Room-temperature ferromagnetic/ferroelectric BiFeO₃ synthesized by a self-catalyzed fast reaction process

Jiangtao Wu,[a] Shaoyu Mao,[*a] Zuo-Guang Ye,[*ab] Zhaoxiong Xie[a] and Lansun Zheng[a]

Bismuth ferrite BiFeO₃ has attracted a great deal of interest because of its multiferroic properties. However, BiFeO₃ synthesized by conventional methods in the forms of single crystals, ceramics or thin films only exhibit ferroelectricity and antiferromagnetic order at room temperature, with weak ferromagnetism appearing at very low temperatures. To fully explore the potential of multiferroism in such applications as new memory devices, it is necessary to synthesize materials that show ferromagnetic order at room temperature as well, which will *a priori* allow for magnetoelectric coupling. In this paper, we report a new synthetic technique for the synthesis of BiFeO₃ that exhibits unusual ferromagnetic properties. This method involves a low temperature fast solid state reaction based on tartaric acid. The mechanism of the reaction deduced from thermogravimetric analysis (TGA) and differential thermal analysis (TGA) suggests that a self-catalyzed process in the presence of iron and bismuth oxides triggers the oxidation of tartaric acid at low temperature and gives out a large amount of heat, which, in turn, leads to the formation of BiFeO₃. The BiFeO₃ synthesized in this way is ferromagnetic. The origin of the unusual ferromagnetism is supposed to be associated with point defects of oxygen vacancies generated during the self-catalyzed extremely fast exothermic reaction, which suppress the spin circular cycloid in BiFeO₃. Ferroelectric hysteresis loops are displayed in the BiFeO₃ samples. The presence of room temperature ferromagnetic and ferroelectric orders makes BiFeO₃ a truly multiferroic material potentially interesting in such applications as magnetoelectric devices.

Introduction

Multiferroic materials exhibit some unique properties with the presence of at least two kinds of long-rang ordering among ferroelectricity (or antiferroelectricity), ferromagnetism (or antiferromagnetism) and ferroelasticity. Single-phase compounds in which both ferromagnetism and ferroelectricity arise independently and may couple to each other to give rise to magnetoelectric interactions are ideal materials for applications, but are unfortunately rare.[1] Bismuth iron oxide, BiFeO₃ (BFO), has attracted increasing attention because it is one of few multiferroic materials at room temperature, which presents interest for potential applications not only in lead-free ferroelectric devices but also in devices using coupled electric polarization and magnetization, such as new generation of memory and sensors. Perovskite BFO has a ferroelectric Curie temperature T_C of 1103 K,[2] and an antiferromagnetic Néel temperature T_N of 643 K.[3] The structure of bulk BFO has been extensively studied. The lattice of BFO crystal is a rhombohedrally distorted perovskite with the unit cell parameters of $a = b = c = 5.634$ Å and $\alpha = 59.348°$.[4] However, bulk BFO presents some issues, namely, the difficulties in preparing single-phase samples, a small remnant polarization (much smaller than the theoretically calculated spontaneous polarization), a high coercive field, a large leakage current and weak magnetoelectric coupling effects. Recently, many attempts have been made in order to overcome these drawbacks. For example, a large ferroelectric polarization and a small net magnetization of the Dzyaloshinskii-Moriya type have been realized on BFO thin films.[5] Single-phase BFO ceramics with a high resistivity and a large polarization were synthesized by a rapid liquid phase sintering technique.[6] BFO powders of nanosize were obtained by mechanochemical synthesis,[7] nonthermal electrochemical synthesis,[8] sol–gel based soft chemical route[9] and hydrothermal synthesis.[10] The solid solution of $(BiFeO_3)_{1-x}(PbTiO_3)_x$ was recently studied and shown to exhibit multiferroic properties.[11]

The weak ferromagnetic character of BFO mainly results from the canting of the antiferromagnetic sublattice which exhibits a spiral spin structure.[12] A number of studies have been carried out to improve the magnetic performance of BFO by chemical or physical modifications. For instance, the effect of yttrium doping on the improvement of the dielectric properties and magnetic switching behavior in BFO was studied by Mishra *et al.*,[13] and the electric-field control of local ferromagnetism in BFO films was reported by Chu *et al.*[14]

For the conventional synthesis of BFO, solid state reaction is the most commonly used method, in which bismuth oxide and iron oxide are milled and heated in a furnace at 810 °C or higher.[15] In general, repeated grinding, pelletizing, high temperature heating, and long reaction durations are needed, because solid state reaction is heterogeneous reaction in which the

[a]State Key Laboratory for Physical Chemistry of Solid Surface & Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China. E-mail: symao@xmu.edu.cn
[b]Department of Chemistry and 4D LABS, Simon Fraser University, 8888 University Drive, Burnaby, British Columbia, V5A1S6, Canada. E-mail: zye@sfu.ca

formation of the product phase is controlled by the diffusion and counter-diffusion of atoms and/or ionic species between reactants and products. It is our belief that, by means of appropriate chemical and structural modifications *via* nouvelle synthetic strategies, it may be possible to modify the antiferromagnetic circular cycloid structure of BFO, giving rise to long-range ferromagnetism at room temperature. In pursuing this concept, we notice that both iron oxide and bismuth oxide are known to be excellent catalysts. They can both absorb and activate oxygen molecules,[16] and thereby, can catalyze some reactive organic substance, such as tartaric acid, glycin, sucrose, *etc.* When these organic substances react with oxygen, they give out a great deal of heat. Through thermodynamics calculation,[17] it is shown that with the help of sufficient heat, iron oxide and bismuth oxide may react with each other to form $BiFeO_3$. On the other hand, fast reaction at very high heating and cooling rates could possibly produce metastable and/or structurally imperfect products which may exhibit new or unusual properties.

In this work, we have developed a new synthetic route for the preparation of multiferroic $BiFeO_3$ by a self-catalyzed low temperature fast solid state reaction of bismuth oxide and iron oxide in the presence of tartaric acid. The BFO powder synthesized is characterized by X-ray diffraction (XRD). Most interestingly, the as-synthesized BFO powder exhibits saturated magnetic hysteresis loop at room temperature and is strongly attracted to a magnet, indicating ferromagnetism in BFO.

Experimental

The chemical reactants used in the synthesis were bismuth oxide (Bi_2O_3), alpha-iron oxide (α-Fe_2O_3), and tartaric acid ($C_4H_6O_6$). All the chemicals were of analytical grade purity without need for further purification. Stoichiometric amounts of iron oxide and bismuth oxide, and 5 mol of tartaric acid per mole of metal ion were mixed in a mortar. The mixture was then heated to 250 °C at which it began to ignite and violently burn. All of these reactions took place in a crucible, which was heated by a heating jacket. After complete combustion, the powder was cooled down to room temperature. The as-prepared powder was separated into two parts by a magnet: a major part (with a yield of about 75%) was attractive to the magnet, and a minor part did not respond to the magnetic attraction.

X-ray powder diffraction (XRD) was performed on both the magnetically attractive powder and the non-magnetic powder using Cu Kα radiation (X'pert PRO, PANalytical B.V., Holland). The data were taken with a step size of 0.0167° and a step time of 10 s. Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out on a simultaneous TGA/DSC apparatus (SDT Q600, TA Instruments-Waters LLC, USA) at a heating rate of 10 °C/min. Magnetic measurements were performed using a Superconducting QUantum Interference Device (SQUID, MPMS-XL-7, Quantum Design Inc., USA). Scanning electron microscopy (SEM) was carried out on a Field Emission Scanning Electron Microscope (Hitachi S-4800, Hitachi Ltd, Japan). Polarization-electric field hysteresis loops were measured using a Precision Workstation Ferroelectric Test System (RT 6000, Rayto, USA). X-ray photoelectron spectroscopy (XPS, PHI660) was performed using a monochromatic Mg Kα X-ray source.

Results and discussion

Phase analysis and microstructure

Fig. 1 shows the XRD patterns of the magnetic powder (A) and non-magnetic powder (B) obtained by this reaction process. According to the JCPDS powder data (Card No.86-1518), the XRD pattern (A) of the sample responsive to magnet belongs to pure perovskite phase of $BiFeO_3$ with the $R3c$ space group. On the other hand, the non-magnetic powder (B) contained the non-reacted phases of Bi_2O_3 and Fe_2O_3. Therefore, the synthetic process developed in this work, involving self-combustion in the presence of tartaric acid, resulted in $BiFeO_3$ of perovskite structure in majority, which is magnetically attractive. Compared to the soft chemical route,[9] this technique has allowed us to obtain $BiFeO_3$ by a one–step process that took place instantaneously (in less than 5 min.) at a temperature below 300 °C.
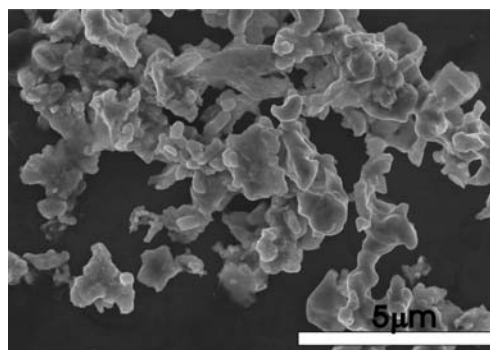
Fig. 2 shows the SEM image of as-prepared (magnetic) BFO powder separated by magnet. The average particle size is found to be approximately 100 nm. The formation of agglomerated clusters indicates that the sample was partly melted during the reaction, which suggests that the reaction involved very high temperature (see Section below).

Reaction mechanism

It is well know that the organic substances such as tartaric acid, glycin, sucrose, *etc.*, could not burn easily in air. Instead, they
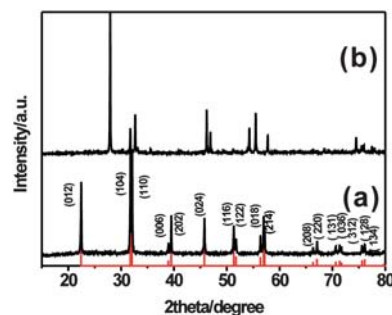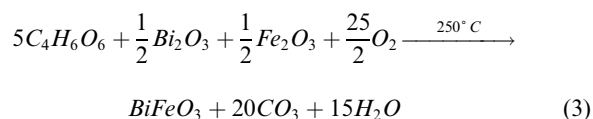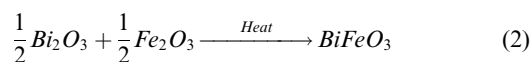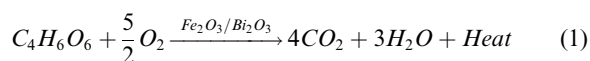

Fig. 1 XRD patterns of (a) the magnetically attractive $BiFeO_3$ (BFO) powder prepared by a self-catalyzed low-temperature fast solid state reaction. Red lines indicate the powder data of JCPDS Card No. 86-1518 for $BiFeO_3$, and (b) the non-magnetic power which shows the non-reacted starting reactants of Bi_2O_3 and Fe_2O_3.

Fig. 2 SEM image of as-prepared (magnetic) BFO sample.

simply carbonize into carbon first, and the carbon begins to burn as the temperature is further increased. However, with the help of appropriate solid state catalyst(s), such as iron oxide, bismuth oxide, nickel oxide, *etc.*, these organic compounds can react, at a relatively low temperature, with activated oxygen molecules which are adsorbed on the surfaces of the metal oxide catalyst(s),[18,19] giving out a great deal of heat. This heat, in turn, promotes the reaction of Bi_2O_3 and Fe_2O_3 to form BFO in the present case.

The chemical reactions leading to BFO are described as follows:

$$C_4H_6O_6 + \frac{5}{2}O_2 \xrightarrow{Fe_2O_3/Bi_2O_3} 4CO_2 + 3H_2O + Heat \quad (1)$$

$$\frac{1}{2}Bi_2O_3 + \frac{1}{2}Fe_2O_3 \xrightarrow{Heat} BiFeO_3 \quad (2)$$

$$5C_4H_6O_6 + \frac{1}{2}Bi_2O_3 + \frac{1}{2}Fe_2O_3 + \frac{25}{2}O_2 \xrightarrow{250°C}$$

$$BiFeO_3 + 20CO_3 + 15H_2O \quad (3)$$

Such a self-catalyzed reaction process started in Reaction (1) with the combustion of tartaric acid in the presence of Bi_2O_3 and Fe_2O_3, which served as catalysts. This reaction produced a large amount of heat, which, in turn, promoted the reaction of Bi_2O_3 and Fe_2O_3, leading to the formation of perovskite $BiFeO_3$ within a very short period of time (less than 5 min) [Reaction (2)].

To prove this reaction mechanism, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out at a heating rate of 10 °C min^{-1} in the temperature range of 30–500 °C in air, on four different samples: (A) pure tartaric acid, (B) 10 N tartaric acid mixed with iron oxide, (C) 10 N tartaric acid mixed with bismuth oxide, and (D) 10 N tartaric acid mixed with both iron oxide and bismuth oxide.

Fig. 3 (a) shows the TGA curves of these four samples. It can be seen that pure tartaric acid experiences two weight losses at 250 °C and 470 °C, respectively. In contrast, other samples of tartaric acid in the presence of Bi_2O_3, or Fe_2O_3, or (Bi_2O_3 + Fe_2O_3) show one weight loss only at approximately 250 °C. This different thermal behavior suggests that the tartaric acid underwent a catalyzed oxidation at 250 °C with α-Fe_2O_3 or Bi_2O_3, or both, acting as catalyst(s).

Fig. 3 (b) gives the DTA curves of the corresponding 4 samples. It can be seen that all four samples exhibit a first peak at 165 °C, which is associated with the melting of the tartaric acid, and a second peak at 250 °C, resulting from the decomposition of the tartaric acid into H_2O and carbon. Both peaks are endothermic. The third peak is an exothermic one. It appears at 470 °C for pure tartaric acid, at which the amorphous carbon begins to burn. In comparison, for the mixture of tartaric acid and iron oxide, this exothermic event appears as a broadened peak at a much lower temperature (between 250 °C and 350 °C). For the mixture of tartaric acid with Bi_2O_3, two exothermic peaks appear at 280 °C and 415 °C, respectively. For the mixture of tartaric acid with both Fe_2O_3 and Bi_2O_3, a single exothermic event occurs at 275 °C. A possible reason for Bi_2O_3 to have two exothermic peaks is that Bi_2O_3 absorbs fewer oxygen molecules
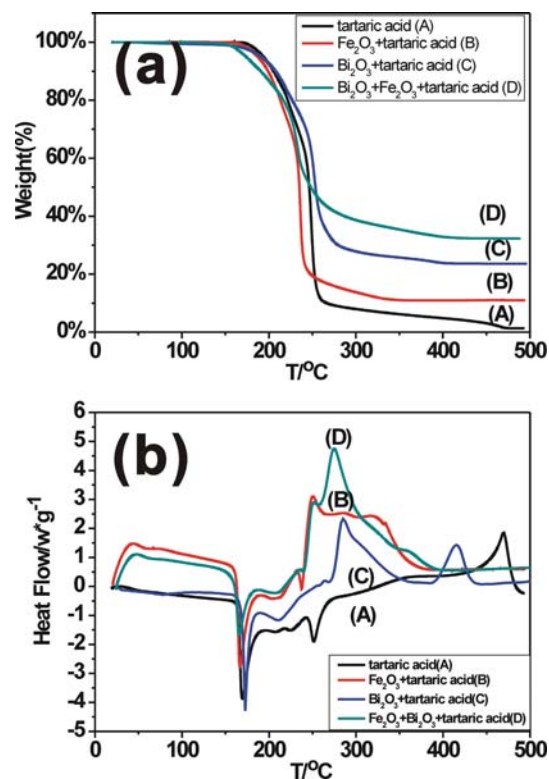

Fig. 3 (a) Thermogravimetric analysis (TGA) curves of (A) pure tartaric acid, (B) tartaric acid mixed with iron oxide, (C) tartaric acid mixed with bismuth oxide, and (D) tartaric acid mixed with both iron oxide and bismuth oxide. (b) Differential thermal analysis (DTA) curves in air of (A) pure tartaric acid, (B) tartaric acid mixed with iron oxide, (C) tartaric acid mixed with bismuth oxide, and (D) tartaric acid mixed with both iron oxide and bismuth oxide, measured in air upon heating at 10 °C min^{-1}.

that can penetrate into the bulk and has a higher activation energy for the oxygen exchange reaction,[16] so its ability to catalyze the tartaric acid oxidation is weaker than in the mixtures (B) and (D). From the TGA and DTA curves we can conclude that iron and bismuth oxides can indeed catalyze the oxidation of tartaric acid effectively by decreasing the reaction temperature by approximately 200 °C. The catalyzed oxidation of $C_4H_6O_6$ gives rise to a great deal of heat which in turn triggers the reaction of Bi_2O_3 and Fe_2O_3 to form BFO [Reaction (3)].

## Physical and chemical characterizations of BiFeO₃

Since the $BiFeO_3$ powder synthesized by this self-catalyzed reaction technique is attractive to a magnet, it is of interest to characterize the magnetic properties of BFO in detail and to understand the origin of the (ferro)magnetism. Fig. 4 (a) presents the variation of the magnetization of the $BiFeO_3$ powder as a function of magnetic field, measured at 300 K and 5 K. A slim magnetic hysteresis loop is displayed under a field of ±20000 Oe with a (weak) remanent magnetization of 1.8 emu/g at 300 K and 3.0 emu/g at 5 K, respectively. The magnetization is saturated at a relatively small field of about 500 Oe (see Inset of Fig. 4(a)). This magnetic hysteresis loop indicates that the as-prepared BFO powder is indeed ferromagnetic at room temperature, with a very small coercive field of 140 Oe at 300 K and 300 Oe at 5 K. There
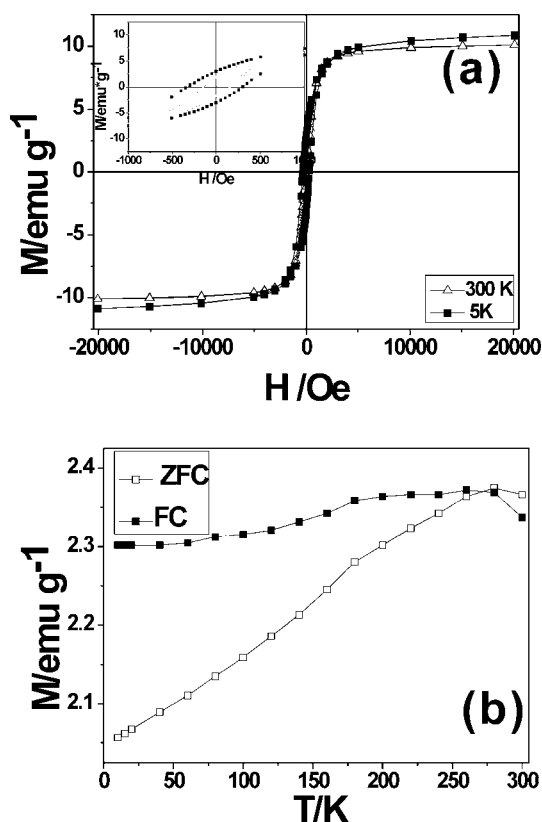
Fig. 4 (a) Magnetization (M) versus field (H) curve for the BiFeO$_3$ powder measured at 300 K and 5 K. Inset shows the details of the M–H hysteresis loop displayed at a field of ±1000 Oe. (b) Zero-field-cooled (ZFC) and field-cooled (FC) magnetization measured below room temperature at a field of 100 Oe.

is no significant difference in the magnetic properties at 300 K and 5 K. This displayed ferromagnetic behavior is consistent with the above observation that the BFO powder is strongly attracted by a magnet, confirming its ferromagnetism. This ferromagnetic behavior is very unusual given that the BFO samples prepared so far in the forms of single crystals, ceramics or thin films have been known to exhibit antiferromagnetic properties.

In order to investigate the nature of ferromagnetism in BFO, the magnetic measurements were carried out upon both zero-field-cooling (ZFC) and field-cooling (FC), in the temperature range of 5 to 300 K. Fig. 4 (b) gives the temperature dependences of the ZFC and FC magnetizations which exhibit different values
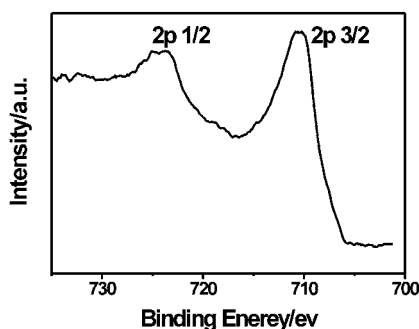
below 275 K (the drop of curves near 300 K is believed to arise from the thermal fluctuation when approaching the upper limit of temperature). The difference becomes more significant at lower temperatures, with the FC magnetization being higher than the ZFC one. This magnetization behavior of BFO powder is different from that of single crystal which was reported to undergo spin-glass ordering below 120 K.[20] Since BFO is known to be antiferromagnetic below $T_N = 643$ K,[3] the splitting of FC and ZFC magnetization curves suggests some kind of irreversibility effect on the magnetic properties, which could arise from the breaking of antiferromagnetic ordering, giving rise to ferromagnetic behavior in the BFO powder.

To understand the chemical origin of the ferromagnetism in BFO, the composition of the as-prepared ferromagnetic BFO powder was determined by XPS based on the spectra of the Fe 2p core levels in terms of binding energy. As shown in Fig. 5, the BFO sample exhibits 2p core levels binding energy of 711.6 eV (Fe 2p$_{3/2}$ without broaden or satellite peak) and 723.7 eV (Fe 2p$_{1/2}$), corresponding to those of Fe^{3+} ion. No other reduced states, such as Fe^{2+} or Fe^0, can be found in the XPS spectrum.[21] In addition, the reactant being α-Fe$_2$O$_3$, it is not likely to convert into γ-Fe$_2$O$_3$. These XPS results suggest that the unusual ferromagnetism detected in BFO powder cannot be associated with any impurity phases, such as Fe, FeO, Fe$_3$O$_4$ and γ-Fe$_2$O$_3$, which can be excluded from the sample, but instead, it is an intrinsic property of the BiFeO$_3$ prepared by the self-catalyzed reaction process.

It is well known that the magnetic structure of BFO exhibits an inherent antiferromagnetic order of circular cycloid magnetic structure with a critical particle size of 62 nm.[22] The particle size of BFO obtained in the current synthetic process is larger than 100 nm, which is beyond the critical size of 62 nm, so the observed ferromagnetism cannot be from the size effect, but more likely from the point defects associated with oxygen vacancies. During the self-catalyzed reaction process, local regions can be heated up to a high temperature in a very short time period, and then cooled down at a high rate. Consequently, a large amount of point defects are expected to form, which mostly consist of oxygen vacancies. It is reasonable to postulate that these point defects could destroy the super-exchange interactions of Fe^{3+}–O^{2-}–Fe^{3+}, and introduce other kinds of exchange interactions. Any of these interactions could change the magnetic moments and directions of the original circular cycloid spin arrangements of the magnetic sublattices and partly destroy the spin-canted magnetic structure, resulting in uncompensated

Fig. 5 XPS spectrum of Fe 2p core levels of the as-prepared BiFeO$_3$.
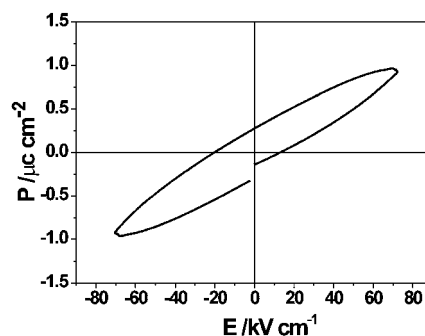
Fig. 6 Polarization-electric filed hysteresis loop of a BiFeO$_3$/PVA pellet displayed at room temperature.

magnetization and thereby a net magnetization and the ferromagnetism. Such ferromagnetism is weak by nature, which explains the low saturation magnetization (Fig. 4).

To confirm the role of point defects and to verify the proposed mechanism of induced ferromagnetism in BFO, the as-prepared ferromagnetic BFO powder was annealed at 650 °C for 2 h in O_2 atmosphere and cooled down to room temperature upon natural oven-cooling. It was found that the ferromagnetism of BFO disappeared after annealing. It becomes clear that the annealing process has reduced the amount of point defects significantly, reestablishing the original antiferromagnetism in BFO. Therefore, it can be concluded that the BFO powders synthesized by this self-catalyzed fast reaction process exits in a metastable state which contains a considerable amount of point defects associated with oxygen vacancies. These point defects destroy the circular cycloid spin arrangement inherently present in canonical BFO, resulting a spontaneous magnetization M, and thereby the unusual ferromagnetism.

In order to detect its ferroelectricity while preserving its chemical nature (defects) and physical properties, the as-prepared (magnetic) $BiFeO_3$ powder is hot-pressed (with a pressure of 15 MPa) into pellets using polyvinyl alcohol (PVA, at a concentration of 6%) as binding agent (the mass ratio of PVA was 3%) for ferroelectric measurement. As shown in Fig. 6, a polarization-electric field hysteresis loop was displayed at room temperature under an applied field of ±80 kV/cm, indicating ferroelectric behavior for the BFO powders synthesized (since PVA is nonferroelectric). The remnant polarization (Pr) and the coercive field (Ec) are found to be 0.28 μC/cm2 and 13 kV/cm, respectively.

Conclusions

We have developed a new synthetic technique for the preparation of multiferroic $BiFeO_3$ *via* a self-catalyzed low temperature fast solid state reaction process. This method consists of mixing the constituent oxides with tartaric acid, and heating the mixture to a moderate temperature of 250 °C. The metal oxides catalyze the oxidation reaction of the tartaric acid, giving out a great deal of heat, which in turn promotes the reaction of the iron and bismuth oxides to form BFO. This technique shows several advantages over the conventional solid state synthesis: (1) Repeated grinding and pelletizing of the reactants are avoided as the starting metals oxides, which serve as the catalysts for the oxidation of tartaric acid at moderate temperature, are uniformly mixed and the atomic diffuse is facilitated through the melting and oxidation of the tartaric acid; (2) The reaction takes place under a very moderate heating, thus it is an energy saving process; (3) The reaction time is very short as the whole process is completed in less than 5 min; (4) It is a one-step process to the synthesis of BFO; (5) The equipment needed is simple. It is reasonable to anticipate that this green, energy-saving, fast and convenient technique can become an effective method for the synthesis of many more inorganic functional materials, as long as the starting metal oxides can catalyze the oxidation of certain organic substances.

Interestingly, the $BiFeO_3$ powders prepared by this self-catalyzed process exhibit ferromagnetism at room temperature. The origin of the unusual ferromagnetism in the samples (which can be strongly attracted to a magnet) is attributed to the effect of point defects associated with oxygen vacancies, which are formed during the fast reaction process involving rapid heating/cooling process. The presence of point defects is believed to destroy the inherent circular cycloid spin arrangements in canonical antiferromagnetic BFO, giving rise to macroscopic magnetization and thereby the ferromagnetism. More detailed investigation is needed to determine the magnetic structure and to better understand the magnetic interaction mechanisms in the metastable ferromagnetic BFO. Ferroelectricity was also displayed in the BFO/PVA samples. In this way, we have proved that the $BiFeO_3$ powder prepared by this technique is indeed simultaneously ferromagnetic and ferroelectric, *i.e.* a true multiferroic at room temperature. With the presence of both ferromagnetic and ferroelectric orders, the magnetoelectric interactions are *a priori* permitted. It is thus interesting to explore the possible magnetoelectric coupling in the ferroelectric/ferromagnetic BFO and related materials.

Acknowledgements

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