Primary Particle Size Effect on Phase Transition in $Ba_2In_2O_5$

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INTRODUCTION

Oxygen-ion conductors have been extensively studied as a consequence of their potential technological applications, such as oxygen sensors and monitors, electrolytes in solid oxide fuel cells, and oxygen permeable membranes [1]. Oxide ceramics with cubic perovskite or related structures may exhibit high oxygen-ion conductivity [1]. The mixed oxide $Ba_2In_2O_5$ adopts an orthorhombic structure from room temperature up to 925 ^oC with cell parameters a = 0.608 nm, b = 1.679 nm and c = 0.589 nm [2]. At that temperature, an order-disorder phase transition occurs and the crystalline structure changes to tetragonal symmetry. A second-order phase transition at 1040 ^oC turns the crystalline structure to cubic perovskite, when the anionic vacancies are in a fully disordered state [3, 4], and the mixed oxide exhibits pure ionic conduction with unity ionic transport number [5, 6]. In this work the primary particle size effect on the order-disorder phase transition temperature of $Ba_2In_2O_5$ was investigated by in situ high-temperature X-ray diffraction and electrical conductivity measurements.

EXPERIMENT

$Ba_2In_2O_5$ was prepared by the conventional mixing of starting oxides/carbonates or nitrate precursors followed by solid state reaction at high temperatures. Sintering of pellets was carried out at 1300 or 1350 ^oC. Structural characterization was done by X-ray diffraction (XRD) using a conventional diffractometer (D8 Advance, Bruker-AXS) and the XPD D10B beam line of the Brazilian Synchrotron Light Laboratory (LNLS). The crystal structures of $Ba_2In_2O_5$ were determined through Rietveld refinement using GSAS. The primary particle sizes were determined from broadened diffraction lines directly from refined patterns [7]. Phase transition study was carried out by in situ high-temperature X-ray diffraction (at LNLS) and electrical conductivity by impedance spectroscopy measurements (HP 4192A LF impedance analyzer).

RESULTS AND DISCUSSION

Room temperature X-ray diffraction results show that all prepared materials were well crystallized brownmillerite-type structure with orthorhombic symmetry. Fig. 1 shows, as an example, the diffraction pattern of a sample prepared from nitrate precursors. In this case, the XRD pattern was obtained in the XPD D10B beam line of LNLS. A special setup [8]

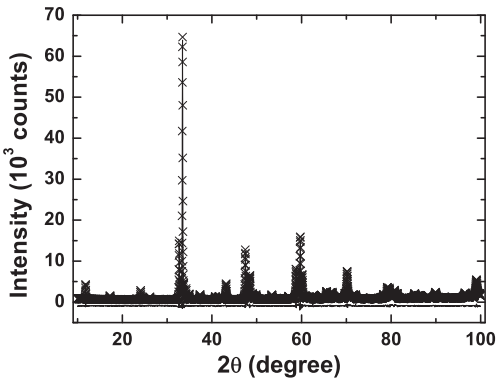

FIG. 1: Room temperature X-ray diffraction pattern of $Ba_2In_2O_5$.

was used for in situ high-temperature X-ray diffraction study of the order-disorder phase transition in $Ba_2In_2O_5$. Fig. 2 shows XRD patterns detected in the room temperature to 950 ^oC temperature range in the specimen prepared from nitrate precursors. It is evident that at 825 ^oC the phase transition has already started. This temperature is relatively lower than that reported in the literature. Fig. 3 shows Arrhenius plots

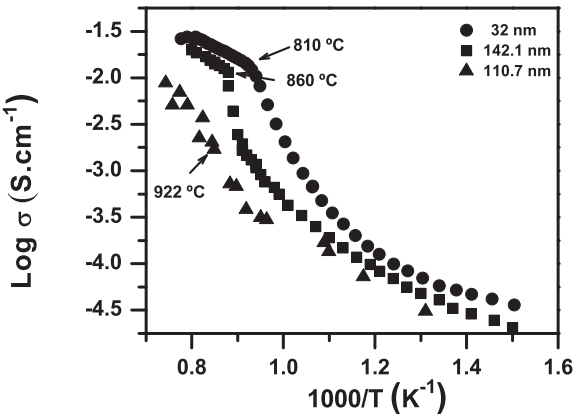

FIG. 2: *In situ* high-temperature X-ray diffraction patterns of $Ba_2In_2O_5$.

of the electrical conductivity of $Ba_2In_2O_5$ sintered materials. There is a continuous increase in the electrical conductivity with increasing temperature, and suddenly a sharp increase in the magnitude of the conductivity reveals the first order phase

transition. It is important to note that the onset of the order-disorder phase transition vary with the particle size. Specimens with primary particle size of 110 nm have an onset temperature of about 922 ^{o}C in agreement with reported values [2, 4], whereas for samples with particle size of only 32 nm that temperature is only 810 ^{o}C. The difference in the phase transition temperature of samples prepared from oxides deserves attention. The main difference in these samples is the room temperature particle size. In addition, this variable influences the cell parameters and the cell volume. It is generally known that the lower is the particle size the higher is the surface energy of a system. Moreover, surface energy is known to have an effect on crystal lattice distortion, which in turn affects the phase transition temperature. Thus, it seems that the primary particle size is the dominating factor affecting the phase transition temperature in $Ba_2In_2O_5$ mixed oxide.

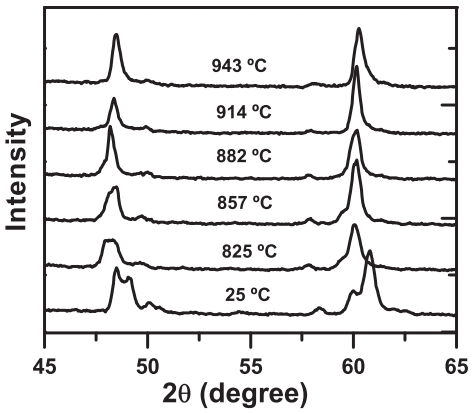

FIG. 3: Arrhenius plots of the electrical conductivity of $Ba_2In_2O_5$ sintered materials with different primary particle sizes.

CONCLUSION

The overall results indicate that the phase transition temperature in $Ba_2In_2O_5$ decreases with decreasing of the primary particle size. This was the first noticed correlation between this structural parameter and the macroscopic electrical conductivity property.

ACKNOWLEDGEMENTS

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