Rapid Communication

Phase transitions, electrical conductivity and chemical stability of BiFeO₃ at high temperatures

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A B S T R A C T

The multiferroic perovskite BiFeO₃ is reported to display two first order structural phase transitions. The structural phase transition at $925 \pm 5\,^{\circ}\mathrm{C}$ is demonstrated to be first order by calorimetry and dilatometry. Electrical conductivity measurements revealed that the high temperature phase above $925 \pm 5\,^{\circ}\mathrm{C}$ is semiconducting, in disagreement with recent reports. The sign and magnitude of the volumes of transition reflect the sign and magnitude of the discontinuities in electrical conductivity across the two first order phase transitions. A high partial pressure of oxygen was demonstrated to stabilise BiFeO₃ towards peritectic decomposition. Finally, the origins of the commonly observed decomposition of BiFeO₃ at high temperatures are discussed.

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1. Introduction

The perovskite BiFeO₃ has become the centre of research on multiferroics due to its robust room-temperature multiferroism with a Néel temperature of 370 °C and a Curie temperature of 820–830 °C [1]. Bulk BiFeO₃ at ambient conditions is a rhombo-hedrally distorted perovskite with the space group $R3c$. Although the temperature–pressure phase diagram of BiFeO₃ has recently received considerable attention, the structural phase transition sequence and the properties at high temperatures are debated. The paraelectric structure (β-phase) above T_C was first demonstrated to belong to the orthorhombic space group $Pbnm$ by Arnold et al. [2]. A structural transition at $925 \pm 5\,^{\circ}\mathrm{C}$ to a γ-phase has also been reported [3,4], but the vicinity to the peritectic temperature [4,5] of 933–934 °C has hampered characterisation of the γ-phase and the β–γ transition. Palai et al. proposed a nearly second order transition to a cubic $Pm\bar{3}m$ γ-phase [3], while a first order transition with a small negative volume of transition, $\Delta_{trs}V$, to an orthorhombic γ-phase was found by Arnold et al. [6]. For isostructural BiFe₀.₇Mn₀.₃O₃ the structural phase transition sequence $R3c$ – $Pbnm$ – $Pm\bar{3}m$ was inferred, with a positive $\Delta_{trs}V$ for the $Pbnm$ – $Pm\bar{3}m$ transition [7]. At ambient conditions, bulk BiFeO₃ is a semiconductor with a relatively low band gap of 2.2–2.8 eV [8,9]. Theoretical studies have found that the band gap of cubic BiFeO₃ is zero [3,8], and an insulator–metal transition

associated with the β–γ transition has been reported [3,6]. Isostructural BiFe₀.₇Mn₀.₃O₃ exhibited semiconductivity also in the γ-phase [7]. Moreover, it seems to be a consensus that BiFeO₃ is metastable at temperatures above 800 °C [1].

In this paper the two structural phase transitions at high temperatures are shown to be first order by thermal analysis. Semiconducting behaviour is found for all three polymorphs of BiFeO₃. Moreover, we challenge the idea that thermodynamic instability in the paraelectric phase is an intrinsic property of BiFeO₃. We argue that the commonly observed decomposition at high temperatures below the peritectic decomposition temperature can be rationalised from chemical incompatibility of BiFeO₃ towards supporting materials rather than intrinsic instability.
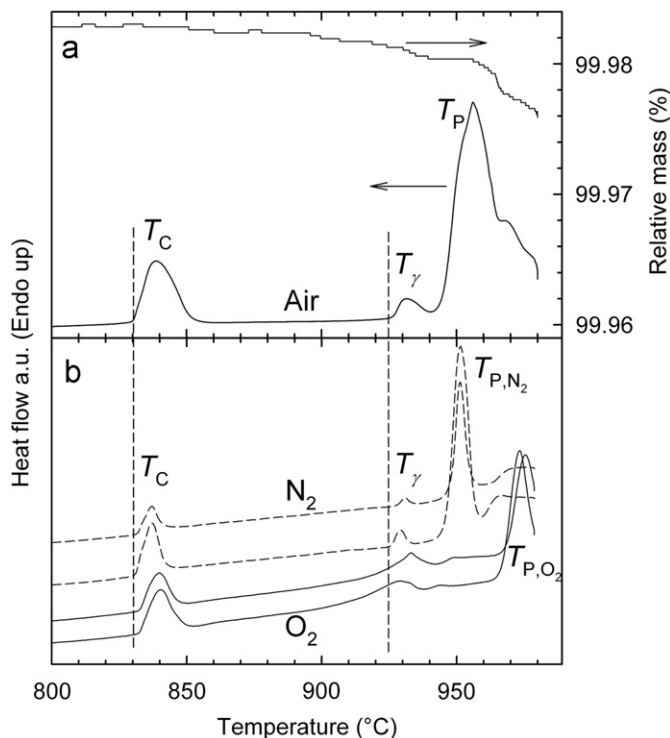
2. Experimental

Bulk BiFeO₃ was prepared by solid state reaction between dried Bi₂O₃ and Fe₂O₃ as described elsewhere [10]. Differential thermal analysis (DTA) was performed with a Netzsch STA 449 C Jupiter in synthetic air, 99.999% O₂ and 99.999% N₂ atmosphere with $10\,^{\circ}\mathrm{C\,min^{-1}}$ heating and cooling rates on ~0.2 g powder samples. Thermal expansion and volumetric changes due to phase transitions of polycrystalline BiFeO₃ were investigated by dilatometry in synthetic air with a Netzsch DIL 402 C dilatometer using $5\,^{\circ}\mathrm{C\,min^{-1}}$ heating and cooling rates. The experimental setup and sample preparation for four-point conductivity measurements have been reported elsewhere [7].

3. Results

Three thermal events are evident from the differential thermal analysis (DTA) data in Fig. 1(a), with onsets at 830 ± 5, 925 ± 5 and $940 \pm 5\,^\circ\text{C}$. The temperature of the ferroelectric transition T_C at $830\,^\circ\text{C}$ is in good accordance with previous studies [3,4,10,11]. The endothermic peak at $925\,^\circ\text{C}$ is interpreted as the temperature, T_γ, of the transition from the orthorhombic β-phase to the γ-phase. An endothermic peak at about 925–$930\,^\circ\text{C}$ has also previously been reported [3,4,10]. The distinct thermal signature points to a first order phase transition. Peritectic decomposition at T_P gives rise to the largest endothermic peak, with onset at $940 \pm 5\,^\circ\text{C}$. The decomposition at the peritectic temperature involves partial melting of the solid, thus the large amount of heat associated with this reaction. Given that the transition at T_C is strongly first order, the relative magnitudes of the endothermic events point to a less abrupt first order transition at T_γ, in line with our recent report on $BiFe_{0.7}Mn_{0.3}O_3$ [7]. Onset of mass loss at approximately T_γ was observed and the loss increased when crossing T_P (Fig. 1(a)). The enhanced mass loss above T_P can be explained by the higher vapour pressure of Bi_2O_3 above the Bi_2O_3-rich liquid formed at T_P. The influence of atmosphere on the phase transitions is shown in Fig. 1(b); two measurements on pristine samples in each atmosphere are reported to show the reproducibility of the experiments. Neither T_C nor T_γ is sensitive to the atmosphere, and no systematic difference in T_C and T_γ was found. An increase in the onset temperature of peritectic decomposition in O_2 atmosphere was observed and reproduced. Although a subtle endothermic peak was observed just above T_γ for both measurements in O_2, it is too small to correspond to peritectic decomposition. In O_2 atmosphere the peritectic decomposition starts at approximately $960\,^\circ\text{C}$, which has also

been reported as the decomposition temperature of $Bi_2Fe_4O_9$ [3,5].

At T_C the volume of transition, $\Delta_{trs}V(T_C)$, is large and negative, as shown by thermal expansion measurements (dilatometry) of a dense ($>93\%$) polycrystalline sample, see Fig. 2. At T_γ the thermal expansion across the phase transition identifies $\Delta_{trs}V(T_\gamma)$ as positive. Both discontinuous volume and thermal hysteresis, as shown in the inset of Fig. 2, is consistent with a first order phase transition at T_γ. Apparent thermal contraction between T_C and T_γ, and the different thermal expansion upon heating and cooling, can be attributed to creep, which is commonly observed for polycrystalline samples at high temperatures. The volume change and transition temperatures were reproduced several times to rule out the possibility of systematic errors due to these effects. Absolute values of $\Delta_{trs}V$ could not be determined from the dilatometer data, but the sign and relative magnitudes of the thermal expansion anomalies at T_C and T_γ unambiguously show that $\Delta_{trs}V(T_C) < 0$, $\Delta_{trs}V(T_\gamma) > 0$ and $|\Delta_{trs}V(T_C)| \gg |\Delta_{trs}V(T_\gamma)|$, as also found for $BiFe_{0.7}Mn_{0.3}O_3$ by dilatometry and high temperature X-ray diffraction [7]. The steep rise in volume upon cooling through T_C is due to the large $\Delta_{trs}V(T_C)$ of $BiFeO_3$, as discontinuous expansion across a first order phase transition yields sharper signals in this experimental setup than discontinuous contraction.

The electrical conductivity of a polycrystalline sample across the two structural transitions is displayed in Fig. 3(a). O_2 atmosphere was used in accordance with the DTA results in Fig. 1(b). The discontinuous increase in the conductivity across the ferroelectric T_C is in accordance with previous investigations, and the negative sign of $\Delta_{trs}V(T_C)$. At $T_{\gamma,h}$ we observe a change of the slope $d\sigma/dT$ from positive to negative upon heating, which was also observed by Palai et al. [3] who interpreted this as an insulator to metal transition. Upon increasing temperature the slope $d\sigma/dT$ changes sign again to positive. The γ-phase, with a larger molar volume (from $\Delta_{trs}V(T_\gamma) > 0$), is expected to be less conducting than the denser β-phase. When entering the β-phase upon cooling at $T_{\gamma,c}$ the conductivity increases abruptly, consistent with the smaller molar volume of the β-phase compared with the γ-phase. The sign and magnitude of the discontinuous conductivity anomalies at T_C and T_γ reflect the sign and magnitude of the thermal expansion anomalies found by dilatometry in Fig. 2, $\Delta_{trs}V(T_C) < 0$ and $\Delta_{trs}V(T_\gamma) > 0$. A finite, narrow temperature interval with negative $d\sigma/dT$ slope is therefore only observed due to the kinetics of the phase transition, and does not reflect an insulator to metal transition.
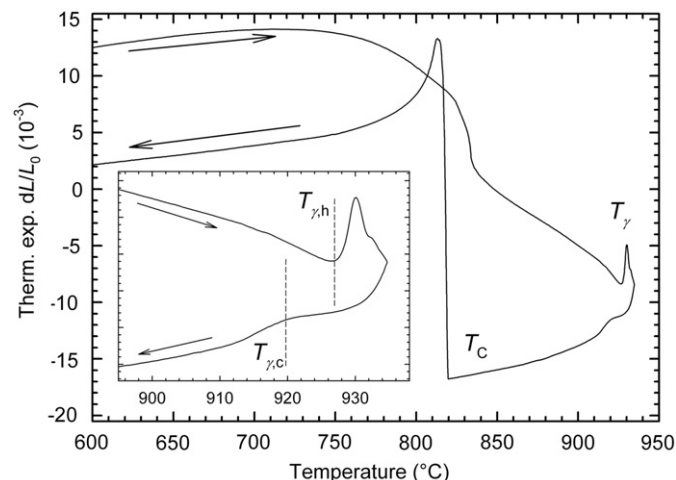

Fig. 1. (a) Differential thermal analysis (DTA) and thermogravimetry (TGA) of $BiFeO_3$ bulk powder in air. (b) DTA of $BiFeO_3$ bulk powder in N_2 (dashed lines) and O_2 (solid lines) atmospheres. The ferroelectric Curie temperature, transition to the γ-phase and the peritectic decomposition temperature are denoted as T_C, T_γ and T_P, respectively. Vertical dashed lines are guides to the eye.
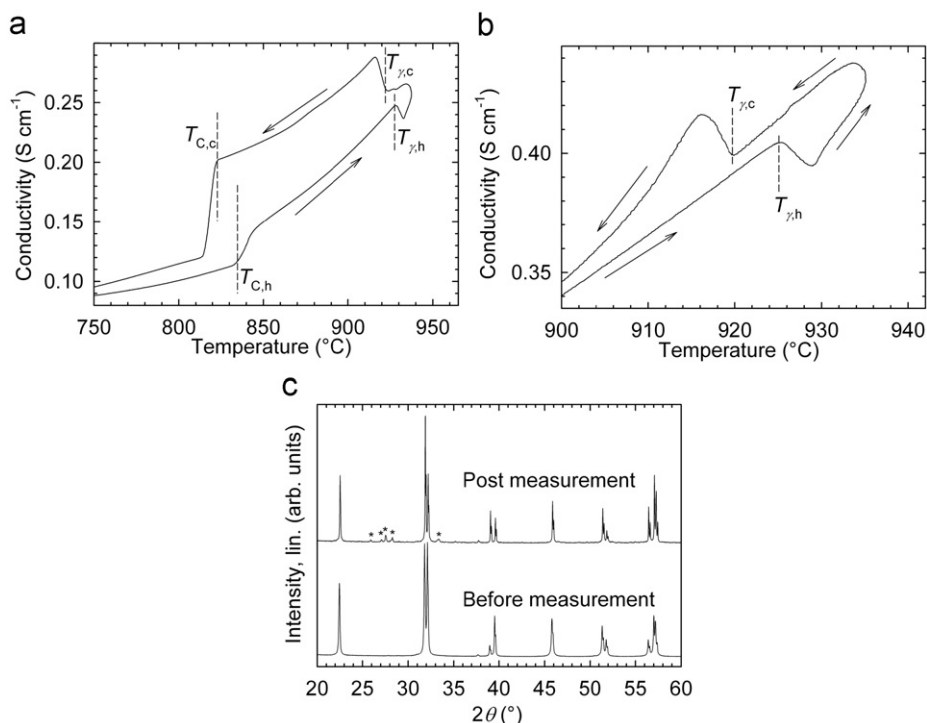

Fig. 2. Thermal expansion (dilatometry) of a dense $BiFeO_3$ polycrystal in air. Inset: zoom-in on the transition to γ-phase, T_γ. Subscripts "h" and "c" refer to the transition upon heating and cooling, respectively.

Fig. 3. (a) Electrical conductivity of a dense $BiFeO_3$ polycrystalline bar. (b) Electrical conductivity of a pristine, dense $BiFeO_3$ polycrystalline bar, zoomed in on the conductivity across the transition from the β- to the γ-phase. The measurements were done in O_2 atmosphere. Subscripts "h" and "c" refer to the transition upon heating and cooling, respectively. (c) XRD patterns of $BiFeO_3$ before and after conductivity measurement in O_2 atmosphere in (b), reflections from secondary phases are denoted with asterisks (*).

The electrical conductivity of a pristine polycrystalline $BiFeO_3$ sample was measured in O_2 atmosphere to confirm the reproducibility of the experiment, and the conductivity across T_γ upon heating and cooling is shown in Fig. 3(b). Significant thermal hysteresis and discontinuous electrical conductivity confirm the first order nature of this reversible, first order phase transition. Discontinuous electrical conductivity across $T_{\gamma,h}$ and $T_{\gamma,c}$ is in concordance with $\Delta_{trs}V(T_C) > 0$. The difference in absolute conductivity upon heating and cooling is related to possible creep and minor deformation of the sample. Some interface reaction between the Pt electrodes and the sample is also expected [12]. Only negligible amount of secondary phases was present in the sample in Fig. 3(b) after measurements in O_2 atmosphere, as shown in Fig. 3(c). Conductivity measurements were also carried out in N_2 atmosphere (not shown), but peritectic decomposition prevented measurement of the conductivity across T_γ.

4. Discussion

The phase transitions studied in this work are first order from discontinuous volume and enthalpy. Discontinuous electrical conductivity across the phase transitions at T_C and T_γ correspond to the first order nature of the transitions, the relative magnitude of the calorimetric peaks in Fig. 1, and both the sign and relative magnitude of the thermal expansion anomalies from dilatometry in Fig. 2. A reduction in molar volume at T_C is accompanied by increased electrical conductivity, and vice versa at T_γ. All three polymorphs displayed semiconductivity, in agreement with our previous study [7,11], but in disagreement with the work by Palai et al. [3].

High temperature characterisation of $BiFeO_3$ has proven difficult, with poor reproducibility between different laboratories and experimental setups. Decomposition below the peritectic temperature of 933–934 °C has been frequently reported in the literature [2–4,7,11,13]. DTA measurements (Fig. 1) imply that $BiFeO_3$ is more stable in O_2 than air and N_2 atmosphere, thus a higher partial pressure of oxygen stabilizes $BiFeO_3$, in agreement with a titration study by Li and MacManus-Driscoll [14]. Thermal reduction of a fraction of Fe^{3+} to Fe^{2+} in the acidic Bi-rich liquid formed during peritectic decomposition may contribute to the observed mass loss above T_P in Fig. 1(a). However, the insensitivity of T_C and T_γ to the atmosphere demonstrates that the structural phase transitions are not accompanied by thermal reduction of the oxidation state of Fe.

$Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$ are commonly found impurities in $BiFeO_3$ prepared by solid state reaction [15]. The Gibbs energy of reaction (1), $\Delta_{r(1)}G_m^o$,

$$12\ Bi_2Fe_4O_9 + Bi_{25}FeO_{39} = 49\ BiFeO_3 \tag{1}$$

is close to zero, but increasingly negative with increasing temperature above 800 °C [16]. This explains the success of the "rapid liquid phase sintering" [17] in obtaining phase pure $BiFeO_3$ at 880 °C. Ignoring mass loss through evaporation of bismuth oxides, $BiFeO_3$ is thus stable towards decomposition to $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$ in the paraelectric β-phase. Evaporation of bismuth oxides from $BiFeO_3$ would yield coexistence of $BiFeO_3$ and $Bi_2Fe_4O_9$ according to the phase diagram [3,5]. The vapour pressure of BiO (g) (BiO is the dominant gaseous bismuth oxide species above 800 °C) can be estimated by the thermodynamics of the reaction:

$$8\ BiFeO_3 = 4\ BiO\ (g) + 2\ Bi_2Fe_4O_9 + O_2(g) \tag{2}$$
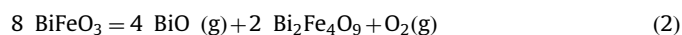
Thermodynamic calculations with FactSage show that the vapour pressure of BiO (g) over pure Bi_2O_3 (l) is less than 10^{-6} atm at 1200 K [18]. The presence of iron oxide in the system will reduce the activity of BiO (g); hence the vapour pressure of BiO (g) is therefore significantly lower above solid $BiFeO_3$ than the vapour pressure above pure liquid Bi_2O_3. However, in experiments using powder or thin films, where the mass is relatively

small and the surface large, evaporation of BiO (g) may be significant, particularly if the sample is exposed to a gas flow, resulting in the formation of $Bi_2Fe_4O_9$. For bulk material the loss of Bi through BiO (g) should be less pronounced. Equilibrium (2) explains the stabilisation of $BiFeO_3$ from peritectic decomposition in O_2 relative to N_2 atmosphere [14] by Le Chatelier's principle.

Since $\Delta_{r(1)}G_m^o$ is close to zero the phase equilibrium is sensitive to the presence of impurities. Valant et al. showed that minor amounts of Al_2O_3 or SiO_2 drive reaction (1) towards the left hand side, as Al_2O_3 and SiO_2 is more soluble in $Bi_2Fe_4O_9$ and $Bi_{25}FeO_{39}$, respectively, than in $BiFeO_3$ [15]. Unfortunately, Al_2O_3 and SiO_2 are primary constituents of refractory materials commonly in contact with $BiFeO_3$ during high temperature experiments. Hence decomposition at $BiFeO_3/Al_2O_3$ and $BiFeO_3/SiO_2$ interfaces must be anticipated, as pointed out in the case of SiO_2 already in 1972 by Bucci et al. [19]. Moreover, platinum is often used as electrodes or heating strips in high temperature diffraction experiments with the Bragg–Brentano geometry. The binary Pt–Bi phase diagram displays several intermetallic phases [20], revealing affinity between Bi and Pt, suggesting that interface reactions will occur at high temperatures, as reported by Yakovlev et al. [12]. Based on this reasoning, we propose that decomposition of $BiFeO_3$ in the paraelectric β-phase (below T_P) is due to *chemical incompatibility* towards the materials in contact with the sample rather than *intrinsic thermodynamic instability*. E.g. alloying of Bi into adjacent Pt at high temperatures requires reduction of Bi from +3 to 0, thus a high partial pressure of oxygen stabilises $BiFeO_3$ from interface reaction with Pt. Finding materials chemically inert towards $BiFeO_3$ would substantially ease high temperature characterisation, and is also important for integration of $BiFeO_3$ into electronic circuitry.

5. Conclusion

Upon increasing temperature, $BiFeO_3$ goes through two reversible, first order structural phase transitions at 830 ± 5 and $925 \pm 5\,^\circ C$. The former transition is strongly first order with a large, negative volume and an associated discontinuous increase in electrical conductivity. The latter transition is also first order, but with a small, positive volume of transition and an associated decrease in electrical conductivity. Semiconducting behaviour was found for all three polymorphs in both O_2 and inert atmosphere. O_2 atmosphere was found to increase the stability in vicinitiy of the peritectic decomposition temperature. Based on thermodynamic considerations, it is proposed that chemical incompatibility with sample supporting materials, rather than intrinsic thermodynamic instability, is the most common cause of the frequently observed decomposition of $BiFeO_3$ in the paraelectric phase.

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