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# High temperature phase transformation in rhombohedral bismuth strontium oxide

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## Abstract

A combined DSC and high temperature XRD study of the phase transformation reported for the $\beta$-phase solid solution $(Bi_2O_3)_{1-x}$ $(SrO)_x$ was undertaken for the composition $Bi_{1.6}Sr_{0.2}O_{2.6}$. The DSC and high temperature XRD results were in good agreement. A reversible phase transformation was observed over a narrow temperature range around 650°C, characterized by a large increase in the $c$ lattice parameter, although, both the low and high temperature phases have the same crystal symmetry. Published by Elsevier Science B.V.

*Keywords:* Bismuth strontium oxide; High temperature X-ray diffractometry; Ionic conductor; Differential scanning calorimetry; Phase transformation

## 1. Introduction

Over 50 years ago, Sillén and Aurivillius [1] reported that bismuth oxide, with partial substitution of $Bi^{3+}$ by the alkali earths $Sr^{2+}$, $Ba^{2+}$, or $Ca^{2+}$, forms an intermediate solid solution with hexagonal (rhombohedral) symmetry, which has been well established by X-ray [1,2], electron [3,4], and neutron [5] diffraction. The room temperature structure is based on space group $R\bar{3}m$ (#166), and consists of layers of BiO-(Sr,Bi)O-BiO, with the alkaline earth solute ion substituting only into the middle oxide layer. The valence difference between the Bi and alkaline earth ion is compensated through the creation of oxygen vacancies in the solid solution. These solid solutions have been shown to be oxygen ion conductors with high ionic conductivity [6–9], particularly, at high temperatures.

That a high temperature phase transformation takes place in the β-phase solid solution has been well established by observation of an endothermic DTA peak [8–10], a sharp discontinuity in the lattice parameters [10–15], and an order of magnitude increase in the ionic conductivity [7,8,10–15]; nevertheless, this phase boundary was omitted from a recent phase diagram [16,17]. The high temperature phase has the same space group symmetry as the low temperature phase, although, the unit cell has a larger $c$ axis lattice parameter and the distribution of the oxygen ions is modified. The present paper presents the results obtained from differential scanning calorimetry (DSC) and high temperature X-ray diffraction (HTXRD) on this high temperature phase transformation in the $\beta$-phase $(Bi_2O_3)_{0.8}(SrO)_{0.2}$ composition.

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## 2. Experimental

A sample batch with composition $x$=0.20 was prepared from $Bi_2O_3$ (99.999%) and $SrCO_3$ (99.999%) powders. This composition may be described either as $Bi_{1.6}Sr_{0.2}O_{2.6}$ or $Bi_{0.89}Sr_{0.11}O_{1.44}$, depending on the convention used, which has previously led to some confusion in comparing results in the literature (see reference [4] for such an example). These powders were mixed and ground, and then calcined in air for 20 h at 800°C in platinum crucibles. The reacted powders were crushed, ground, pressed and fired three times, and no evidence of unreacted precursors or impurity phases was observed by XRD. The final powders were annealed for 2 h at 800°C and then cooled in the furnace to room temperature.

A differential scanning calorimeter (Stanton-Redcroft DSC1500) was used to study the thermal events that occur in the $Bi_{1.6}Sr_{0.2}O_{2.6}$ powder sample, during heating and cooling between 20°C and 750°C. A 117 mg specimen was heated and cooled at a rate of 20°C/min in air flowing at 50 ml/min. Platinum sample pans and lids were used along with 66 mg of sapphire in the reference material pan. The temperature scale of the DSC was calibrated in the region of interest by using the solid state transitions of the ICTAC standards, $K_2SO_4$ and $BaCO_3$, at 582°C and 808°C, respectively.

High temperature X-ray diffraction patterns were obtained with an automated diffractometer (Scintag PADX) incorporating a high temperature chamber (Bühler), position sensitive detector (mBraun), 2 kW copper target X-ray tube, and diffracted beam beta filter (nickel foil). The sample was mounted within the high temperature chamber on a platinum-rhodium heater strip, the temperature of which was measured and controlled to ±1°C over the full experimental range, using a Pt/Pt-13% Rh thermocouple spot welded to the heater strip. Instrument alignment was confirmed using silicon and lanthanum hexaboride NIST powder standards [SRM 640 b and SRM 660, respectively]. Samples were prepared by depositing a small quantity of finely ground powder onto the center of the platinum-rhodium heater strip. The temperature gradient over a length of ±2.5 mm from the center of the hot zone has been previously shown, to be less than ±2°C [18] for this furnace. To improve the thermal contact between the powder sample and the heater strip, a drop of acetone was added to distribute the powder evenly over the center of the strip and then allowed to evaporate fully before initiating diffraction scans. Out of concern for a possible reaction of platinum with bismuth, Guillermo et al. [12] used gold foils and crucibles for their high temperature experiments; however, platinum heater strips were used in the HTXRD experiments of Levin and Roth [19], who did not report any deleterious effects. Our experiments were performed with a platinum-rhodium heater strip in 1 atm of air without any apparent degradation of either sample or heater strip. Powder samples were examined at temperatures up to 750°C, with the high temperature diffractometer from 20° to 70° 2$\theta$, a range which included twenty well-resolved diffraction peaks. In the temperature range of most interest, i.e. from around 600°C to 750°C, the diffraction patterns were taken at 5°C increments during heating and cooling cycles, and the process was repeated to check for reproducibility. The temperature was ramped at 20°C/min between setpoints, with a 2 min hold time before collecting data to ensure temperature stability. Using the position sensitive detector in scanning mode at 5°2$\theta$/min, each diffractogram took 10 min to collect.

Diffraction patterns were analyzed using commercial software [Jade version 3.1, Materials Data, Livermore, CA]. Peaks were indexed by direct comparison with the diffraction data originally published by Sillén and Aurivillius [1], allowing for peak shifts due to the lower strontium concentration in the present composition, and the lattice parameters were refined along with the sample surface displacement.

## 3. Results

Fig. 1 shows the heating and cooling DSC curves for the $Bi_{1.6}Sr_{0.2}O_{2.6}$ powder. Two reversible thermal events were seen to occur in the range of 20–750°C. The first of these transitions observed during heating, is an endothermic peak that has an extrapolated onset temperature of 669°C. During cooling, this transition occurs as an exothermic peak having an extrapolated onset temperature of 654°C. A second transition occurs at 710°C during heating and 678°C during cooling. This second transition appears to

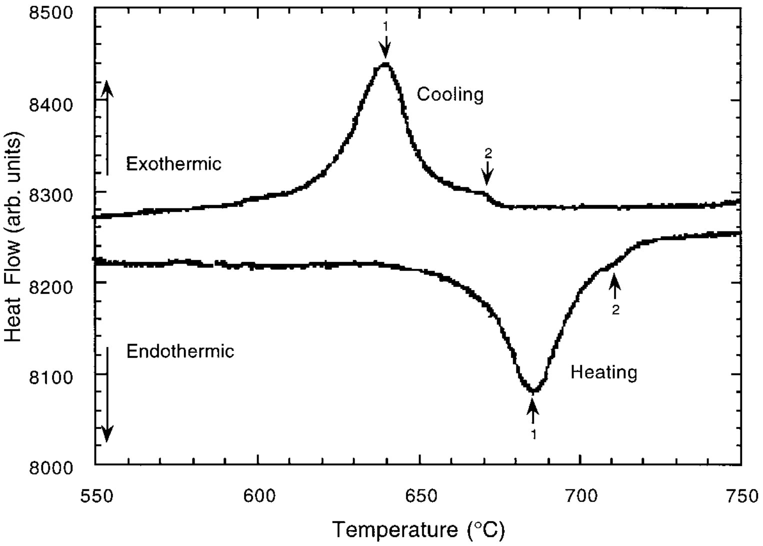

Fig. 1. Heating and cooling DSC curves taken at 20°/min. The phase transformation (1) occurs with an onset temperature around 650°C, with some hysteresis between heating and cooling. The small second event (2) also occurs on heating and cooling.

be related to a step change in the specific heat capacity of the material, the origin of which is currently unknown.

The diffraction patterns could be indexed as a single hexagonal phase with slightly broadened diffraction peaks at all temperatures, except for the narrow range of temperatures for which both the high and low temperature hexagonal phases coexist. The room temperature lattice parameters were $a$=3.970(1) Å and $c$=28.121(6) Å, in good agreement with previously published values [1,12]. As reported previously [3,4], the peaks of the $\beta$-phase samples are somewhat broader than those of the diffraction profile standard [NIST SRM660] $LaB_6$ powder over the same range of 2θ under the same instrumental conditions. The shift in the position of the 00.9 Bragg peak (at around 3.13 Å at room temperature) is the simplest indicator of the phase change from the low temperature to high temperature phase, as shown by the high temperature X-ray diffraction data in Fig. 2. The peak splitting observed in the region of the transformation demonstrates that this transformation is characterized by a discrete change in the lattice dimensions, rather than a continuous evolution from one phase to the other. The transformation temperature range, as characterized by the relative proportion of the peak area of the low and high temperature 00.9 Bragg peaks, has a midpoint around 665°C on heating, as shown in Fig. 3 and at around 630°C on cooling, as shown in Fig. 4. These differences between the heating and cooling transformation temperatures are in reasonable agreement with the DSC measurements. In Fig. 3 and particularly in Fig. 4, some fluctuations in the transformation curves are observed on the high temperature side of the transformation. The nature of this effect is presently unclear, but it appears to correlate in temperature with the second DSC transition discussed previously in Fig. 1.

These changes in the respective lattice parameters over a narrow temperature range confirm previous reports [10–15] and provide new insight into the $\beta_2 \leftrightarrow \beta_1$ phase transformation. The expansion of the $c$ parameter indicates a relaxation of the bonds in directions parallel to the c axis of the hexagonal cell. Recent high temperature neutron diffraction data [5] have supported the hypothesis that this is due to a migration of the oxygen ions into planes normal to this axis. In contrast, relatively small changes are observed in the $a$ parameter due to the constraints imposed by the more strongly bonded atomic planes.

It is observed in Fig. 2 through Fig. 4 that the integrated areas of all of the diffraction peaks are

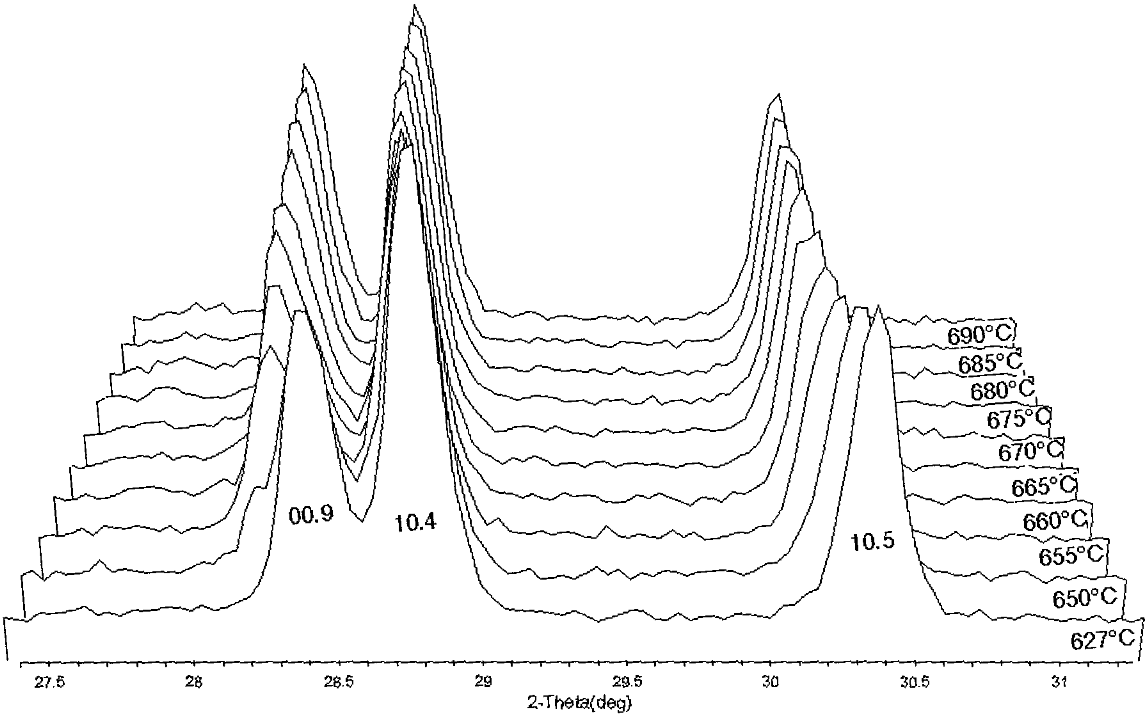

Fig. 2. Superimposed HTXRD patterns taken at intervals on heating from 627°C to 690°C. The phase transformation modifies the peak intensities and causes discrete shifts in all the diffraction peaks, but particularly in the 00.9 reflection.

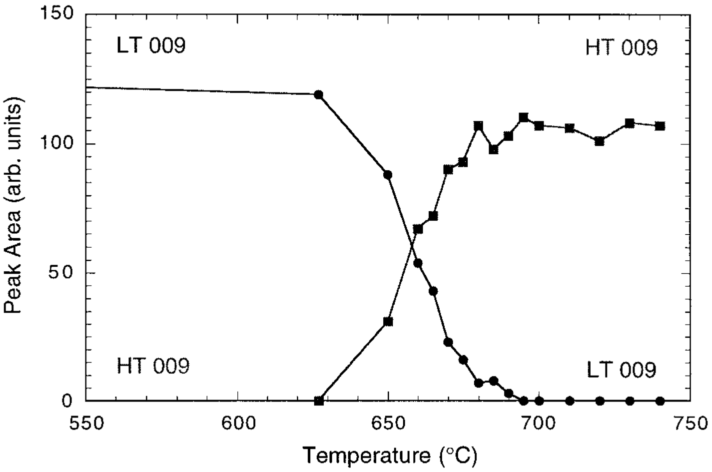

Fig. 3. Plot showing the low and high temperature 00.9 diffraction peak areas as a function of temperature during the heating cycle. The HT phase begins to form around 640°C, is 50% transformed by 655°C, and is fully transformed by about 695°C.

somewhat reduced above the transformation temperature, and this effect was found to be fully reversible on cooling. This observation suggests that the transformation may involve a modification of the cation sublattice in addition to the anion sublattice, since a reordering of the $O^{2-}$ ions should not alter the relative

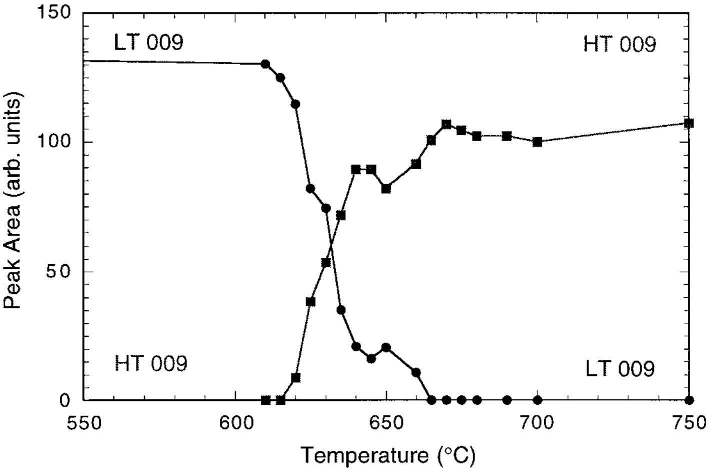

Fig. 4. Plot of the 00.9 diffraction peak area as a function of temperature during the cooling cycle. The LT phase begins to form around 660°C, is 50% transformed by 630°C, and is fully transformed by about 615°C.

intensities of the diffraction peaks so significantly, given the relatively low X-ray scattering factor of oxygen compared to that of bismuth and strontium. The form of the modification of the lattice which generates the lattice expansion $\Delta a$, $\Delta c$, and $\Delta V$, must be such that it increases the mobility of anions in layers which lie normal to the z axis, to account for the observed increase in anionic conductivity [10–15]. This increased conductivity has thus been attributed to thermal excitation of oxygen anions into weakly-bound sites between the cation layers, which provide higher mobility in agreement with the neutron diffraction findings [5]. The reversible changes in diffraction peak intensities observed here have not been reported previously, although, it is unclear whether this amplitude reduction is generally true for the solid solution, or whether it has some dependence on composition.

## 4. Discussion

The present work illustrates the advantage of combining information from complementary methods, in order to determine accurate phase diagrams. This is of particular importance in systems such as $Bi_2O_3$–SrO, where high temperature phases exist which cannot be stabilized at room temperature. Analysis by high temperature X-ray diffraction requires little sophistication when the phase transformation includes a significant structural change, but considerably more care was required to analyze the $\beta_2 \leftrightarrow \beta_1$ transformation, in which the structural changes were much more subtle. In this case, the information provided by the differential scanning calorimetry justified a detailed examination of the diffraction pattern in the temperature range around 650°C.

The first DSC peak is clearly correlated with a change in the structure of the material, as demonstrated by the HTXRD results. The second DSC event at higher temperature was shown by HTXRD measurements to be correlated with structural changes, but the nature of this event is not understood at this time. It is possible that this second transformation involves some subtle ordering in the structure, for which tube-based X-rays are not the most reliable probe. Synchrotron X-rays afford an opportunity to select suitable wavelengths to distinguish site occupancies of different ions, and high temperature neutron diffraction has already been demonstrated to be effective for the study of changes in oxygen site occupancy associated with the $\beta_2 \leftrightarrow \beta_1$ phase transformation [5]. Therefore, it is reasonable to propose that a synchrotron or neutron diffraction study at high temperature might be attempted to clarify the nature of the second transformation.

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