

Investigation of reactions between BaTiO_3 and $\text{La}(\text{Ni},\text{Co})\text{O}_3$ by diffusion couples

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The diffusion of cations and the formation of compounds at the interface of diffusion couples of BaTiO_3 and $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_3$ have been investigated by scanning electron microscopy and energy dispersive X-ray spectroscopy. The firing conditions have been varied with respect to firing temperature, firing time and heating rate. At the interface between BaTiO_3 and $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_3$ a layer of a perovskite type compound with varying composition is formed. Ti and La ions diffuse preferentially towards the reaction layer from the BaTiO_3 and the $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_3$, respectively. A consequence of the preferred diffusion of Ti towards the reaction layer is a depletion of Ti and the enrichment of Ba within the BaTiO_3 adjacent to the interface causing the formation of overstoichiometric BaTiO_3 (with respect to Ba), which is known to exhibit pronounced grain growth inhibition. The zone of reduced grain size is found to reach approximately 200 μm into the BaTiO_3 bulk.

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1. Introduction

Barium titanate (in the following denoted as BT) is a widely used ferroelectric material for ceramic multilayer capacitors. The perovskite type compound $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_3$ (in the following denoted as LNC) is a good electronic conductor with the metallic characteristics of LaNiO_3 , stabilized by cobalt for higher sintering temperatures [1, 2]. Technological application as an electrode material for BaTiO_3 -based capacitors is hindered by the inhibition of densification of ceramics consisting of these two materials [3, 4]. Investigation of the sintering of BT/LNC powder mixtures also showed inhibited grain growth combined with increased porosity resulting in a lower final density in comparison with the sintering of “pure” BT and LNC powders [5].

In this paper we report on the investigation of diffusion couples, which should serve for the study of the interfacial region, the estimation of diffusion lengths and the effects of the interaction on the bulk of the materials. It was decided to choose a representative model system for LNC electrodes in BT ceramics. For this purpose a sandwich structure consisting of an LNC layer between two layers of BT was prepared. With scanning electron microscopy and EDX (energy dispersive X-ray spectroscopy) interdiffusion and compound formation and their influence on the densification and the grain growth in the boundary region was evaluated.

2. Experimental

For BT a commercially available high purity powder (BT02 from SAKAI) with a medium grain size of 0.2 μm and a Ba/Ti atomic ratio of 0.999 (according to the product data sheet) was chosen. LNC was prepared by co-precipitation from nitrate solution with sodium hydroxide. The washing of the precipitate was done by repeated dispersion in deionized water and was monitored by a sodium sensitive electrode. The synthesis of this perovskite compound was done at 850°C for 6 hrs in air. Experimental details are given elsewhere [3]. The powder was characterized by grain size analysis (Cilas Granulometer HR 850 B, Alcatel) and exhibits a median grain size of 0.96 μm . Phase formation was confirmed with X-ray diffraction (Siemens D5005).

From these powders sandwich pellets consisting of two layers of BT (each appr. 2 mm thick) with a 250 μm thick layer of LNC in between were prepared by uniaxial pressing in an 8 mm diameter steel die with a pressure of 100 MPa. To avoid influences from a more or less complex binder burn-out the powders were pressed without any use of binder. The pellets were fired in a tube furnace equipped with an Eurotherm 818P controller in air. Firing temperature was varied between 1200 and 1275°C with dwell times of 1, 2 and 6 hrs and different heating rates (2.5°C/min and 10°C/min).

For the microstructural investigation the samples were mounted in epoxy resin in a cross-sectional orientation and then cut and polished using standard

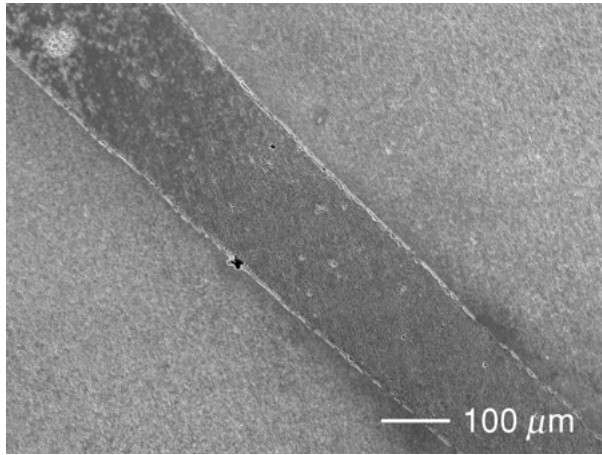


Figure 1 SEM image of a LNC-layer between BT in a sandwich structure diffusion couple (sintered at 1250°C for 2 hrs with a heating rate of 10°C/min).

metallographic techniques. A JEOL JSM 5800 scanning electron microscope (SEM) equipped with a Link ISIS 300 EDX system from Oxford Instruments was used for the microstructural analysis. Prior to analysis in the SEM, the samples were coated with carbon to provide electrical conductivity and to avoid charging effects. The typical microstructure of such a diffusion couple is given in Fig. 1

3. Results and discussion

In all cases a pronounced reaction layer was found to form between the BT- and the LNC-layer during firing. The thickness of this layer increased slightly (appr. 10%) with the firing temperature (Fig. 2). Firing time had no significant influence on the thickness of the reaction layer (Fig. 3).

Apparently material adjacent to that reaction layer was transported towards the boundary region and a zone of increased porosity is found along the layer within the BT as well as in the LNC. These pores coalesce during longer firing time and form elongated voids parallel to the reaction layer (Fig. 3). Lowering the heating rate from 10°C/min to 2.5°C/min causes a broadening of the porous region in the BT layer adjacent to the reaction layer (Fig. 4). The reaction layer shows a pronounced warping especially after longer firing time. This warping gives hint to internal stresses occurring in the reaction layer due to different expansion coefficients of the materials or different sintering rates.

Grain size and porosity within the LNC layer is found to be quite homogeneous, whereas the BT layer was finely grained near the BT/LNC boundary (medium grain size similar to the starting powder, 0.2 μm) and with well grown grains with a medium grain size of 1–2 μm approximately 2 mm away from the boundary (Fig. 5). The zone of inhibited grain growth reached

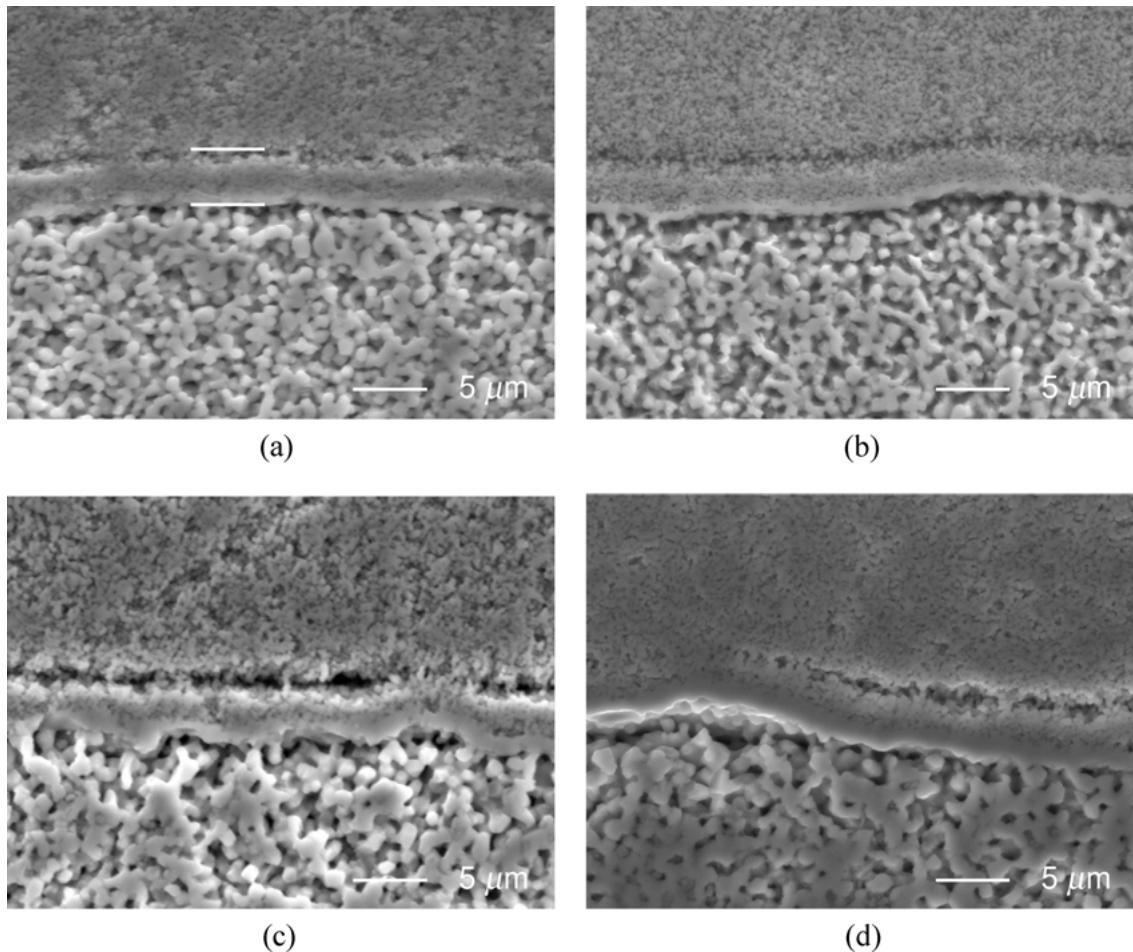


Figure 2 SEM images of interfaces between LNC (coarse grained, lower part) and BT (fine grained, upper part) in sandwich structure diffusion couples with reaction layer (indicated by white lines in a): (a) fired at 1200°C for 1 h, heating rate 10°C/min, (b) fired at 1225°C for 1 h, heating rate 10°C/min, (c) fired at 1250°C for 1 h, heating rate 10°C/min, and (d) fired at 1275°C for 1 h, heating rate 10°C/min.

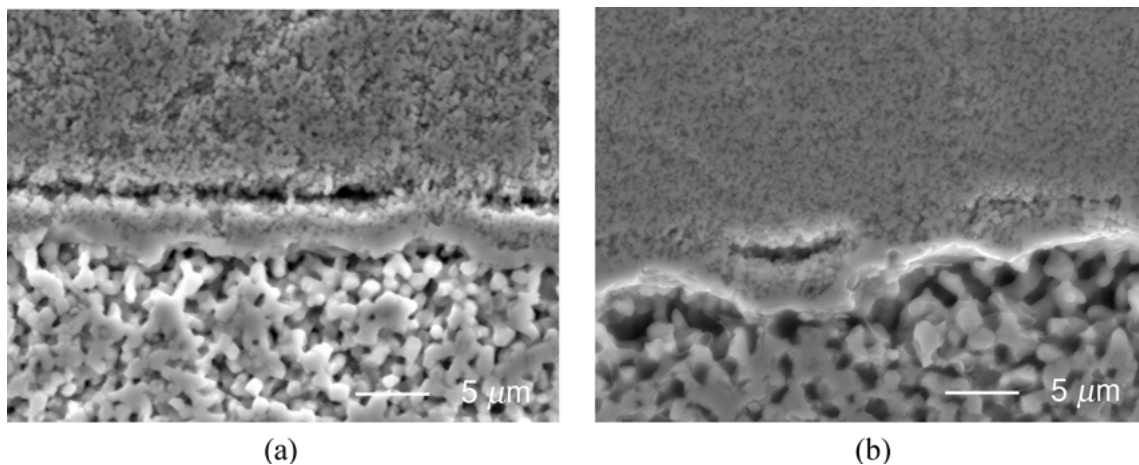


Figure 3 SEM images of interfaces between LNC (coarse grained, lower part) and BT (fine grained, upper part) in sandwich structure diffusion couples after different sintering time (a: 1250°C for 1 hr, 10°C/min, b: 1250°C for 6 hrs, 10°C/min).

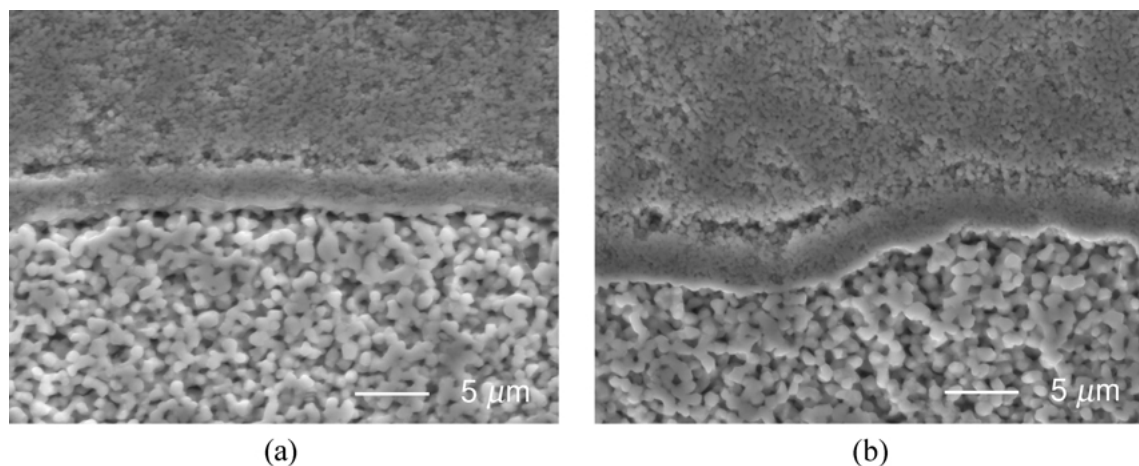


Figure 4 SEM images of interfaces between LNC (coarse grained, lower part) and BT (fine grained, upper part) in sandwich structure diffusion couples after sintering with different heating rate (a: 1200°C for 1 h, 10°C/min, b: 1200°C for 1 h, 2.5°C/min).

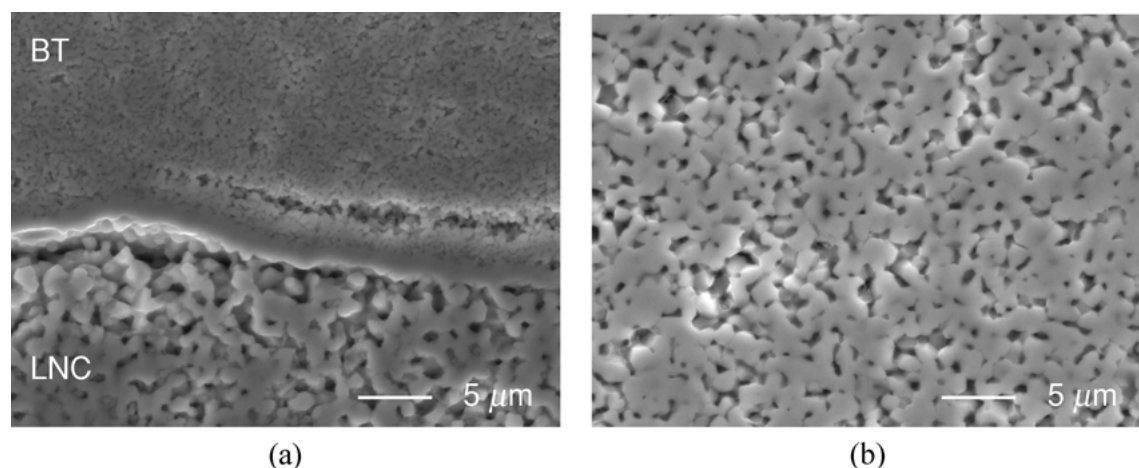


Figure 5 SEM images of interface (a) with finely grained BT, and (b) BT appr. 2 mm away from BT/LNC interface. Sample fired at 1275°C for 1h at a heating rate of 10°C/min.

about 200 μm from the interface into the BT bulk with a gradual increase of the grain size. The inhibition of grain growth leads to a difference in the densification between the BT near the LNC layer and the BT farther away (in powder mixtures a decrease of linear shrinkage of about 30% was observed due to the addition of 5 mol% of LNC to BT [5]). This difference causes a

stress in the BT which is released by cracking of the BT from the side of the pellet (Fig. 6).

EDX-analysis revealed that the above mentioned reaction layer in itself consisted of a BT-rich part with a fine microstructure and a rather dense La-rich zone, but contained all ions of the starting compounds throughout the whole layer (Fig. 7). It is remarkable that

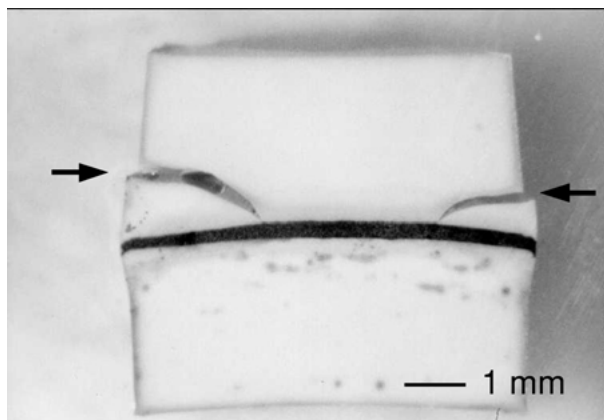


Figure 6 Photograph of cross section of diffusion couple (sintered at 1250°C for 6 hrs with a heating rate of 10°C/min) showing cracks (marked by arrows).

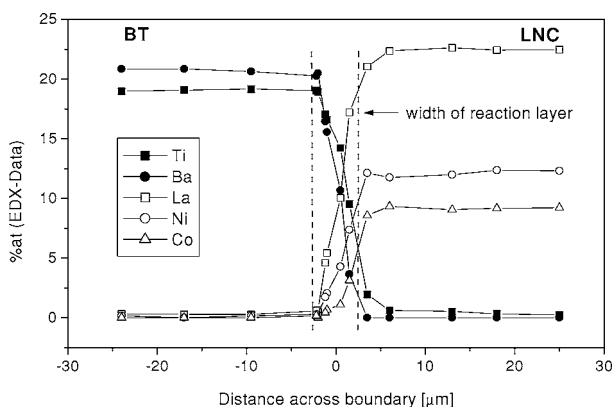


Figure 7 Diffusion profile of Ba, La, Ti, Ni and Co across the reaction layer from EDX-data. The dashed line indicates the width and the location of this layer. Sample was fired at 1250°C/1 h, 10°C/min.

the Ba/Ti-ratio in the reaction layer was always lower than in the BT-layer (i.e., Ti-rich). Within the La-rich zone the Ti-concentration exceeds the Ba-concentration more than two times. The ratio between La and the sum of Ni and Co was found to be around 2:1 within the reaction layer (in LNC this ratio is 1:1). But due to the higher content of Ti the ratio between A-site cations (La and Ba) and B-site cations (Ti, Ni and Co) remained around one throughout the whole layer, indicating a perovskite type reaction product (i.e., (La, Ba)(Ni, Co, Ti)O₃) with gradually changing composition. With these findings a preferred diffusion of Ti from BT and La from LNC towards the reaction layer is clearly indicated. The formation of a Ba₂TiO₄ phase was not observed.

Ti was found to diffuse into the LNC-layer much faster than Ba. Within the BT-layer only La was found in significant amounts in samples fired at higher temperatures (1275°C). Diffusion of Ni and Co into the BT-layer as well as Ba into the LNC-layer seems to be restricted to a few microns. The diffusion profiles of the ions exhibited only minimal changes with firing time or temperature. Fig. 8 shows the profiles at different firing temperatures for Ti. A noticeable impact on the diffusion profile of Ti was found only by lowering the heating rate (Fig. 9).

To sum up the following points can be stated. The formation of a solid solution between BT and LNC was

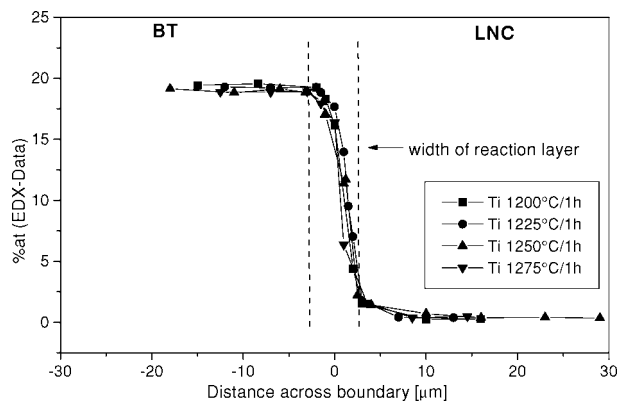


Figure 8 Diffusion profiles of Ti across the reaction layer at various firing temperatures from EDX-data. The dashed line indicates the width and the location of this layer.

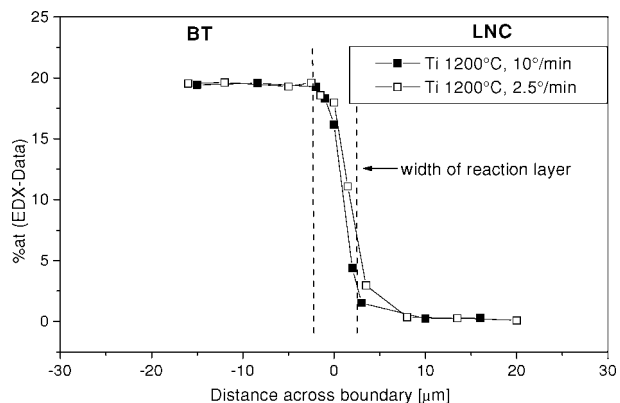


Figure 9 Diffusion profiles of Ti across the reaction layer after different heating rates from EDX-data (firing time 1 h). The dashed line indicates the width and the location of this layer.

demonstrated by X-ray diffraction on powder mixtures [5]. In diffusion couples it was found that at the interface between BT and LNC a layer of a perovskite type compound (La, Ba)(Ni, Co, Ti)O₃ with the composition varying from a BT rich side to a LNC rich side is formed. That reaction layer acts as a sink for Ti diffusing from BT. Note that the compounds containing Ba, La, Ti and Co with perovskite structure are already described in literature [7, 8]. Ti ions are diffusing from BT into the reaction layer.

The changes in the diffusion profile of Ti suggest that the heating rate has a higher influence on diffusion than firing time and temperature. This would imply, that the diffusion starts at temperatures below the maximum firing temperature and could be mainly a surface diffusion (in the range where a swelling was observed in powder mixtures [5], approximately 1000°C). With the Ti concentration exceeding the Ba concentration in the reaction layer an indication is found for the depletion of Ti and the enrichment of Ba within the BT layer. This would cause the formation of overstoichiometric BT (with respect to Barium).

In the literature a great number of reports about the effect of stoichiometric deviations on the sintering behavior of BaTiO₃ is found. Although the content is partly contradictory, it is generally accepted that an excess of BaO typically inhibits grain growth, whereas an excess of TiO₂ enhances grain growth [9]. In the recent

literature it was confirmed by Choi and Kim [10], that already a small excess of BaO inhibits grain growth. It is assumed that the solubility of BaO in BaTiO₃ is around 100 ppm and in samples with Ba/Ti-ratio > 1.001 the formation of barium orthotitanate Ba₂TiO₄ is observed [11]. This compound was found in some samples of powder mixtures but was not detected in the BT-region of diffusion couples. This would mean that the Ti deficiency is below that limiting amount of 100 ppm. This assumption is plausible, if one estimates that the Ti excess in the relatively thin reaction layer (3–4 μm) originates from the zone of inhibited grain growth, which reaches approximately 200 μm into the bulk of BT. This grain growth inhibition, that is accompanied by a decreased shrinkage of the BT, further causes mechanical stress within the BT bulk.

The formation of the porous regions on both sides of the BT/LNC boundary could originate from the Kirkendall effect, which is caused by a preferred diffusion of one species in a multi-component system. Such a formation of voids due to the Kirkendall effect was, for example, also observed in BaTiO₃/SrTiO₃ diffusion couples [6]. By EDX data it is shown, that in our case the diffusing ions are the Ti-ions from the BT but also the La-ions from the LNC. A simple explanation following classical Kirkendall theory is complicated by the fact that these two ions diffuse in opposite directions within two different crystallographic sites.

4. Conclusions

In diffusion couples it was found that at the interface between BT and LNC a layer of a perovskite type compound with varying composition is formed. Ti ions diffuse from BT into this reaction layer. From the LNC a preferred diffusion of La into that reaction layer is observed. This results in a porous zone between the bulk ceramic (both BT and LNC) and the reaction layer which could be explained by the Kirkendall effect.

The influence of the heating rate on the diffusion profile of Ti rather than that of firing time and temperature indicates, that the diffusion starts at temperatures below

the maximum firing temperature. The diffusion of Ti from BT towards the BT/LNC interface further results in a depletion of Ti and the enrichment of Ba within the BT bulk adjacent to the interface and would cause the formation of overstoichiometric BT (with respect to Barium), which is known to exhibit pronounced grain growth inhibition. The zone of reduced grain size is found to reach approximately 200 μm into the BT bulk. This grain growth inhibition, which leads also to a decreased shrinkage of the BT, further causes mechanical stress within the BT bulk.

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