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Refinement of Bi_2WO_6 and Bi_2MoO_6 polymorphism

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ABSTRACT

Bi_2WO_6 (BW) and Bi_2MoO_6 (BM) single-layer Aurivillius phases have been prepared by crystal growth and solid-state reactions, and their thermal and electrical properties have been studied with the aim of gaining detailed insight into their polymorphism. The results demonstrate that both compounds exist in four polymorphs: low-temperature polar orthorhombic (γ), polar orthorhombic (γ'''), nonpolar orthorhombic (γ'') and high-temperature monoclinic nonpolar (γ'). Accordingly, they undergo three phase transitions: $\gamma \rightarrow \gamma'''$ (ferroelectric–ferroelectric phase transition between two polar phases), $\gamma''' \rightarrow \gamma''$ (ferroelectric–paraelectric transition from polar to nonpolar phase) and $\gamma'' \rightarrow \gamma'$ (reconstructive transition between two nonpolar phases). BW has been shown experimentally for the first time to have an intermediate orthorhombic phase (γ'') in a temperature range as narrow as 30 °C between its ferroelectric–paraelectric and reconstructive structure phase transitions. The ferroelectric–paraelectric transition of BW can be detected by dielectric measurements, and its reconstructive transition, by calorimetry, which has enabled their temperatures to be determined: 930 and 960 °C, respectively. Calorimetry data confirm that the $\gamma \rightarrow \gamma'''$ phase transition occurs at 310 °C in BM and at 640–660 °C in BW. BW single crystals exhibit a weak lambda-type dielectric anomaly at 640 °C, suggesting that the $\gamma \rightarrow \gamma'''$ phase transition is ferroelectric–ferroelectric. The ferroelectric transition in the $n = 1$ materials BW and BM involves a change from polar orthorhombic to nonpolar orthorhombic symmetry, rather than to tetragonal (4/*mmm*).

1. Introduction

The isostructural Bi_2WO_6 (BW) and Bi_2MoO_6 (BM) are the simplest ($n = 1$) members of the large family of layered perovskite-related compounds with the general formula $(Bi_2O_2)(A_{n-1}B_nO_{3n+1})$ (Aurivillius phases). The structure of these compounds consists of alternating Bi_2O_2 sheets and perovskite-like layers of corner-linked BO_6 octahedra [1]. Many Aurivillius phases are ferroelectrics, oxygen ion conductors and catalysts [2–4]. Ferroelectric ordering in most multi-layer Aurivillius phases typically leads to a transition from a tetragonal (4/*mmm*) to a polar orthorhombic structure. An exception was found for $Sr_{0.85}Bi_{2.1}Ta_2O_9$, in which an intermediate orthorhombic (*mmm*) paraelectric phase has been found. At higher temperatures it has transformed into tetragonal nonpolar phase (4/*mmm*) [5]. The phase transitions of BW and BM have been studied for more than four decades now, but the number of transitions and their detailed nature are not yet fully clear [6–20].

In the early work on BM [9,10], three polymorphs were mentioned: low temperature (γ), intermediate (γ'') and high temperature (γ'). At room temperature BM is in a polar state (γ-phase) and has space group $P2_1ab$ with unit-cell parameters $a = 5.5131$, $b = 16.2266$, and $c = 5.4896$ Å [6]. At 604 °C, ferroelectric–paraelectric phase transition [20] into the paraelectric phase γ'' takes place. γ''-Phase is likely to have orthorhombic symmetry [21,22] rather than tetragonal, as in the case of some multi-layer Aurivillius phases. That the γ''-phase is nonpolar is evidenced by the fact that the second harmonic generation signal from BM disappears at this temperature [15]. In addition, the ferroelectric–paraelectric transition shows up as a dielectric anomaly at 604 °C [15]. According to Watanabe and Kodama [13], this transition is also seen at 604 °C in differential thermal analysis (DTA) scans as a weak thermal event owing to the proximity of this transition to the second order transition. According to several reports [10,15–17], γ-phase persists only to 310–350 °C. It seems likely that, at these temperatures, BM undergoes a phase transition $\gamma \rightarrow \gamma'''$ into the phase, which we designate as γ'''. This transition is evidenced by the X-ray investigations [15], changes in its Raman spectrum [16,17]. There is good reason to believe taking into account the thermal evolution of the lattice parameters [15,22] that γ'''-phase as γ-phase is orthorhombic and polar (2*mm*) since next transition at 604 °C is ferroelectric–paraelectric. At higher temperatures, there is a strong DTA peak due to the $\gamma'' \rightarrow \gamma'$ reconstructive structure phase transition, which is essentially irreversible

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[13]. This transition has not been revealed by the other methods. The γ'-phase has a monoclinic structure ($P2_1/c$) with considerable structure realignment with the formation of MoO_4 tetrahedra instead of MoO_6 octahedra being in lower temperature phases (γ, γ''', and γ'') [4]. The temperature of $\gamma'' \rightarrow \gamma'$ transition varies from 640 to 670 °C, depending on the heating rate. With decreasing heating rate, the temperature of the reconstructive transition approaches that of the ferroelectric–paraelectric transition [13].

Unlike BM in BW only three phases were revealed experimentally (γ, γ''' and γ'). At room temperature BW is in a polar state and has space group $P2_1ab$ with parameters $a = 5.458$, $b = 16.43$, and $c = 5.437$ Å (γ-phase) [12]. BW is a well-known ferroelectric compound with high Curie temperature T_c in the range 930–960 °C during heating and at about 840 °C during cooling [15,23–28]. A disappearance of second harmonic of laser irradiation at 930 °C [26] indicates that ferroelectric–paraelectric transition in BW takes place at this temperature. DTA and dilatometry data reveal only one the intensive peak at temperature near 930–960 °C connected with the reconstructive transition into γ'-phase, which, in contrast to γ'-BM phase, contains layers of stoichiometry WO_4 with WO_6 octahedra sharing edges and corners [14,18,30]. At that, the symmetry of BW changes from polar orthorhombic to nonpolar monoclinic ($A2/m$) [18], which is lower than the symmetry of the ferroelectric phase γ, in addition significant structure rebuilding takes place [14,18]. Such symmetry changes are atypical of ferroelectric–paraelectric transitions. In contrast to BM, no nonpolar paraelectric orthorhombic phase of BW (such as γ'') has been identified to date, even though there is some evidence for such a phase: Yanovskii et al. [24] observed DTA peaks at 920 and 960 °C on heating, and Maczka et al. [19] reported a high-pressure (6.2 GPa) ferroelectric transition of BW to a centrosymmetric orthorhombic (*Bmab*) phase. Based on symmetry analysis, Rae et al. [29] predicted space group *Fmmm* for the paraelectric phase of BW. It seems likely that, at normal pressure, BW also has nonpolar orthorhombic phase between the ferroelectric–paraelectric and reconstructive transitions, but in a narrow temperature range. Thus further research is needed to resolve the problem of the γ''-phase existence. As regards other BW phases, it was found, using dilatometry, DTA and temperature evolution of Young's modulus [14,30] and X-ray diffraction (XRD) [15], to undergo at 662–690 °C a transition from low temperature orthorhombic phase γ with space group $P2_1ab$ to γ'''-phase with an unidentified space group. Recent neutron diffraction work [18] has confirmed that BW undergoes a transition to a polar orthorhombic phase (space group $B2cb$) at 660 °C, analogous phase transition was observed for BM near 310 °C.

So, the data about the number and nature of phase transitions in BW and BM are not full and clear. To gain detailed insight into the polymorphism of these compounds, we relied on electrical measurements and calorimetry.

2. Experimental

BW and BM ceramic samples in polar orthorhombic γ-phase were prepared by solid-state reactions from extrapure-grade Bi_2O_3, WO_3 and MoO_3 in stoichiometric proportion. Compositions were obtained as ceramic samples annealed in the platinum crucibles in air. BW ceramic was fired in two steps: at 700 °C for 24 h and then at 850 °C for 72 h with intermediate regrinding. BM was fired at 560 °C for 72 h, since the γ-phase of BM exists only below 600 °C. We also used BW single crystals prepared by spontaneous crystallization from fluxes [15]. The purity of the phases was checked by XRD characterization of powder samples at room temperature using a DRON-2.0 diffractometer (Cu K_α radiation, $2\theta = 20$–$60°$ with a step of 0.05°). The thermal behavior of BW (single crystals and ceramic) and BM (ceramic) was studied by differential scanning calorimetry (DSC) and thermogravimetry (TG) in air using a NETZSCH STA 449 C system (30–1000 °C, Pt crucibles). The heating/cooling rate was varied from 0.5 to 40 K min^{-1}. To ascertain that the results were reproducible, three measurement cycles were carried out for each sample. Dielectric permittivity and electrical conductivity of ceramic and single crystal samples were measured as a function of the temperature from 20 to 1000 °C at 1 MHz by a two-probe technique using a Tesla BM 431 E bridge and platinum electrodes. The heating rate was 10 K min^{-1}.

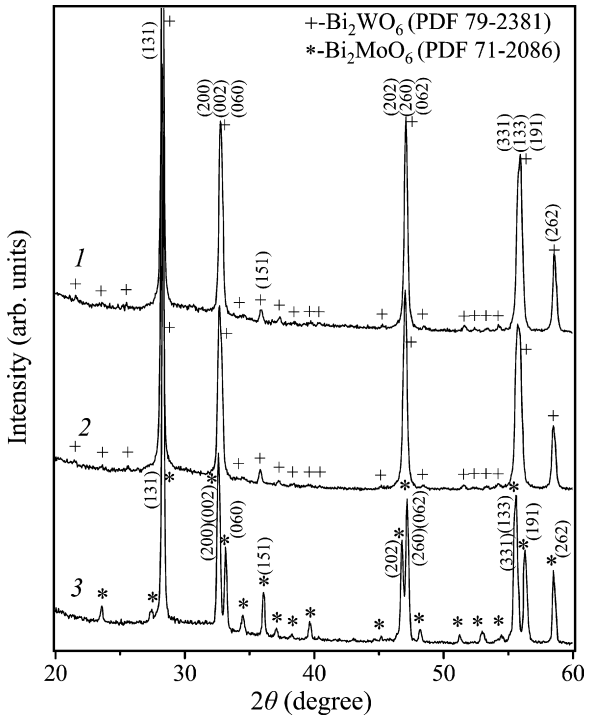

Fig. 1. Powder XRD patterns of ground (1) Bi_2WO_6 single crystals, (2) Bi_2WO_6 and (3) Bi_2MoO_6 ceramic samples. Indexes of strong reflexes are pointed out.

3. Results and discussion

Weight losses of synthesized samples were not observed by thermogravimetric measurements.

X-ray phase analysis (Fig. 1) showed that the BW and BM samples were single-phase in agreement with early data [7,31–33]. The unit-cell parameters of BW ceramic were determined to be $a = 5.465$, $b = 16.40$ and $c = 5.449$ Å, and those of BM, $a = 5.498$, $b = 16.21$ and $c = 5.484$ Å.

3.1. Polymorphism of Bi_2MoO_6

Fig. 2 presents the DSC curves in the range 500–800 °C, with two phase transitions. The heating curve shows a very

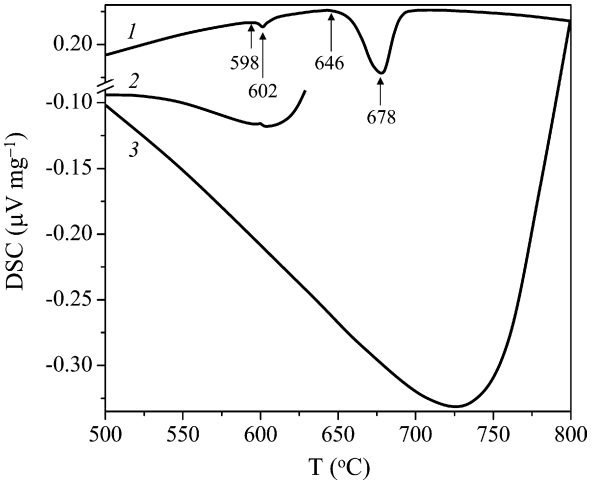

Fig. 2. DSC (1) heating up to 800 °C, (2) cooling from 640 °C (before the $\gamma'' \rightarrow \gamma'$ transition) and (3) cooling from 800 °C (after the $\gamma'' \rightarrow \gamma'$ transition) scans for Bi_2MoO_6; heating/cooling rate, 10 K min^{-1}. Arrows indicate onset and peak temperatures of events corresponding to $\gamma''' \rightarrow \gamma''$ and $\gamma'' \rightarrow \gamma'$ transitions; °C.