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Investigation of the sintering of barium titanate ceramics by oxygen coulometry

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Abstract

The oxygen coulometry method by solid electrolyte circonia cells was applied to investigate the sintering process of $Ba_{1-x}La_xTiO_3$ ceramics ($0 \leqslant x \leqslant 0.05$). During the heating, three different oxygen release phenomena were observed: (1) the O_2 release due to the formation of Schottky-type oxygen vacancies; (2) the O_2 release caused by the incorporation of the donor impurity during grain growth; and (3) an irreversible oxygen release with an onset temperature between 1000 and 1150°C, for which the cause is not clear. The quantitative data of the effect (2) can be explained on condition that the donors are charge compensated both by electrons and by cation vacancies.

Keywords: $BaTiO_3$ and titanates; Defects; Grain growth; Oxygen coulometry

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1. Introduction

For $BaTiO_3$ as an oxide compound, its deviation from the stoichiometric composition with respect to oxygen determines in a great extent the macroscopic properties of the material. As an example, oxygen vacancies act as donors and can change the electric conductivity in a wide range. Hence, the determination of the amount of oxygen exchange with the ambient atmosphere at elevated temperatures is an important task in the investigation of the defect chemistry of $BaTiO_3$. Another interesting oxygen exchange process occurs during the incorporation of higher valency elements at Ba or Ti sites (donors, e.g. $La_{Ba}^{\bullet}$) if they are introduced as oxides. This process normally takes place during sintering and is strongly related to the grain growth mechanism.[1] Generally, oxygen can be exchanged with the ambient atmosphere both during the formation of the final material, e.g. the sintering process, and/or during the reaching of the equilibrium with the ambient atmosphere with respect of temperature and oxygen partial pressure. To investigate the oxygen exchange, mostly thermogravimetry was used in the past,[2–5] sometimes combined with mass spectroscopy to identify oxygen as the mass changing element.[6]

Until now, no investigations of the oxygen exchange in $BaTiO_3$ by coulometric methods are known. Thus, the aim of this paper is to demonstrate the benefit of the oxygen coulometry method applied on barium titanate ceramics for the investigation of both their defect chemistry and the sintering process.

We report both on the development of a suitable measuring system and on its application on the investigation of the sintering of donor-doped and undoped barium titanate ceramics with variing Ba/Ti stoichiometry.

2. Experimental procedure

2.1. Preparation of specimens

The ceramic powder with a nominal composition of $Ba_{1-x}La_xTiO_3$ ($0 \leqslant x \leqslant 0.05$) was prepared by the classical mixed-oxide powder technique. Partly, 1 mol% TiO_2 or 2 mol% BaO were added. After mixing (agate balls, water) and calcination (1100°C, 2 h) of appropriate amounts of $BaCO_3$ (Solvay, VL600), TiO_2 (Merck,

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no. 808) and $La_2(C_2O_4)_3\bullet 9H_2O$ (SKW Piesteritz), the powder was milled again and densified to disks with a diameter of 12 mm and a height of nearly 3 mm ($m\approx 1$ g). The samples were sintered with heating and cooling rates of 10 K/min in a special gas-tight alumina tube furnace of the coulometry system (see below). To avoid interfering contamination during sintering they were contained in ZrO_2 powder covered Pt dishes.

The microstructure of the polished and chemically etched specimens was examined by optical microscopy.

2.2. Oxygen coulometry

The mean components of the equipment are two identical, electronically controlled, oxygen conducting ZrO_2 Nernst cells (SensoTech, Magdeburg-Barleben, Germany, model Oxylyt 10-21), which exhibit two pairs of electrodes (see Fig. 1). One of them is used for the determining of the oxygen partial pressure, pO_2, of the flowing gas stream by measuring the voltage between the electrodes, U^{cell}, according to the Nernst equation (1).

$$U^{\text{cell}} = \frac{RT}{4F}\ln\frac{p_{O_2}}{p_{O_2}^{\text{ref}}} \tag{1}$$

(R, molar gas constant, T, absolute temperature; F, Faraday constant; pO_2^{ref}, oxygen partial pressure of air as the reference gas).

The second pair of electrodes is used for the transport of a well-defined amount of oxygen between the flowing gas inside the cell and the ambient air by an applied electric current, I. Both electrode pairs are connected by an electronic control circuit with the set point U^{set} and the control variable I in that sense, that a constant output pO_2 (U^{cell}) of the cell is maintained by an oxygen transport into or out of the ZrO_2 tube (see Fig. 1).

The measuring principle is described as follows. After the preparation of the carrier gas (gas mixing and flow control device, Horiba Ltd., Japan) the first cell is used to produce a working gas stream (200 ml/min) with well-defined pO_2 as the ambient atmosphere of the sample to be investigated. After passing the furnace, the gas streams through the second cell, which set point U^{set} is chosen to get a appropriate current I^{pump}. As long as no change of the oxygen partial pressure between the two cells occurs, this current is constant and exhibites the base line of the measurement I_0. If an oxygen exchange between the sample and the ambient atmosphere occurs, e.g. during change of the sample temperature, a changing current I^{pump} will compensate the changed oxygen partial pressure of the output gas stream of the furnace. Thus, the total amount of exchanged oxygen during a time interval $t_2 - t_1$ can be calculated by the following expression.

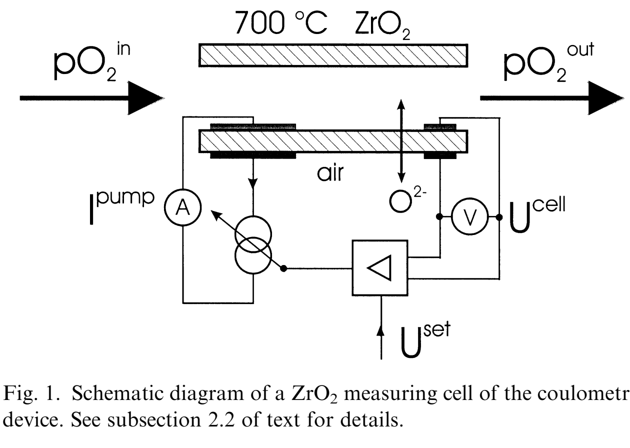

Fig. 1. Schematic diagram of a ZrO_2 measuring cell of the coulometry device. See subsection 2.2 of text for details.

$$\Delta n_{O_2} = \frac{1}{4F}\int_{t1}^{t2}[I^{\text{pump}}(t) - I_0]\,dt \tag{2}$$

A quantitative check of the procedure was performed by the decomposition of BaO_2 and resulted in errors $\leqslant 5\%$ within 10^{-6} and 10^{-5} mol expelled O_2 which is in the same order or a little more than the oxygen exchange of the samples to be investigated.[7]

To separate the influence of alumina (furnace tube and sample holder) and zirconia (sample pad) on the oxygen exchange, empty tests were performed. Only at temperatures higher than 1400°C a remarkable, but small amount of oxygen is expelled during the heating cycle which is caused probably by the formation of oxygen vacancies. All quantitative results were corrected by subtracting that effect of the apparatus.

3. Results and discussion

Fig. 2 shows a typical coulometry measurement of a 0.5 mol% La containing sample. During heating, four peaks of the pumping current I^{pump}, can be observed. As minimum peaks they indicate an oxygen release of the sample.

3.1. Formation of oxygen vacancies

Only peak (IV) which overlaps with peak (III) has a counterpart during the cooling cycle. Hence, only the process(es) which cause that effect are reversible. Obviously, peak (IV) originates from the formation of equilibrium oxygen vacancies according to Eq. (3)

$$0 \leftrightarrow V_O^{\bullet\bullet} + 2e' + \tfrac{1}{2}O_2\uparrow \tag{3}$$

The vacancies are formed both in the specimen and in the alumina and zirconia material of the measuring device. The interesting amount of oxygen which results

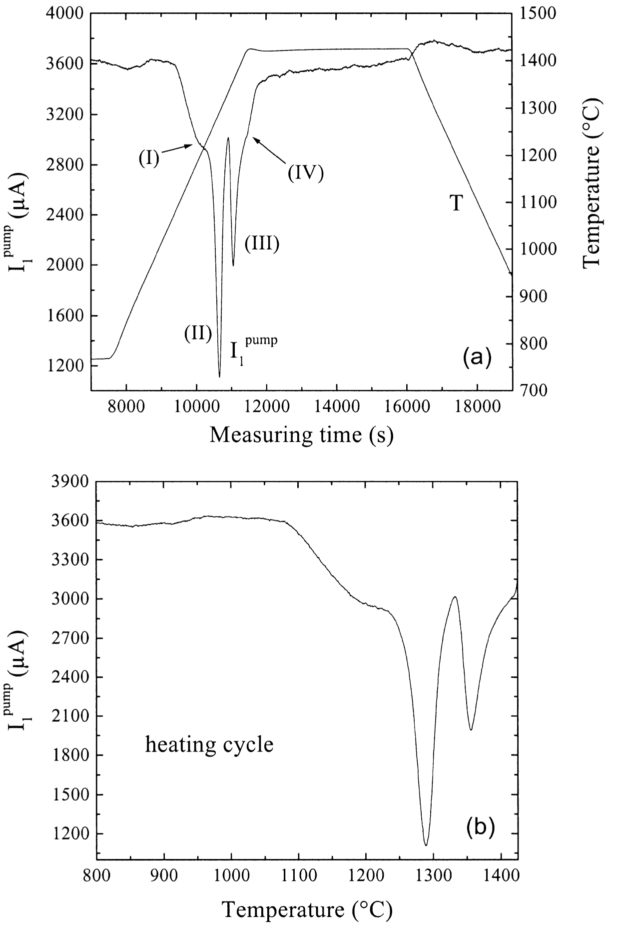

Fig. 2. Pumping current I^{pump} of the coulometry cell in dependence on both (a) time and (b) temperature during the sintering of a sample with 0.5 mol% La and 1 mol% excess TiO_2. Ambient atmosphere: $pO_2 = 2.4$ Pa. Marks (I) to (IV) denote different oxygen release effects, which are discussed in the text.

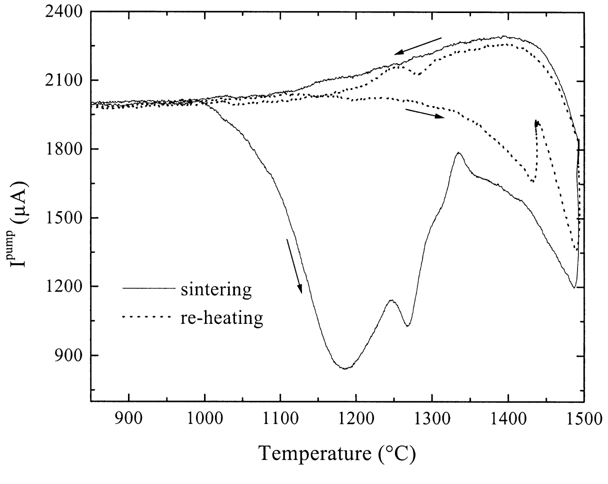

Fig. 3. Pumping current I^{pump} in dependence on temperature during sintering as well as during re-heating of a sample with 0.2 mol% La, 2 mol% excess BaO and 2 mol% SiO_2. Ambient atmosphere: $pO_2 = 2.4$ Pa.

from the specimen is obtained by re-heating of a sintered sample where only peak (IV) occurs. As an example, see Fig. 3. The quantity of the oxygen release allows the calculation of the change of the concentration of the oxygen vacancies. Such a systematic analysis in dependence on temperature, heating rate, oxygen partial pressure and chemical composition is the subject of our further work.

3.2. Incorporation of donor dopant

To attribute the peaks (I)–(III) to particular processes during the sintering, measurements at soaking temperatures of 1200, 1300 and 1430°C were performed. The results together with the related microstructure data are shown in Fig. 4. While a sintering temperature of 1200°C is too low to initiate the anormal grain growth of $BaTiO_3$, the microstructure of the specimens sintered at 1300 and 1430°C exhibits the typical bimodal intermediate and final stage, respectively. The onset temperatures of the peaks (II) and (III) correspond very well with the starting temperatures of the exaggerated grain growth in the presence of a SiO_2 and TiO_2 containing liquid phase, respectively.[8–10] SiO_2 impurities come from the abrasion of the agate balls during milling. Their small amount causes an incomplete grain growth. Hence, peaks (II) and (III) originate from the incorporation reaction of La_{Ba}

$$La_2O_3 + 2TiO_2 \rightarrow 2La^{\bullet}_{Ba} + 2Ti'_{Ti} + 6O^{\times}_{O} + \tfrac{1}{2}O_2 \uparrow \tag{4}$$

which is in accordance to the findings of Drofenik, who stated that in $BaTiO_3$ the endothermic donor incorporation according to Eq. (4) is only possible as long as a constant, sufficient high energy is provided by the stored free surface energy during the exaggerated grain growth.[1]

By means of coulometry measurements at different maximum sintering temperatures and the subtraction of the contributions of the oxygen vacancies both from the specimen and from the apparatus, the amount of expelled oxygen of the sample sintered at 1430°C caused by the La incorporation was determined to 2.6×10^{-6} mol O_2 corresponding to 0.064 mol%. If the total amount of 0.5 mol% La would be incorporated according to Eq. (4) an oxygen release of 0.125 mol% would be expected. Since no La segregation at grain boundaries or triple points was detected, this discrepancy may be explained, if only about 50% of the $La^{\bullet}_{Ba}$ ions are compensated by electrons (Ti'_{Ti}) and 50% e.g. by Ba vacancies according to following equation.

$$La_2O_3 + 3TiO_2 \rightarrow 2La^{\bullet}_{Ba} + V''_{Ba} + 3Ti^{\times}_{Ti} + 9O^{\times}_{O} \tag{5}$$

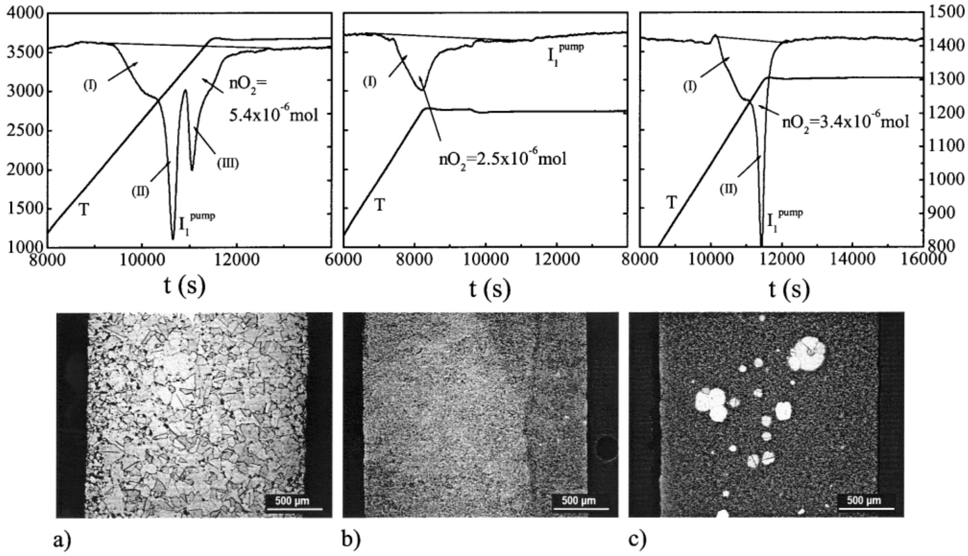

Fig. 4. Pumping current I^{pump} in dependence on time during the sintering of a sample with 0.5 mol% La and 1 mol% excess TiO$_2$ at different maximum temperatures of 1430°C (a), 1200°C (b) and 1300°C (c). Ambient atmosphere: pO$_2$ = 2.4 Pa. Optical micrographs of the corresponding microstructure are also presented (bar = 500 μm). Marks (I) to (III) correspond to Fig. 2.

3.3. *Discussion of peak (I)*

The reason of the oxygen release peak (I) is not clear until now. Because of its irreversible character it must be related to a process which occurs during sintering. It occurs both in undoped and donor-doped material. While stoichiometric and BaO-excess samples exhibit onset temperatures $\geqslant 1100$°C, an addition of excess TiO$_2$ or SiO$_2$ shifts the onset temperature by about −100 K. Since the coulometry measurements were performed at an oxygen partial pressure of 2.4 Pa, a possible explanation could be the release of air enclosed in intragranular pores during the shrinkage process. But, dilatometric investigations exhibited no correlation to the onset temperature of peak (I). Furthermore, the exhaustion of the greens followed by storing in argon resulted in an only very small reduction of the peak size. The desorption of chemisorbed oxygen caused by the storage of the powder in air seems to be unlikely because of the relative high onset temperatures of 1000 until 1200°C.

4. Conclusions

By means of the oxygen coulometry it is possible to determine quantitatively the oxygen exchange due to the donor incorporation during sintering and due to the formation or annihilation of equilibrium oxygen vacancies as well as the onset temperatures of the corresponding defect reactions in perovskite-type ceramics based on BaTiO$_3$. In the case of La doped material, the oxygen release data can be explained if both electronic and cation vacancy charge compensation take effect.

The oxygen release effect which starts at about 1000–1150°C is not understood and must be the subject of further investigations as well as the investigation of acceptor-doped material.

Acknowledgements

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