



# Investigation of Semiconducting Barium Titanate Ceramics by Oxygen Coulometry

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Submitted February 20, 2003; Revised February 4, 2004; Accepted February 5, 2004

**Abstract.** Donor-doped BaTiO<sub>3</sub> ceramics (0–0.6 mol% Nb) were investigated during the sintering process at an oxygen partial pressure of 2.4 Pa and at a maximum temperature of 1430°C. The occurring oxygen exchange with the ambient atmosphere was monitored quantitatively by oxygen coulometry. The coincidence between the grain growth behavior and the occurrence of distinct oxygen release peaks during the anomalous grain growth reveals that significant amounts of the donor are incorporated and charge-compensated by electrons only under the conditions of the anomalous grain growth. Quantitative analysis of the coulometric data shows that at a doping level of 0.2 mol% nearly all donors are charge-compensated by electrons. With increasing Nb concentration also Ti vacancies gradually begin to serve for compensation. At 0.5 mol% Nb their influence reaches 70 % of the electronic compensation.

**Keywords:** barium titanate, donor-doped, defect chemistry, sintering, oxygen coulometry

## Introduction

The defect chemistry as well as the microstructure of donor(n)-doped, semiconducting BaTiO<sub>3</sub> ceramics crucially govern its material properties used in numerous applications such as PTCR (positive temperature coefficient of resistance) devices, GBBL (grain boundary barrier layer) capacitors and several sensor devices (oxygen, humidity, pressure). The general characteristic of the equilibrium defect chemistry of n-doped BaTiO<sub>3</sub> with donor concentrations  $\geq 1$  mol% seems to be known (see [1] for a recent overview). In a wide range of oxygen partial pressure ( $p_{O_2}$ ) the positive donor is charge-compensated by negative titanium vacancies [2, 3]. Only at very low  $p_{O_2}$  electronic compensation dominates [3]. But, in the case of lowly-doped material, a controversial discussion continues. The most recent example is the proposal of Morrison,

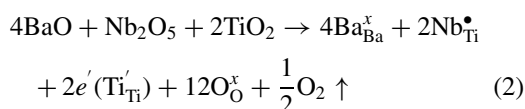
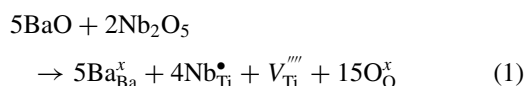
Coats, Sinclair, and West [4], who stated that in air-sintered samples the donor ( $La^{3+}$ ) is exclusively compensated by Ti vacancies and the electrical conductivity of the material only results from oxygen vacancies but not from the donor doping. A critical discussion of this hypothesis was given in [1].

A special property of n-doped BaTiO<sub>3</sub> ceramics, related also to non-equilibrium processes like sintering and grain growth, is the well-known doping anomaly, which is still not well understood. The anomaly is that for donor concentrations higher than a critical value (depending on  $p_{O_2}$  and specific surface of the starting powder) the material becomes insulating and simultaneously the anomalous grain growth, which is usually accelerated by liquid phase sintering, is more or less inhibited. In the literature, that anomaly was often explained by a change of the charge-compensation species from electrons to cation vacancies. But especially the abrupt change of the grain growth behavior cannot be interpreted in this manner. A possible explanation was given by Drogenik [5, 6], who stated

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(1) that the endothermic incorporation process of the *electron-compensated* donor is only possible as long as a constant, sufficiently high energy is provided by the stored free surface energy of the primary grains during the anomalous (exaggerated) grain growth (AGG), and (2) that the grain growth is inhibited if the necessary incorporation energy exceeds the surface energy as the driving force of the grain growth.

For all the mentioned questions the knowledge of the kind of charge-compensation of the donor is of crucial importance both in the equilibrium state and during non-equilibrium processes like the donor incorporation during heating. Following simplified equations describe the two significantly different incorporation variants for vacancy, Eq. (1), and electronic, Eq. (2), compensation with  $\text{Nb}_{\text{Ti}}^{\bullet}$  as the donor impurity and  $V_{\text{Ti}}^{\prime\prime\prime}$  as the cation vacancy, e.g.<sup>1</sup>



Generally, only the compensation by electrons is accompanied by an oxygen release regardless of the complexity of the incorporation reaction. Hence, both compensation mechanisms can be distinguished experimentally. In the past, measurements of the weight change due to the exchanged oxygen were mostly used for that purpose [7–9]. All that data are related to integral changes between equilibrium states at fixed temperature and  $p\text{O}_2$  and exhibit no information about the kinetics of the oxygen exchange process. Recently, it was shown by the authors that oxygen coulometry as an alternative method to thermal gravimetric analysis (TG) can be used for the quantitative determination of the oxygen exchange of doped  $\text{BaTiO}_3$  ceramics both under equilibrium and non-equilibrium conditions [10]. Compared to TG in most cases the coulometric technique has a better detection limit for mass changes and it is oxygen sensitive.

Thus, the aim of this paper is a systematic investigation of Nb-doped  $\text{BaTiO}_3$  ceramics with respect to their oxygen exchange during sintering to get quantitative data about the donor incorporation in dependence on the progress of the sintering process.

## Experimental

Ceramic powders with a nominal composition of  $\text{BaTi}_{1-x}\text{Nb}_x\text{O}_3 + 4.0 \text{ mol\% TiO}_2 + 0.6 \text{ wt\% SiO}_2$  ( $0 \leq x \leq 0.007$ ) were prepared from following starting materials:  $\text{BaTiO}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$  and  $\text{Nb}_2\text{O}_5$  (all chemicals were pure > 99 wt%, for preparation details see [5]). The green pellets (0.5–1 g) were sintered in a special gas-tight furnace of the coulometric measuring system [10] at a maximum temperature of 1430°C in an ambient atmosphere of  $p\text{O}_2 = 2.4 \text{ Pa}$ .  $\text{ZrO}_2$  powder ( $\approx 250 \text{ mg}$ ) was used as a sample pad to avoid interfering contamination of the Pt crucible. During sintering the oxygen exchange was quantitatively monitored by an apparatus with cells for oxygen pumping and detecting based on  $\text{ZrO}_2$  ceramics. The measuring principle is described elsewhere [10].

The microstructure of the polished and chemically etched specimens was examined by optical microscopy and by scanning electron microscopy (SEM). The distribution of the Nb donor inside the sintered samples was investigated by wavelength-dispersive X-ray electron probe microanalysis (Cameca, France). Within the accuracy of this method, neither inhomogeneities inside the grains nor segregation at the grain boundaries could be detected in coarse-grained samples (<0.6 mol% Nb).

## Results and Discussion

Figure 1 shows the oxygen pumping current of the coulometric measuring cell as well as the sample temperature versus time during the sintering (complete heating and cooling cycle) of a specimen doped with 0.3 mol% Nb as an example. Deviations of the pumping current  $I$  from the equilibrium value  $I_0$  (dotted line) indicate oxygen release (decreased current) and oxygen uptake (increased current), respectively. Four different oxygen release peaks can be observed during the heating cycle, denoted with increasing temperature by numbers I–IV. Peaks (I) and (IV) result from the formation of Schottky-type equilibrium oxygen vacancies. Peak (I) depends significantly on the quality of the ceramic powder and originates partly from the decreased  $p\text{O}_2$  of the ambient atmosphere since the powders are prepared usually in air. Whereas peaks (I) and (IV) can be observed both in undoped and in doped samples, peaks (II) and (III) only occur in donor-doped material. Their onset temperatures of 1260°C and 1320°C, respectively,

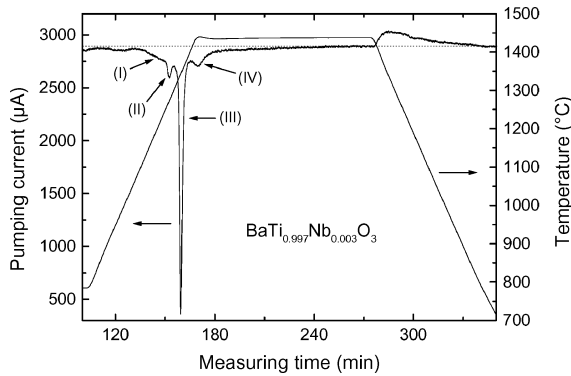


Fig. 1. Pumping current of the coulometric measuring cell and the temperature of a 0.3 mol% Nb-doped BaTiO<sub>3</sub> sample in dependence on time during the complete sintering cycle. Marks (I)–(IV) are explained in the text.

correspond very well with the starting temperatures of the AGG in the presence of a SiO<sub>2</sub> and TiO<sub>2</sub> containing liquid phase, respectively [11, 12]. The microstructure of specimens sintered slightly above these temperatures is bimodal or coarse-grained, corresponding to the intermediate and final sintering stage, respectively [10]. Hence, the irreversible oxygen release related to the peaks (II) and (III) originates from the donor incorporation reaction (2) which is related to the charge-compensation by electrons. The quantity of electron-compensated Nb<sub>Ti</sub><sup>•</sup> lattice defects was determined according to the following procedure. The total amount of exchanged oxygen during a time interval  $t_2 - t_1$  can be calculated by the following expression with  $F$  being the Faraday constant.

$$\Delta n_{O_2} = \frac{1}{4F} \int_{t_1}^{t_2} [I(t) - I_0] dt \quad (3)$$

All data were corrected by measurements without a specimen. Generally, the total exchanged oxygen caused by the creation and annihilation of Schottky-type oxygen vacancies of the alumina furnace tube and the zirconia sample pad, amounts less than 10% of the simultaneous effects of the specimen. In Fig. 1, the small deviations from the equilibrium current  $I_0$  at temperatures below 1100°C are caused by the sample pad. The results of the oxygen release, related to electron-compensated Nb incorporation in the doping range of between 0.1 and 0.5 mol%, are shown together with the mean grain size in Fig. 2. According to Eq. (2) the

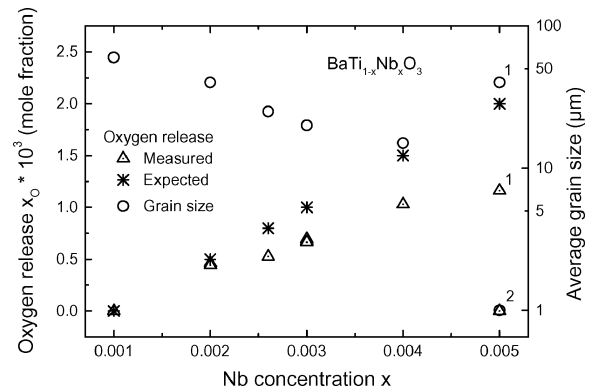


Fig. 2. Measured and expected oxygen release  $x_O$  (see text) of BaTi<sub>1-x</sub>Nb<sub>x</sub>O<sub>3</sub> ceramics during the sintering versus Nb concentration  $x$ . Additionally, the mean grain size is shown. Marks 1 and 2 denote two different samples of the same Nb concentration with different microstructure.

concentration of the electron-compensated Nb<sub>Ti</sub><sup>•</sup> donor is  $[\text{Nb}_{\text{Ti}}^{\bullet}]_{\text{el. comp.}} = 2x_O = 4x_{O_2}$ , with  $x$  as the mole fraction of the released oxygen atoms or molecules, respectively. Since the measurements were performed at a reduced pO<sub>2</sub> of 2.4 Pa, the critical donor concentration is shifted to a value between 0.5 and 0.6 mol%. Therefore, the sample with 0.5 mol% Nb exhibits ambivalent behavior. Whereas the sample labeled “1” shows both the AGG and distinct peaks (II) and (III), the grain growth of the sample labeled “2” is completely inhibited and peak (III) is absent. Only peak (II) is slightly developed. All samples with concentrations  $\geq 0.6$  mol% Nb exhibit the behavior of sample “2” with gradually vanishing peak (II). Hence, at least under the applied ambient conditions ( $T$ , pO<sub>2</sub>) the *electron-compensated* incorporation of significant amounts of Nb into the lattice only occurs during the AGG, which supports the model mentioned above [5, 6].

The sample with 0.1 mol% Nb exhibits no peaks (II) and (III) and, moreover, in the whole sintering cycle its curve of the pumping current is almost identical with that one of the undoped sample within the accuracy limit. This can be interpreted by the well-known accidental acceptor impurity of BaTiO<sub>3</sub> which naturally occurs unless highly-purified raw materials are used [13]. Thus, electronic charge-compensation only occurs, if the donor concentration exceeds the acceptor level. The effect that Nb<sub>2</sub>O<sub>5</sub> grains are dissolved in the liquid phase and/or run out together with it during the final sintering stage seems to be unlikely but cannot be excluded. Under the assumption that for all samples

approximately 0.1 mol% of the Nb dopant must not be considered for the charge balance, the expected oxygen release  $x_O$  for exclusive electronic compensation was calculated and presented in Fig. 2. The comparison with the measured values shows that only at a doping level of 0.2 mol% electrons are dominating for charge-compensation of the remaining donor. The difference between expected and measured values, which can be attributed to the titanium vacancies as the other charge-compensating species, gradually increases with increasing Nb content. In 0.2 mol% Nb-doped samples, at most 10 % of the remaining donors are compensated by titanium vacancies. This portion reaches 40% at 0.5 mol% Nb.

The quantitative results of the oxygen uptake during the cooling process which can be attributed to the reoxidation of the Schottky-type oxygen vacancies created during heating in dependence on the doping concentration are shown in Fig. 3. The minimum of the amount of incorporated oxygen somewhat below the critical concentration can be interpreted as follows. Until the start of the significant AGG near 1320°C the oxygen release of all samples investigated shows equal behavior caused by creation of Schottky-type vacancies. Whereas for undoped, 0.1 mol% doped, and samples with inhibited grain growth this oxygen release gradually increases until the maximum temperature, the Schottky-type vacancy related peak (IV) is strongly depressed (see Fig. 1) for specimens with a doping level between 0.2 and 0.5 mol% (sample 1). This is caused by the blocked bulk diffusion of oxygen vacancies in electronically compensated donor-doped BaTiO<sub>3</sub> [14],

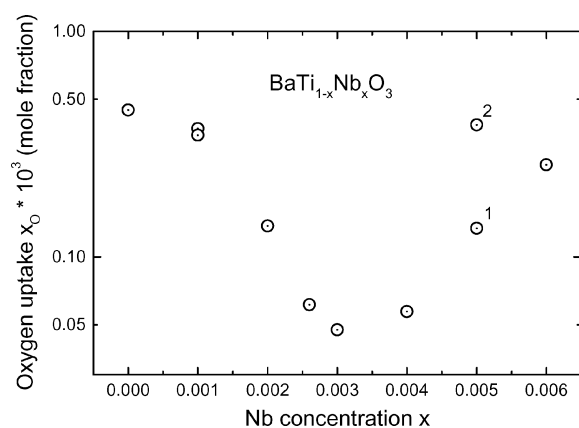


Fig. 3. Measured oxygen uptake  $x_O$  of BaTi<sub>1-x</sub>Nb<sub>x</sub>O<sub>3</sub> ceramics during the sintering (cooling cycle) versus Nb concentration  $x$ . For marks 1 and 2 see caption of Fig. 2.

since at this sintering stage the grains are already grown and the bulk diffusion became dominating. Hence, the minimum oxygen uptake between 0.3 and 0.4 mol% Nb can be explained by the different kinetics of the oxygen transport processes during heating/cooling with a finite rate of 10 K/min. Thus, the samples with a doping level between 0.2 and 0.5 mol% do not reach their equilibrium oxygen vacancy concentration during heating and the subsequent soaking time of about one hour at  $\approx 1430^\circ\text{C}$ . Consequently, less vacancies have to be annihilated during cooling apart from the fact that the oxygen transport also into the lattice is strongly slowed down during the cooling step.

### Summary

The coulometric measuring of the oxygen exchange during the sintering ( $p_{\text{O}_2} = 2.4 \text{ Pa}$ ) of coarse-grained BaTiO<sub>3</sub> ceramics of a doping level between 0.2 and 0.5 mol% Nb shows the occurrence of four successive oxygen release processes (heating cycle). Two of them are attributed to the creation of Schottky-type oxygen vacancies which can be observed also for samples with lower and higher Nb concentrations, respectively. The other two processes are related to the donor incorporation mechanism which holds for charge-compensation by electrons and do not occur with specimens of doping levels  $x < 0.002$  and  $x > 0.005$ . The observed coincidence of these processes with the grain growth behavior supports the thermodynamic model of the doping anomaly of donor-doped BaTiO<sub>3</sub> [5]. At least for an oxygen partial pressure of 2.4 Pa the donor can only be incorporated and charge-compensated by electrons under the conditions of the anomalous grain growth. By quantitative analysis of the coulometric data the concentration of Nb donors which are charge-compensated by electrons was determined. Under the assumption that 0.1 mol% of Nb is charge-compensated by naturally occurring acceptor impurities, the portions of the remaining Nb donors, which are compensated by electrons and by titanium vacancies, respectively, can be estimated. At  $x = 0.002$ , the majority of the donors is compensated by electrons. With increasing Nb concentration the Ti vacancies gradually begin to serve for compensation and reach a percentage of 40% at 0.5 mol% Nb. The quantitative differences in the reoxidation processes of the samples with varying donor concentration can be explained by the strongly reduced chemical bulk diffusion coefficients of the specimens

in which donors are charge-compensated by electrons.

### Acknowledgment

Financial support from the International Bureau of the German Ministry of Education and Research and from the Slovenian Ministry of Education, Science and Sport in the framework of the bilateral cooperation in Science and Technology is gratefully acknowledged.

### Note

1. Here and in the following the Kröger-Vink notation of defects is used.

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