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Thermodynamic quantities and oxygen nonstoichiometry of undoped $BaTiO_{3-\delta}$ by thermogravimetric analysis

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ABSTRACT

Thermogravimetry analysis was performed to determine the oxygen nonstoichiometry of oxides by using a home-made experimental set-up with Cahn D200 microbalance for an undoped $BaTiO_{3-\delta}$ specimen. The relative partial molar enthalpy and entropy of oxygen for undoped $BaTiO_{3-\delta}$ were also calculated from the slope and intercept of the $\delta - P_{O_2} - T$ relation, respectively. The negative signs of partial molar enthalpy and entropy in the oxygen deficient regime indicated that the incorporation of oxygen is an exothermic process. The values for K_i and K_{Re} of the undoped $BaTiO_{3-\delta}$ are best described by the following equations:

$$K_i/\mathrm{cm}^{-6} = (1.69 \pm 1.51) \times 10^{46} \exp\left(-\frac{2.93 \pm 0.23\,\mathrm{eV}}{kT}\right)$$

$$K_{Re}/\mathrm{cm}^{-9} = (7.15 \pm 5.55) \times 10^{73} \exp\left(-\frac{5.80 \pm 0.15\,\mathrm{eV}}{kT}\right)$$

The difference in n–p transition P_{O_2} compared with reference should be further understood by identifying the cation nonstoichiometry and the value of impurity defects for the clarification of defect structure.

1. Introduction

It has long been the basic rule of solid state ionics that both the transport and thermodynamic properties of the oxide utilized in electrochemical applications are strongly influenced by the nature of the defect system of oxides that should be subjected to the external thermodynamic conditions [1,2]. Chemical potentials may be assigned to all elements in redox reactions involving the structure elements of oxide and equilibrium conditions are formulated when the free energy change of the reaction equals the difference of the sums of chemical potentials of elements at the product and reactant sides of the reaction [3]. Because mass action law defines the relationship between oxygen partial pressure (P_{O_2}) and the defect concentration in crystal oxides during redox reactions, much interest has been focused on precisely how to extract the internal/external reaction constants from various experimental measurements. Several defect-related transport properties, including optical, electrical, and electrochemical measurements, have been applied to obtain the thermodynamic quantities of oxides [4–7].

Among these techniques, thermogravimetric analysis (TGA) has been recognized as one of the most valuable tools for directly clarifying the defect concentrations of oxides as a function of the thermodynamic control parameters by measuring the weight change of oxide caused by the redox reactions until it reaches a new equilibrium state determined by the change of thermodynamic conditions such as temperature and P_{O_2} [8–10]. The weight change can then be directly converted into the corresponding variation of oxygen nonstoichiometry, δ, of the oxide specimen. However, despite the clarity in TGA's working principles, its application to determine the oxygen nonstoichiometry has not been considered a trivial matter. Moreover, because the weight change undergoing redox reactions may be interfered with by multiple spurious weight changes caused by environmental and structural factors, the exact measurement of the pure weight change by redox reactions from oxides has been recognized as a critical hurdle that must be overcome, especially in the case of very narrow oxygen stoichiometric oxides. Especially, for the perovskite oxides showing n- to p-type transition in an extended range of P_{O_2} at elevated temperature, the nonstoichiometric variation with P_{O_2} is expected to be so negligible

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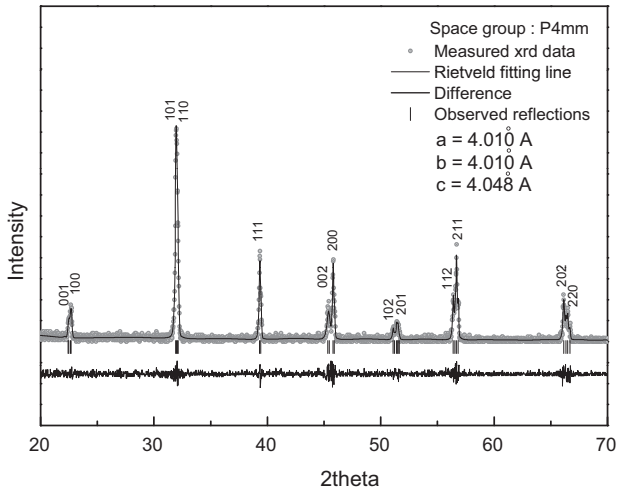

Fig. 1. Room temperature X-ray diffraction (XRD) patterns of $BaTiO_{3-\delta}$.

(corresponding to around several micrograms difference in weight) in the electron/hole mixed conduction regions that only a few TGA has been successful due to the difficulty in experimental resolution [11].

In this work, we report a newly built, home-made experimental set-up consisting of an asymmetric TGA system with Cahn D200 microbalance and is then applied to evaluate the thermodynamic quantities and oxygen nonstoichiometry of $BaTiO_{3-\delta}$ as a function of temperature ($1073 \leq \mathrm{Temp/K} \leq 1273$) and P_{O_2} ($-18 \leq \log P_{O_2}/\mathrm{atm} \leq 0$) corresponding to the very narrow oxygen nonstoichiometric change ($\approx 10^{-4}$ mol). On the basis of the defect chemistry widely discussed in the literature, the nonstoichiometry, δ, was successfully determined with non-linear functional fitting. Furthermore, the relative partial molar enthalpy and entropy of oxygen for undoped $BaTiO_{3-\delta}$ were also calculated from the slope and intercept of the $\delta - P_{O_2} - \mathrm{T}$ relation,

2. Experimental

2.1. Sample preparation

"Undoped" polycrystalline $BaTiO_{3-\delta}$ specimens were prepared by conventional solid state reaction method. The starting materials of $BaTiO_{3-\delta}$ (Alfar Aesar, 99.99%) in powder form were pressed into pellets, cold-isostatic-pressed, and sintered at 1623 K for 5 h in air. It should be mentioned that 5 ppm of Fe and Al by weight were identified as impurities based on the certificate of analysis given by company. During the sintering, these $BaTiO_{3-\delta}$ specimens on a first-layer $BaTiO_{3-\delta}$ substrate were fully covered by $BaTiO_{3-\delta}$ starting powders to prevent any possible reaction. The densities of the resultant disks were 90% of the theoretical values. X-ray diffraction (XRD) spectra confirmed the single phase tetragonal $BaTiO_{3-\delta}$ (space group, *P4mm*) as shown in Fig. 1, in agreement with the literature [12,13]. The specimens for TG measurements were cut out of the sintered disk into around 781 mg cylinder. Because the oxygen nonstoichiometry of yttria-stabilized zirconia (YSZ) does not need to be considered like the coulometric titration measurements, relatively light, 781 mg specimens were prepared.

2.2. Experimental set-up

TGA determines the weight change of a specimen in relation to the change in P_{O_2} and temperature. Therefore, such analysis relies on a high degree of precision in three measurements: weight, P_{O_2}, and temperature change. The experimental apparatus of asymmetric TGA with Cahn D200 microbalance that was used to make these three precise measurements is shown in Fig. 2. Spurious weight changes caused by the thermal convection flow within the reactor are mainly ascribed to the temperature difference along the hang-down wire [14]. To minimize the thermal convection flow reaching the specimen and causing some disturbance to the specimen, a home-made reflector was designed. The plausible electrostatic effect of the microbalance due to the application of friction to the gas flow was minimized by using the metal end-cap connected to a ground connection [15]. To minimize the thermal diffusion due to the difference in the thermal diffusivity of the component gases, 90% ultra-high purity (UHP) N_2 carrier gas was used and the mixture gas was produced by flowing through a mixing bath zone [16,17]. The radiation effect due to the asymmetric design of TGA was minimized by placing an oval mirror inside the tube connected to the microbalance [11]. The input power stability was assured by using a constant voltage, constant current, uninterruptible power supplier. The inherent effects due to the asymmetric design of TGA, including upthrust buoyancy [17,18], thermomolecular force [17], and high-temperature aerodynamic effects [15,19], were corrected by subtracting the spurious weight change of a dummy test with alumina from the real measurements. The flow of the N_2 protective gas through a counter weight reactor prevents any corrosive gas flow into the microbalance. The effects from the reactor tube size and hang-down wire diameter were also considered in our experimental design. To minimize the temperature variation near the microbalance and balance controller, a temperature-programmed heater and air conditioner were used. Finally, the vibration effect, one of the most important and serious obstacles to high resolution, was relieved by using a two-step, anti-vibration pad on a 200 kg metal ground pad.

The P_{O_2} was controlled by a N_2/O_2 gas mixture at higher P_{O_2} and a CO/CO_2 gas mixture at lower P_{O_2}, with UHP N_2 carrier gas at a constant flow rate of 180 sccm, while the total flow rate of the gas mixture to the reactor was maintained at 200 sccm for all measurements. Each gas flow during the TG measurements was controlled with a mass flow controller (MKS) and the rate was measured with a flow calibrator (Digital flowmeter, Optiflow 570). The equilibrium P_{O_2} was determined from the open circuit potential of a YSZ-based oxygen sensor after the reactor and near the specimen within the reactor. The temperature of oxygen sensor located in outside of reactor was maintained as same as the reactor temperature, maintained within 1 K of the target temperature. The both YSZ oxygen sensors calibrated in terms of standard gas and temperature.

The relationship between the oxygen nonstoichiometric variation and the measured weight change can be described as

$$\Delta\delta = \frac{\Delta w}{M_O}\frac{M_S}{w_S} \tag{1}$$

by assuming that only oxygen exchange from the specimen occurs and changes the specimen weight, where $\Delta\delta$ is the oxygen nonstoichiometric variation, Δw the weight change of the specimen, w_S the initial specimen weight, M_O the oxygen atomic weight, and M_S denotes the molecular formula weight of the specimen.

3. Results and discussion

After subtracting the spurious weight change due to the many factors described in experimental section, Fig. 3 shows a typical weight change profile upon oxidation and reduction as a function of time for the $BaTiO_{3-\delta}$ specimen with ± 0.5 μg resolution, in which the measured relative weight change of around 3 μg corresponds to an oxygen nonstoichiometric change of less than around 10^{-4} mol. Our TGA system was able to clearly distinguish the oxygen nonstoichiometric change of less than 10^{-4} mol for the $BaTiO_{3-\delta}$ specimen at 1273 K with 200 sccm total gas flow dynamic condition with ± 1.5 μg resolution in the worst case over all the measurement ranges. By cyclic operation of oxidation and reduction at a given temperature, we confirmed the reproducibility of the measurement by demonstrating its return to the starting values.

Despite the debate regarding the electrically compensating defect species for oxygen vacancies, especially about cation defects, the absolute nonstoichiometry of undoped $BaTiO_{3-\delta}$ was successfully extracted from the coulometric titration measurements based on defect chemical rationale by considering acceptor-type impurities, where n- to p-type transition occurs [20,21]. One should note that the analysis of absolute nonstoichiometry of undoped $BaTiO_{3-\delta}$ was also successful based on Schottky-Wager disorder [22]. With only P_{O_2} dependence of the mass changes from TGA, the majority defects species may not be clarified especially within *n–p* transition regime due to the same oxygen partial pressure dependence of oxygen vacancy concentration, regardless of cation defect or acceptor impurity. Therefore, the oxygen nonsotichiometry caused from the variation of cation ratio, Ba/Ti, was not considered in this work to make the analysis simple as possible, and one may define the external and internal equilibria as

$$O_O^x = V_O^{\bullet\bullet} + 2e^{/} + \frac{1}{2}O_2(g); \quad K_{Re} = [V_O^{\bullet\bullet}]n^2 P_{O_2}^{1/2} \tag{2}$$

$$0 = e^{/} + h^{\bullet}; \quad K_i = n \cdot p \tag{3}$$