.6\%$). According to the refinement results, the quantity of the possible impurity phase, if it exists, should be below XRD instrumental resolution. Keeney *et al.* [13,17] had reported that the magnetic secondary phase from Co substituted Aurivillius-type multiferroic thin film is a CoFe_2O_4 type spinel phase. However, for our ceramic, it is very difficult to distinguish the possible impurity phases from the main Aurivillius phase by the XRD analysis, because the positions of the main peaks of the possible magnetic inclusions (e.g., CoFe_2O_4) and the part peaks of the Aurivillius phase appear to overlap, as shown in Fig. 1a.

Figure 1 Characterizations of BFCT polycrystalline ceramic. (a) Observed (red solid circles), calculated (black solid lines) and difference (blue solid line) XRD patterns of BFCT. No second phase is detected. XRD patterns of $\text{BiFe}_{0.75}\text{Co}_{0.25}\text{O}_3$, CoFe_2O_4 , Fe_3O_4 and Co_3O_4 are shown for reference. (b) SEM image of the BFCT ceramic.

The SEM image of the BFCT was taken from fresh fracture surface and shown in Fig. 1b. The ceramic prepared using the hot-press sintering technique is very dense with well compact grains and its relative density determined by the Archimedes method is ~93%.

M - H hysteresis loops of the BFCT measured at different temperatures are shown in Fig. 2a, and the remnant magnetization ($2M_r$) and the saturation magnetization (M_s) extracted from these hysteresis loops are illustrated in Fig. 2b. $2M_r$ and M_s decrease as the testing temperature increases, but still maintain acceptable values when the temperature reaches to 373 K, indicating a fairly RT operation stability for device applications. It is noted that $2M_r$ and M_s of the BFCT at RT are approximate 2.4 and 7.7 emu g⁻¹, respectively. This $2M_r$ value is about three orders of magnitude higher than that of Bi₇Fe₃Ti₃O₂₁ (~2.67 memu g⁻¹) [18] and Bi₅Fe_{0.5}Co_{0.5}Ti₃O₁₅ (~7.8 memu g⁻¹) [11]. From Fig. 2a, the material's Curie temperature (T_C) can be deduced among 673–753 K, which is much higher than the RT. Lu *et al.* [19] had reported an exchange interaction (e.g., exchange bias) between two magnetic phases can also provide a sensitive

Figure 2 Room temperature magnetic property of the BFCT ceramic. (a) M - H hysteresis loops of BFCT at 298, 398, 498, 598, 673 and 753 K. The inset shows an enlarged central region. (b) $2M_r$ and M_s of BFCT vs. temperatures.

way to identify the ferrimagnetic phase. But this method requires a ferrimagnet/antiferromagnetic interface formed at the grain surface, and it is hardly to quantify the magnetic secondary phase. In addition, no distortion of the M - H hysteresis loops was observed in our ceramic sintered at 1153 K, suggesting that the exchange interaction between the main phase and the magnetic secondary inclusions (if it exists) is very weak. Therefore, new methods or sensible techniques have to be developed to identify and quantify the magnetic secondary phases.

According to the above results of magnetic measurements, we deduced that the decisive magnetic second phase inclusion, if it exists, may be the CoFe₂O₄ type spinel phase. The reasons may include as follows: 1) T_C of CoFe₂O₄ ferrite particles is near ~700 K [20], and $2M_r$ and M_s of bulk CoFe₂O₄ at RT are about 53 and 79 emu g⁻¹ [21] (higher than the values of CoFe₂O₄ ferrite particles, $2M_r$ ~29 emu g⁻¹ and M_s ~62 emu g⁻¹), respectively, meaning that a low content can make a big magnetic response; 2) Co₃O₄ is an antiferromagnet (T_N ~30 K) [22] and the T_C of Fe₃O₄ was reported a value of ~875 K [23], which are both beyond 673–753 K limits; 3) because the BFCT was calcined at 1023 K and sintered at 1153 K, it seems that the Fe₃O₄, if it exists, should be oxidized to α -Fe₂O₃ (normally, Fe₃O₄ initially forms γ -Fe₂O₃ at about 450 K, and then changes to α -Fe₂O₃ at about 623 K [24]). Yet, α -Fe₂O₃ is a weak ferromagnetic material at RT and its magnetization is less than 1 emu g⁻¹ [25]; 4) the BiFe_{0.75}Co_{0.25}O₃ has the magnetic property ($2M_r$ ~9 emu g⁻¹ and M_s ~13 emu g⁻¹) in the same order with that of the BFCT, implying that a low content of BiFe_{0.75}Co_{0.25}O₃ only has a little small magnetic response. Therefore, we will focus our discussion on the ferromagnetic second phase CoFe₂O₄.

Fig. 3 shows thermo-gravimetric (TG) curves of

Figure 3 Thermo-gravimetric curves of CoFe₂O₄ at three times thermo-cycling measurements under a 0.02 T applied magnetic field with a heating/cooling rate of 20 K min⁻¹.

CoFe_2O_4 at three times thermo-cycling measurements under a 0.02 T applied magnetic field with a heating/cooling rate of 20 K min^{-1} . A T-TG loop is clearly observed. What's more, this loop can be well repeated by multi-measurements, indicating that the TMG technique has a good response to magnetic materials. The curves measured at the heating processes and the cooling processes do not overlap each other, indicating a thermal hysteresis. We also note that a sharp weight loss of CoFe_2O_4 occurs at approximately 721 K in the TG curve at heating processes, however, a sharp weight gain occurs at approximately 670 K at cooling processes. These features imply that the ferrimagnetic

CoFe_2O_4 phase may be identified by the sharp weight loss/weight gain using the TMG technique in Aurivillius-type multiferroic material, if it is assumed that it does not interact with the Aurivillius phase matrix, in view of considerable evidences of phase separation between CoFe_2O_4 spinel phase and perovskite structures such as BiFeO_3 [26], BaTiO_3 [27] and PbTiO_3 [28].

Fig. 4 shows weight loss and DTMG curves of the BFCT at the heating processes through seven times thermo-cycling measurements. The 1st–4th conditions were measured at the heating rate of 20 or 5 K min^{-1} under 0.02 T, and the 5th–7th conditions were measured at the heating

Figure 4 Thermo-gravimetric and the DTMG curves of the heating processes of the BFCT through seven times thermo-cycling measurements with/without applied magnetic field. All the cooling processes are at the rate of 20 K min^{-1} without applied magnetic field.

rate of 20 or 5 K min⁻¹ under 0 T. All cooling processes (no shown) are at the cooling rate of 20 K min⁻¹ without applied magnetic field. The 1st TG curve is different from that of the 2nd and 3rd, due to the possible existence of water, pores or specific distribution of magnetic domains in initial sample. The 2nd–4th curves have the similar trends, indicating that the phenomena can be well repeated. However, the different heating rates result in a small shift of the peaks from the DTMG curves, indicating the existence of a thermal hysteresis which is consistent with above discussion. From the 1st–4th measurements, we can find that the FM–paramagnetic (PM) transition of the sample has a broad temperature range, about 660–740 K, in the TG curves, and this transition consists of about three peaks in DTMG curves. What's more, the weight loss temperature of CoFe₂O₄ (~721 K) is within this temperature range. This phenomenon implies that the BFCT sample may contain the CoFe₂O₄ inclusions. The 5th TG curve is near horizontal, confirming that the thermal active contribution is very small. Similar curves from the 5th–7th measurements indicate that the phenomena without applied magnetic field can be also well repeated, even though the heating rates are different. If we subtract the 5th TG curve from the 2nd TG curve, the weight loss from the only contribution of the FM–PM transition will be detected. That is how to deduct the influence of thermal active to weight loss.

To detect the sensitivity of this method, some relevant tests were also done. Fig. 5 shows the weight loss and the DTMG curves of the ZrO₂-*x* wt.% CoFe₂O₄ (*x* = 0.5, 1, 3, 6, 13 and 100), in the same conditions of nitrogen atmosphere at a heating rate of 20 K min⁻¹ with a 0.02 T applied field. Under the magnetic field, weight loss from the thermal active contribution has been automatically deducted. Because the first heating process is easily influenced by the initial condition, each weight loss curve chosen to discuss corresponds to the second heating process of the samples. Since ZrO₂ is not a magnetic material, weight loss after deduction of the thermal active contribution should be derived from the FM–PM transition of the CoFe₂O₄ phase. From Fig. 5, we can acquire three conclusions: 1) even though the weight fraction of CoFe₂O₄ changes in samples, the FM–PM transition positions of the samples are nearly invariable (~721 K); 2) in samples, the lower weight fraction of the CoFe₂O₄ exists, and the smaller variation of weight loss is observed; 3) the accuracy of the DTMG measurement experimentally can reach ~0.5 wt.%. Intriguingly, according to the peak area from the DTMG curves, weight loss of CoFe₂O₄ and ZrO₂-13 wt.% CoFe₂O₄ is about 0.955% and 0.128%, respectively. The value of 0.128%/0.955% is approximate 13.4%, consistent with the weight fraction

Figure 5 Weight loss and the DTMG curves of the ZrO₂-*x* wt.% CoFe₂O₄ (*x* = 0.5, 1, 3, 6, 13 and 100), in the same conditions of nitrogen atmosphere at a heating rate of 20 K min⁻¹ with a 0.02 T applied field. Weight loss from the thermal active contribution has been automatically deducted. The peak area (*S*) calculated from the DTMG curve is also shown.

of CoFe₂O₄ in ZrO₂-13 wt.% CoFe₂O₄. More importantly, this way also adapts to other ZrO₂-*x* wt.% CoFe₂O₄ samples. These results indicate that it is feasible to quantify the weight ratio of CoFe₂O₄ inclusions in Aurivillius-type multiferroic ceramics using this method.

Therefore, the DTMG curve of the BFCT ceramic was fitted and decomposed into individual Lorentz components. The weight loss and fitted DTMG curves of the BFCT sample and reference CoFe₂O₄ are shown in Fig. 6, which had deducted the thermal active contribution. An obvious peak around 721 K could confirm the presence of the CoFe₂O₄ spinel phase in the BFCT ceramic. According to this peak area, the content of the CoFe₂O₄ inclusions can be estimated around 3.6 wt.% (0.034%/0.955%). This

Figure 6 The calculated weight loss (the thermal active contribution is deducted) and DTMG curves of BFCT and CoFe₂O₄, measured at the heating rate of 20 K min⁻¹ with a 0.02 T magnetic field. The DTMG curves were fitted and decomposed into individual Lorentz components. The quantity and corresponding percentage of the contribution to weight loss from each component were shown too.

value is below the detection limit of XRD, consisting with the above XRD result. In our previous work, it was demonstrated that the Bi₇Fe_{2.25}Co_{0.75}Ti₃O₂₁ powder synthesized by the hydrothermal method presents the co-existence of 5- and 4-layer Aurivillius-type perovskite structures [16]. This could account for the rest two peaks at ~687 and ~710 K in Fig. 6. Comparing the contributions from the main Aurivillius phases (85%) and the second phase inclusions (15%) to weight loss, we may determine that the observed magnetic contribution to weight loss in sample is mainly attributed to the Aurivillius phases. Assuming that $2M_r$ and M_s are directly proportional to the weight fraction of the inclusions, 3.6 wt.% of CoFe₂O₄ (considering $2M_r$ ~53 emu g⁻¹ and M_s ~79 emu g⁻¹ [21]) at RT would give a $2M_r$ of 1.9 emu g⁻¹ and M_s of 2.8 emu g⁻¹. The intrinsic $2M_r$ and M_s of the Aurivillius phases at RT can be estimated around 0.5 and 4.9 emu g⁻¹, respectively, by deducting the contribution of the CoFe₂O₄ inclusions. Therefore, we can assert that although the BFCT sample contains 3.6 wt.% of unwanted CoFe₂O₄ inclusions, it has intrinsic ferromagnetism. In addition, we found that this method for the detection and quantification of second phase also adapts to other Aurivillius multiferroic materials, which will be shown in elsewhere.

In addition, the intrinsic FE polarization of the BFCT was confirmed. Fig. 7a presents P - E hysteresis loops measured at RT under different applied fields. Remanent polarization ($2P_r$) and coercive field ($2E_c$) measured under the field of 130 kV cm⁻¹ are approximate 14 μ C cm⁻² and 130

kV cm⁻¹, respectively, which are comparable to Bi₄Ti₃O₁₂ (~15 μ C cm⁻²) [29] and Bi₅Fe_{0.5}Co_{0.5}Ti₃O₁₅ (~13 μ C cm⁻²) [11]. In Fig. 7b, $2P_r$ increases when increasing the driving electric field. However, the P - E loops are still far from saturation (limited by the instrument or by the sample breakdown). This phenomenon is in very good agreement with the previous report [11]. To identify a possibility of artificial polarization from the leakage current, the pulsed polarization PUND measurement was performed and the results are also shown in Fig. 7b. The pulsed remanent polarization ΔP (switched polarization – non-switched polarization) [30] is consistent with $2P_r$ determined from the P - E loops. This result indicates that the leakage current contribution is very small and confirms the existence of intrinsic FE polarization in the specimen.

CONCLUSION

In summary, we developed a comprehensive and reliable method to detect and analyse ferromagnetic inclusions in multiferroic ceramics. The measurement accuracy of the DTMG method experimentally can reach ~0.5 wt.%, far below the detection limit of XRD. Furthermore, we demonstrated its application to the analysis of the BFCT ceramic, in which the CoFe₂O₄ secondary phase was identified and the concentration was estimated to be ~3.6 wt.%. Significantly, the room-temperature and intrinsic multiferroic properties from the main Aurivillius phases were verified, suggesting that the sample is a new single-phase multiferroic material.

Figure 7 Room temperature ferroelectric property of the BFCT ceramic. (a) P - E hysteresis loops of the BFCT ceramic under different applied fields. (b) ΔP from PUND measurement and $2P_r$ from the P - E loops of BFCT at RT.

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Conflict of interest The authors declare that they have no conflict of interest.

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中文摘要 判断新的材料是否是一个室温单相多铁性材料需要认真的鉴定评价, 特别是对于 Aurivillius 相多铁材料. 这类材料中易生成微量的具有铁磁性的杂质, 从而混淆对其本征磁性能的判断. 本论文介绍了一种磁失重方法, 并应用该方法判断和量化了 Aurivillius 相层状结构陶瓷 $\text{Bi}_7\text{Fe}_{2.25}\text{Co}_{0.75}\text{Ti}_3\text{O}_{21}$ 中的磁性杂质. 该方法的测量精度远高于 X-射线仪器的精度, 能够辨别出含量仅为 0.5% 重量的杂质. 最终结果表明陶瓷 $\text{Bi}_7\text{Fe}_{2.25}\text{Co}_{0.75}\text{Ti}_3\text{O}_{21}$ 中的磁性杂质是尖晶石相 CoFe_2O_4 , 其含量约占总质量的 3.6%. 通过该方法同时确定了该陶瓷的室温固有磁性. 本研究不仅展示了磁失重方法, 而且通过固有磁性和固有铁电性的鉴定, 证明了该陶瓷是一种新的室温单相多铁性材料.