

# Sintering inhibition and reactions between $\text{La}(\text{Ni},\text{Co})\text{O}_3$ and $\text{BaTiO}_3$ : powder mixtures

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## Abstract

Powder mixtures of  $\text{BaTiO}_3$  and  $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_3$  have been investigated by heating stage microscopy, scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction in order to study the densification behavior and compound formation. By heating microscopy it was demonstrated, that the addition of a few per cent of each material to the other strongly influences the shrinkage of the ceramics. SEM investigations showed a pronounced change in grain size and porosity throughout the whole range of powder mixtures. X-ray diffraction proved the formation of a solid solution between  $\text{BaTiO}_3$  and  $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_3$  as well as the formation of secondary phases. From these results it is concluded, that densification problems arise mainly from compound formation and a preferred diffusion of Ti from the  $\text{BaTiO}_3$  to the  $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_3$ . © 2002 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

The perovskite type oxide compound  $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_3$  is a good metallic conductor with a conductivity up to 1000 S/cm. Since the parent compound  $\text{LaNiO}_3$  decomposes at 860 °C, the substitution of nickel by cobalt stabilizes the perovskite structure for higher sintering temperatures.<sup>1,2</sup> This material was proposed for replacing noble metal electrodes in electroceramic devices by Katsarakis et al.<sup>2</sup> Barium titanate is still the most important basic material for many passive electroceramic components. Noble metals as electrode material cause a great portion of the production costs especially in the field of multilayer capacitors. Preliminary investigations on simple test structures consisting of  $\text{BaTiO}_3$ - and  $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_3$ -layers showed a pronounced chemical interaction between these two materials and evidence was found, that the densification of both materials is hindered.<sup>3,4</sup> The problem of co-firing is also found in other fields of electroceramic materials for the production of monolithic devices e.g. electronic/ionic conductors (solid oxide fuel cells),<sup>5–7</sup>

ferrites/ferroelectrics (LC-filters),<sup>8</sup> or ferroelectrics/ZnO (capacitor/varistor).<sup>9,10</sup>

In the present report reactions between  $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_3$  and  $\text{BaTiO}_3$  have been investigated in a model system consisting of compressed powder mixtures of these two compounds. Hence, the interfacial area between the two reactants has been maximized.

By investigating powder mixtures a description of the densification and the influence of each compound on the densification behavior of the other is presented. Further, the formation of secondary phases developing between  $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_3$  and  $\text{BaTiO}_3$ , the phase distribution and the microstructure of the heat treated powder mixtures are reported as well as the chemical composition of the occurring phases. For this purpose heating stage microscopy, X-ray diffraction analysis and scanning electron microscopy with EDX (energy dispersive X-ray spectroscopy) were employed.

## 2. Experimental

For  $\text{BaTiO}_3$  (in the text denoted as BT) a commercially available powder (BT02 from SAKAI) with a medium grain size of 0.2  $\mu\text{m}$  and a Ba/Ti atomic ratio of

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0.999 (according to the product data sheet) was chosen.  $\text{LaNi}_{0.6}\text{Co}_{0.4}\text{O}_3$  (in the text denoted as 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 with a sodium sensitive electrode. The synthesis of the perovskite compound was done at 850 °C for 6 hours in air. Experimental details are given elsewhere.<sup>3</sup> The powder was characterized by grain size analysis (Cilas Granulometer HR 850 B, Alcatel) and X-ray diffraction (Siemens D5005). It proved to be single phased and exhibits a medium grain size of 0.96  $\mu\text{m}$ .

These powders were mixed thoroughly in an agate mortar with addition of ethanol. After drying, pellets (6 mm diameter, 3 mm high) were pressed without any binder at a pressure of 100 MPa. The green density of the compacts was in the range of 50–55% of the theoretical density. The experimental set of samples included the pure powders and mixtures of 5, 25, 50, 75 and 95 mol% of BT in LNC.

Shrinkage measurements were carried out on a Leitz heating stage microscope with a heating rate of 10 K/min up to 1250 °C and with additional holding time of 100 min at 1250 °C. The images were analyzed manually with a Zeiss Measuring Microscope. For scanning electron microscopy a Jeol JSM 5800 equipped with a Link ISIS 300 EDX system from Oxford Instruments was used. Samples were polished and coated with carbon. X-ray diffraction patterns of powder mixtures were obtained from a Philips PW 1710 diffractometer with  $\text{Cu } K_\alpha$  radiation.

### 3. Results and discussion

Fig. 1 shows the sintering curves of BT, LNC, and the mixtures obtained from the heating stage microscope. It can be seen, that the onset of the shrinkage for both BT and LNC is around 1010 °C. Furthermore it is obvious, that the final shrinkage achieved at 1250 °C is different. The final densities of the samples were 91% of the theoretical density for BT and 80% of the theoretical density for LNC.

The final shrinkage vs. composition is seen more clearly in Fig. 2. The addition of only 5 mol% LNC to BT reduces the shrinkage ( $\Delta l/l_0$ ) from  $-0.11$  to  $-0.07$ . Addition of 5 mol% BT to LNC has a lower but still distinct impact on the final shrinkage. The mixture of 75 mol% BT and 25 mol% LNC (BT/LNC 75/25) exhibits swelling, which starts at temperatures around 1000 °C (observable in Fig. 1). The expansion could possibly be the consequence of some chemical reaction with a preferred diffusion of one compound into the other. A similar behavior was reported by M. Kosec and D. Kolar<sup>11</sup> on the formation of a solid solution between  $\text{PbZrO}_3$  and  $\text{PbTiO}_3$  in which preferential diffusion of Ti was observed accompanied by a large volume increase during heating. Mixtures with 50 mol% of LNC exhibit a higher shrinkage, which does not differ so much from the shrinkage of mixtures with higher LNC content, however swelling is still observed. In common it can be said, that the influence of LNC in a BT-matrix is higher than that of BT in a LNC-matrix.

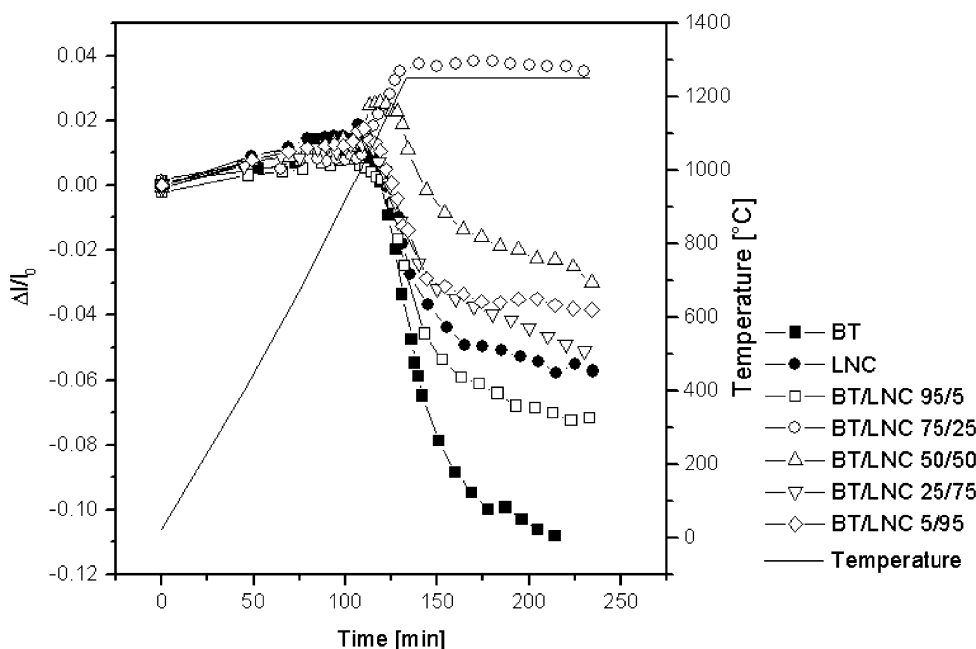


Fig. 1. Shrinkage curves ( $\Delta l/l_0$  vs. time) of BT, LNC and mixtures. The samples were heated with a ramp of 10 °C/min up to 1250 °C followed by a dwell of 100 min.

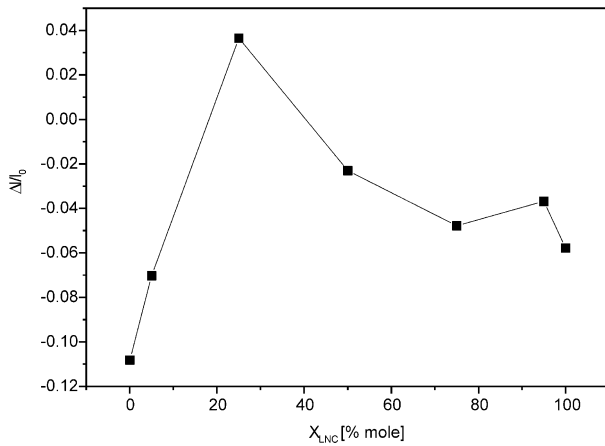


Fig. 2. Final shrinkage  $\Delta l/l_0$  vs. composition of powder mixtures.

Fig. 3a and b shows the microstructures of the pure samples of BT and LNC after firing at 1250 °C for 100 min. The BT grains are regularly shaped with a certain amount of porosity. LNC exhibits a higher porosity, but grains are in contact and common boundaries developed. A few grains consisting mainly of NiO with traces of Co were detected (traces of NiO were also found by X-ray diffraction in the LNC samples). Fig. 3c and d

demonstrate the effect of the addition of 5 mol% of LNC to BT (Fig. 3c) and 5 mol% of BT to LNC (Fig. 3d). In both cases the specimens show very high porosity and consist of small grains with a grain size similar to the starting powder (0.2  $\mu\text{m}$  for BT and 0.96  $\mu\text{m}$  for LNC). According to EDX analysis the finely grained areas in BT/LNC 95/5 (square in Fig. 3c) consist of  $\text{BaTiO}_3$  with traces of La (20.9 at.% Ba, 18.9 at.% Ti, 0.4 at.% La). In the bright and dense areas (circle in Fig. 3c) Ba (14.3 at.%), Ti (15.3 at.%), La (7.0 at.%), Ni (2.6 at.%) and Co (1.3 at.%) are found by EDX. Attention should be paid to the fact that the Ba/Ti ratio in this zone is the reverse of that in the finely grained areas i.e. more Ti than Ba must have been transported to that spot. From the size and the chemical composition of these bright, dense areas we conclude that they are the initial LNC grains, which have reacted with the adjacent BT. Obviously these areas are surrounded by bigger pores. This observation might be explained by the assumption of a higher shrinkage rate of this inhomogeneity according to Evans<sup>12</sup> where it has been shown that inclusions with higher shrinkage rate cause the formation of cracks and pores around such inclusions. In such a case the pores should exhibit an elongated form, which is not stringently confirmed in Fig. 3c.

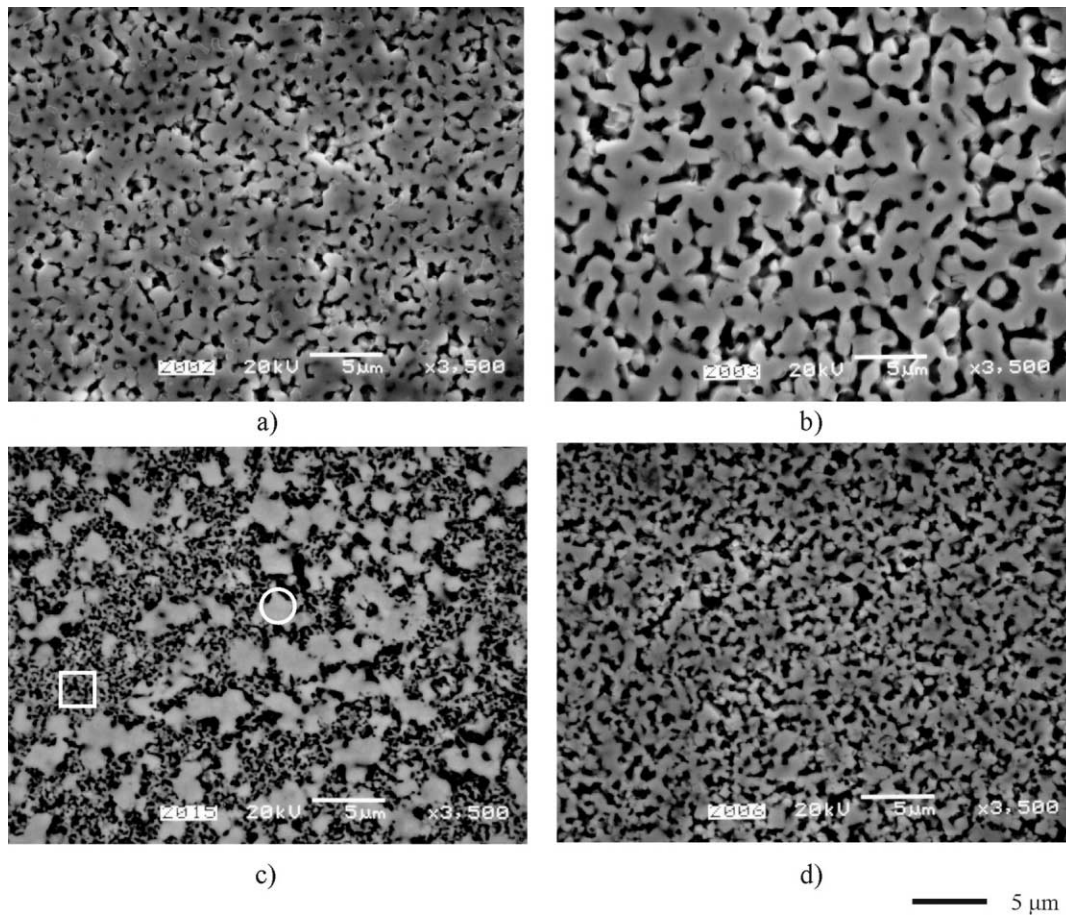


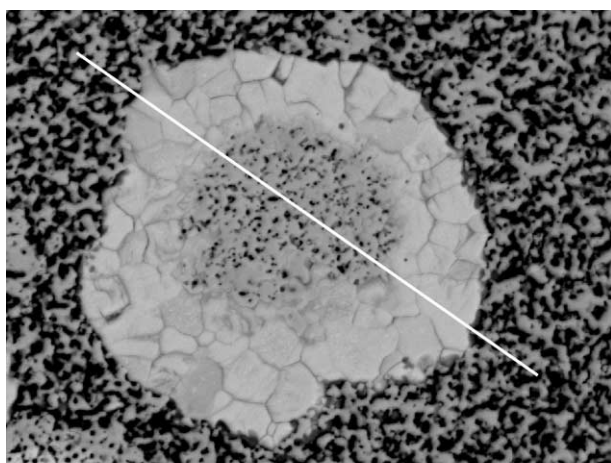
Fig. 3. SEM images of BT (a), LNC (b), BT/LNC 95/5 (c) and BT/LNC 5/95 (d). Samples were fired at 1250 °C, 100 min. The square and circle in (d) indicate the spots of the EDX analysis referred to in the text.

Moreover the size of these bright areas is in the range of the initial grain size of the LNC grains, so a higher densification in these areas is not supported.

Another possibility for an explanation is the assumption that during the reaction between BT and LNC a preferred transport of the BT to the LNC grains takes place, with the effect that the BT around the LNC grains is used up, leaving pores. Such a process is also observed in  $\text{BaTiO}_3/\text{SrTiO}_3$  mixtures and is known as the Kirkendall effect,<sup>13</sup> which explains also the swelling of the specimen because of the additional pore volume.

In samples of BT/LNC 50/50 some agglomerates of BT were found. These agglomerates represent a special case of a diffusion couple with a limited component. Fig. 4 shows such an agglomerate of about 50  $\mu\text{m}$  in diameter after firing at 1250 °C for 100 min. It consists of a finely grained core surrounded by a dense, coarsely grained shell embedded in a porous matrix (comprising BT/LNC 50/50). EDX analysis data across this agglomerate are given in Fig. 5.

EDX analysis of the finely grained core shows the typical composition of  $\text{BaTiO}_3$ . In the coarsely grained shell of the agglomerate the Ba/Ti-ratio transforms in a sudden change to 2:1. This sudden change of the composition and the completely different microstructure and grain size gives rise to the formation of a new compound. At the boundary between the coarsely grained shell and the surrounding matrix it is remarkable, that the Ti-profile intersects the Ba-profile, which would mean that more Ti than Ba diffuses into the matrix. It also agrees with the results of the EDX-analysis of the sample BT/LNC 95/5, where the bright, dense areas (circle in Fig. 3c), which represent the initial LNC grains in the BT matrix, exhibit a Ba/Ti ratio, which is reverse to that of the finely



— 10  $\mu\text{m}$

Fig. 4. Agglomerate of BT in BT/LNC 50/50 sample after firing at 1250 °C for 100 min. EDX analysis data presented in Fig. 5 were taken along the white line.

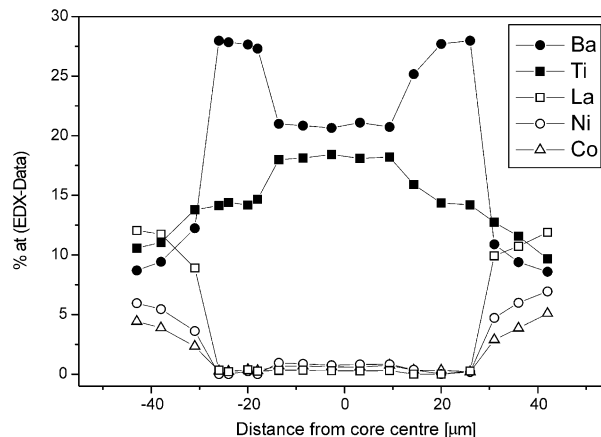


Fig. 5. EDX analysis data for Ba, Ti, La, Ni and Co of the agglomerate along the white line in Fig. 4.

grained areas (square in Fig. 3c). These findings support the assumption of a Ti-depletion of the BT-agglomerate. In the coarsely grained shell of the agglomerate the Ti-concentration gets so low that a new compound with Ba/Ti-ratio 2:1 is formed. For the elements La, Ni and Co it can be said, that their concentration in the surrounding matrix decreases gradually when approaching the boundary to the coarsely grained shell. The concentrations of these elements are beyond detection limit within the coarsely grained shell but traces of Ni and Co can be detected in the finely grained core of the agglomerate. This would mean that these elements diffuse into the BT-agglomerates in an early stage of the firing but do not take part in the formation of the new compound.

X-ray diffraction analysis (Fig. 6) of the specimens after the heating microscope experiments showed a shift of the perovskite peaks, which can be explained by the formation of a solid solution between the two perovskite type compounds BT and LNC. Additionally, peaks of

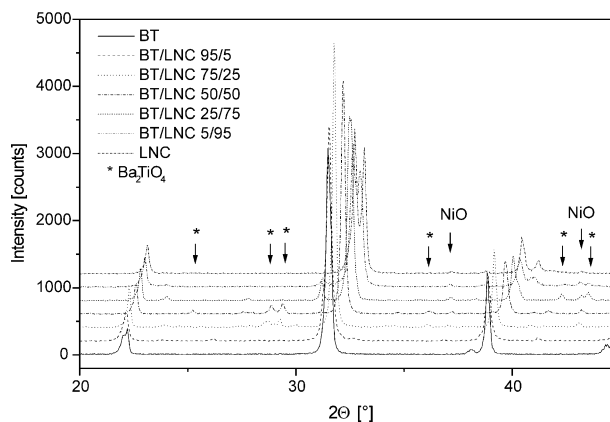


Fig. 6. X-ray diffraction spectra of BT, LNC and powder mixtures, fired at 1250 °C, 100 min. The shift of perovskite peaks indicates the formation of a solid solution. In some compositions barium orthotitanate  $\text{Ba}_2\text{TiO}_4$  and nickel oxide occurs.

secondary phases show up in the diffractograms. The amount of NiO found in the mixtures did not differ significantly from the amounts found in the LNC powders. These results did not change considerably after longer reaction time (up to 48 h at 1250 °C). In the sample BT/LNC (50/50) the secondary phase can be identified as Ba<sub>2</sub>TiO<sub>4</sub> (barium orthotitanate). According to the phase diagram<sup>14</sup> this compound forms, if BaTiO<sub>3</sub> gets Ti-deficient, as there is no solid solution between BaTiO<sub>3</sub> and Ba<sub>2</sub>TiO<sub>4</sub>. This would give further evidence for a preferred diffusion of the Ti ions during the formation of the solid solution between BT and LNC, which can explain the swelling of the BT/LNC 50/50 and BT/LNC 75/25 samples (Fig. 1).

#### 4. Conclusions

From the investigation of powder mixtures of BT and LNC by heating stage microscopy a strong influence of one compound, either BT or LNC, on the shrinkage of the other could be detected. Addition of low amounts of the second compound (5 mol%) decreased the final shrinkage without observable mechanical stresses. Mixtures with a higher amount of the second compound exhibit a swelling of the sample before the start of the shrinkage process. Such a behavior might be connected to a preferred diffusion of one compound and would indicate that these processes take place at rather low temperatures.

SEM investigations revealed a porous and finely grained microstructure in mixtures of BT or LNC with 5 mol% of LNC or BT respectively. Obviously the grain growth during the high temperature treatment is inhibited. EDX analysis and pore structure gave evidence that diffusion takes place to form another compound. From the investigation of BT agglomerates, which exhibit a “core-shell”-structure after heat treatment, it can be concluded that a preferred diffusion of Ti into the surrounding matrix occurs. In the coarse grained shell the Ti-deficiency causes the formation of a new compound, which is also supported by XRD-spectra.

The formation of a solid solution between BT and LNC was demonstrated by X-ray diffraction on powder mixtures. The occurrence of the compound Ba<sub>2</sub>TiO<sub>4</sub> (barium orthotitanate) in some of the powder mixtures supports the assumption of a preferred diffusion of Ti. According to the phase diagram this compound forms as a result of a Ti-deficiency in BaTiO<sub>3</sub>.

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