Solid-State Reactions Occurring during the Synthesis of $CaTiO_3$−$NdAlO_3$ Perovskite Solid Solutions

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The X-ray powder-diffraction technique was used to investigate the solid-state reaction paths to the $0.7CaTiO_3$−$0.3NdAlO_3$ perovskite solid solution. The results show that the perovskite phases $CaTiO_3$ and $NdAlO_3$ are formed prior to the solid solution, regardless of the combination of oxide powders used as reagents. The two perovskites subsequently react to form a solid solution at temperatures above 1200 °C. The reaction between $CaTiO_3$ and $NdAlO_3$ was studied using a diffusion couple, which revealed that the slower kinetics of incorporation of the Al into the forming solid solution results in the formation of an intermediate phase based on hexaluminate $CaAl_{12}O_{19}$. The presence of such inclusions results in the formation of defects in the perovskite matrix phase, which adversely affects the dielectric losses of the sintered ceramics based on the $0.7CaTiO_3$−$0.3NdAlO_3$ solid solution. To minimize the concentration of $CaAl_{12}O_{19}$-based inclusions, a thorough calcination procedure with intermediate homogenizations needs to be conducted at temperatures above 1300 °C.

Introduction

Perovskite solid solutions based on the $CaTiO_3$−$REAlO_3$ (RE = La, Nd, Sm) systems were identified as promising candidates for the synthesis of mid-permittivity-class microwave dielectric ceramics[1] and have thus received much attention in the recent scientific literature.[2−7] A highly positive temperature coefficient of resonant frequency (τ_f = +800 ppm/K), which is inherent to pure $CaTiO_3$, is effectively suppressed by the addition of 30−35 mol % of $REAlO_3$. Apart from temperature-stable resonant frequencies the ceramics based on solid solutions with such compositions exhibit high permittivities (ϵ_r > 40) and high Q-value (Qxf > 40000 GHz), which make them attractive for uses in rapidly developing telecommunication technologies. In the $CaTiO_3$−$REAlO_3$ family, the $CaTiO_3$−$NdAlO_3$-based ceramics are already being used for the commercial production of base-station microwave dielectric resonators in wireless-communication networks.

In the scope of our investigations of the $(1-x)CaTiO_3$−$xNdAlO_3$ system we showed that the two perovskites form solid solutions across the entire compositional range. The ϵ_r and the τ_f of the ceramics based on these solid solutions decrease with the increase in x whereas the Q-value increases.[2,5] The ceramics based on the solid solution with $x = 0.3$ exhibit a temperature-stable resonant frequency (τ_f = +3 ppm/K), a high permittivity (ϵ_r = 45), and a Qxf which can be tuned up to 45000 GHz with the proper choice of processing conditions.[5] Such microwave dielectric properties make ceramics based on the $0.7CaTiO_3$−$0.3NdAlO_3$ solid solution suitable for the production of commercial dielectric resonators. Further investigations into the crystal structure and the microstructure of $0.7CaTiO_3$−$0.3NdAlO_3$ ceramics revealed four distinct microstructural features[5]: antiphase boundaries, twin boundaries, and two types of inclusions rich in Al, spinel-$MgAl_2O_4$, and hexaluminate based on $CaAl_{12}O_{19}$. The twin and antiphase boundaries are formed as a result of the symmetry-breaking structural phase transitions, which occur during cooling from the sintering temperature. The formation of the spinel inclusions is a consequence of the Mg-based impurities, which are probably brought into the system with the $CaCO_3$. The origin of the $CaAl_{12}O_{19}$-based inclusions, however, was not elucidated.

The presence of the inclusions in the microstructure necessarily influences the microwave dielectric properties of the ceramics. Therefore, understanding the mechanism of the formation of these Al-rich hexaluminate inclusions is of crucial importance in controlling the dielectric properties of $0.7CaTiO_3$−$0.3NdAlO_3$ microwave ceramics. The objective of this study was to investigate the solid-state reaction mechanism that occurs during the formation of the $0.7CaTiO_3$−$0.3NdAlO_3$ solid solution to determine the origin of the $CAl_{12}O_{19}$-based inclusions.

Experimental Section

Stoichiometric amounts of reagent-grade powders of $CaCO_3$ (Johnson Matthey 99.95%), TiO_2 (Johnson Matthey >99%),

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Nd_2O_3 (Johnson Matthey 99.99%), and Al_2O_3 (Johnson Matthey 99.99%) were homogenized under ethanol in an ytria-stabilized-zirconia ball-mill using balls with a diameter of 3 mm. Since the Nd_2O_3 powder is strongly hygroscopic, it was dried for 12 h at 850 °C prior to weighing. After homogenization the mixture was dried using a rotary evaporator, pressed into pellets under a pressure of 10 MPa, and fired at several temperatures between 500 and 1400 °C. To study the solid-state reactions that occur at a certain temperature, the reaction mixture was quenched to room temperature after each firing. The phase composition was analyzed using X-ray powder-diffraction analysis with a Philips PW 1710 X-ray powder diffractometer and Cu Kα radiation. Thermal analyses (TG and DTA) were preformed with a Netzsch STA 409 thermal analysis system in an air atmosphere using an Al_2O_3 crucible. Evolved-gas analysis (EGA) was carried out on CO_2^+, H_2O^+, and OH^+ fragments with a Balzers Thermostar GSD 300T quadropole mass spectrometer.

Three additional reaction paths were examined by the use of alternative reagents such as $CaTiO_3$ and $NdAlO_3$. $CaTiO_3$ was obtained by prereacting a homogenized mixture of $CaCO_3$ and TiO_2 at 1200 °C whereas $NdAlO_3$ was prepared by prereacting Nd_2O_3 and Al_2O_3 at 1600 °C. In one case a stoichiometric mixture of the perovskites $CaTiO_3$ and $NdAlO_3$ was fired at several temperatures between 500 and 1400 °C. In the second case $CaTiO_3$ was fired in the same temperature range with stoichiometric amounts of Nd_2O_3 and Al_2O_3 whereas in the third case $NdAlO_3$ was fired with stoichiometric amounts of $CaCO_3$ and TiO_2.

For the purpose of studying the reaction between the pre-reacted $CaTiO_3$ and $NdAlO_3$ a diffusion couple was prepared. A pellet of the $NdAlO_3$ pre-sintered at 1600 °C was embedded in a powder of $CaTiO_3$ and isostatically pressed under 700 MPa. After firing at 1350 °C, the diffusion couple was polished and the interface analyzed with a JEOL JSM-5800 scanning electron microscope (SEM) equipped with the Oxford Link-Isis energy-dispersive X-ray analysis systems (EDS).

The lattice parameters of the perovskite solid solution were calculated by the whole powder-pattern decomposition method,[8] using the computer program TOPAS-R (Bruker AXS, Karlsruhe, Germany).

The microwave dielectric measurements of the ceramic samples sintered at 1350 °C were performed with an HP 8719C network analyzer using a cavity-reflection method. The Q-values of the $TE_{01\delta}$ resonance mode were determined from a Smith chart by analyzing the S_{11} parameter as proposed by Kajfez and Hwan.[9] The permittivities were calculated from the same resonance frequency using the Itoh-Rudokas model.[10]

Results and Discussion

The X-ray analysis of the commercial reagent powders used for the synthesis of the $CaTiO_3$−$NdAlO_3$ solid solutions revealed that the dried Nd_2O_3 powder consisted of two polymorphs, hexagonal A-Nd_2O_3 and a small amount of cubic C-Nd_2O_3. The TiO_2 powder contained some anatase phase in addition to rutile; the $CaCO_3$ powder consisted of pure calcite; and the Al_2O_3 powder was pure α-Al_2O_3. After the homogenization the mixture of these powders also contained some $Nd(OH)_3$, which suggests that the Nd_2O_3 reacts with water contained in the alcohol (Figure 1). Similar mixtures of reagent powders were used to synthesize the $CaTiO_3$−$NdAlO_3$ solid solutions in the majority of our previous experiments.[2,4,5]

To determine the temperatures marking the onset of solid-state reactions among the reagent powders, we performed a thermal analysis. From the DTA and TG

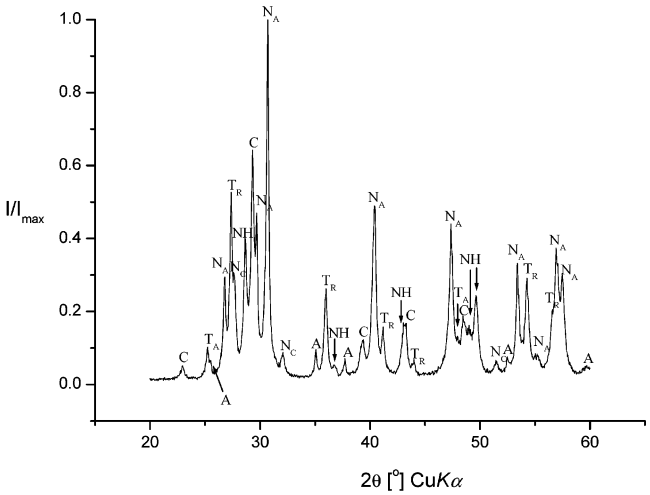

Figure 1. X-ray diffraction pattern of the $CaCO_3$, TiO_2, Nd_2O_3, and Al_2O_3 reaction mixture after homogenization. (C = $CaCO_3$, T_A = TiO_2-anatase, T_R = TiO_2-rutile, N_C = C-Nd_2O_3, N_A = A-Nd_2O_3, NH = $Nd(OH)_3$, A = Al_2O_3).

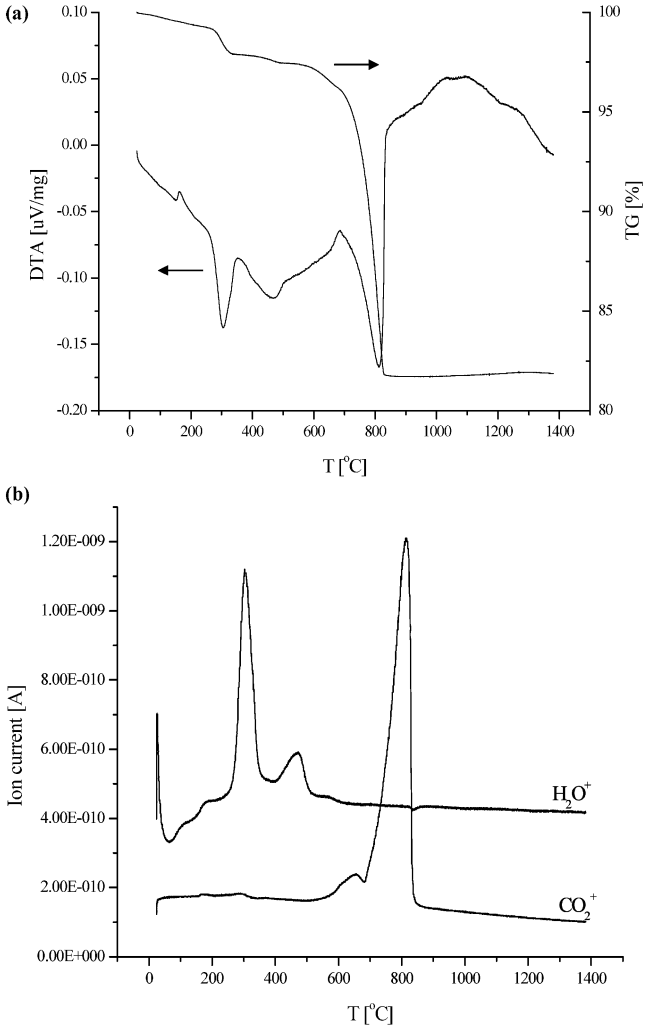

Figure 2. (a) TG, DTA, and (b) EGA curves of the $CaCO_3$, TiO_2, Nd_2O_3, and Al_2O_3 reaction mixture recorded in the temperature range 20−1400 °C with a heating rate at 5 K/min.

curves shown in Figure 2a it can be seen that the first reactions to occur in the range between room temperature and 811 °C are endothermic, and they are accompanied by a weight loss. According to the EGA curve, shown in Figure 2b, the two endothermic reactions

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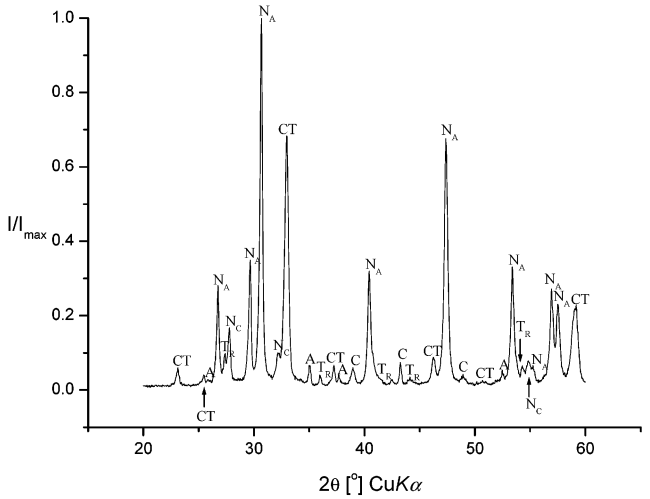

Figure 3. X-ray diffraction pattern of the $CaCO_3$, TiO_2, Nd_2O_3, and Al_2O_3 reaction mixture after firing at 850 °C/2 h. (CT = $CaTiO_3$, C = CaO).

which occur at 304 and 466 °C result in the release of H_2O from the reaction mixture, and a reaction at 811 °C results in the release of CO_2. The two peaks indicating the loss of water can be attributed to the two-stage decomposition mechanism of $Nd(OH)_3$, which was proposed by Klevtsov.[11] According to this mechanism, $Nd(OH)_3$ decomposes to Nd_2O_3 and water vapor via the intermediate compound NdOOH. Inspection of the CO_2^+ peak in the EGA curve reveals that at a heating rate of 5 K/min the decomposition of the $CaCO_3$ in the reaction mixture takes place in the temperature range 650−850 °C, which is in accordance with the decomposition of pure $CaCO_3$. Furthermore, the DTA curve exhibits a broad exothermic peak between 850 and 1300 °C. The exothermic effect can be attributed to the solid-state reactions among the reagent powders.

The X-ray diffraction analysis of the reaction mixture after firing at 850 °C reveals the presence of $CaTiO_3$ (Figure 3). On the basis of this result, we can conclude that apart, from the decomposition of $Nd(OH)_3$ and $CaCO_3$, the formation of $CaTiO_3$ is the only reaction that occurs up to 850 °C. The exothermic effect of this reaction is masked by the endothermic decomposition of the $CaCO_3$ and therefore does not show in the DTA curve. The formation of the $CaTiO_3$ below 850 °C can proceed via two possible solid-state reactions, which may occur simultaneously. The TiO_2 powder can either react directly with $CaCO_3$ powder, thus causing its decomposition, or the reaction takes place between TiO_2 and the CaO released after the thermal decomposition of $CaCO_3$. Such a two-stage mechanism where a carbonate is first thermally decomposed to CO_2 and an oxide which subsequently reacts with another oxide to form a new compound was already proposed for the case of the solid-state synthesis of $BaTiO_3$ from $BaCO_3$ and TiO_2.[12]

The presence of the CaO in the reaction mixture after firing at 850 °C for 2 h, however, indicates that the thermal decomposition of $CaCO_3$ proceeds faster than the formation of $CaTiO_3$ (Figure 3). Up to this temperature the Nd_2O_3 and Al_2O_3 powders remain unreacted.

Firing the reaction mixture at temperatures in the range between 1000 and 1200 °C leads to additional

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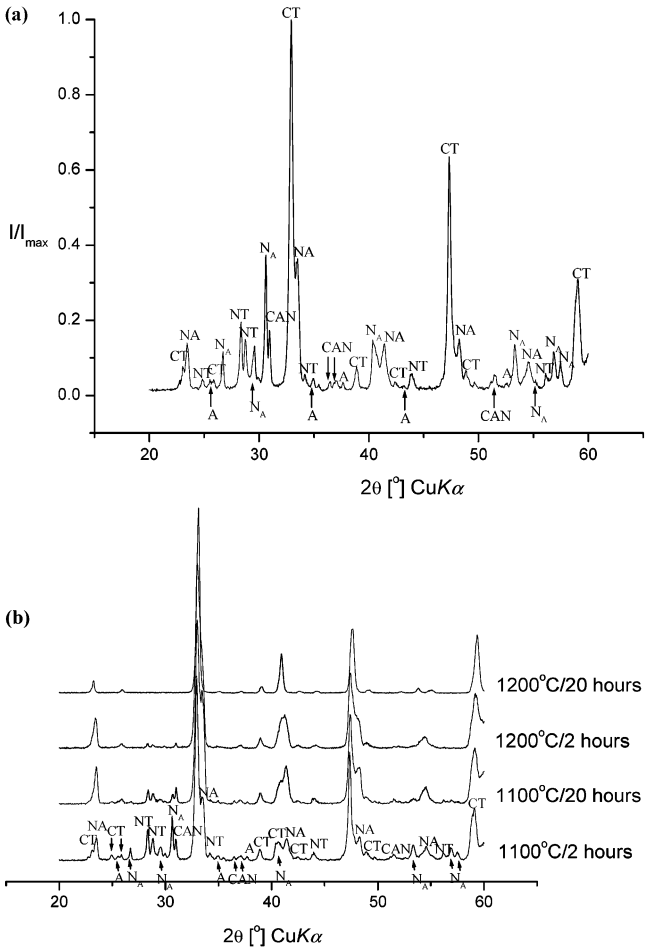


Figure 4. X-ray diffraction pattern of the $CaCO_3$, TiO_2, Nd_2O_3, and Al_2O_3 reaction mixture after firing at (a) 1000 °C/2 h and (b) at 1100 °C and 1200 °C. (NA = $NdAlO_3$, NT = Nd_2TiO_5, CAN = $CaNdAl_3O_7$).

solid-state reactions that result in the formation of three new phases: Nd_2TiO_5, $CaNdAl_3O_7$, and $NdAlO_3$. However, above 1100 °C the Nd_2TiO_5 and $CaNdAl_3O_7$ react, forming the perovskites $CaTiO_3$ and $NdAlO_3$ (Figure 4).

According to the X-ray spectra shown in Figure 4b, the final reaction, which leads to the formation of the $0.7CaTiO_3$−$0.3NdAlO_3$ solid solution, takes place between the two perovskites $CaTiO_3$ and $NdAlO_3$ at temperatures above 1200 °C.

With the use of alternative reagents, we examined three additional paths to the $0.7CaTiO_3$−$0.3NdAlO_3$ solid solution. When prereacted powders of $CaTiO_3$ and $NdAlO_3$ are used, the solid solution forms by a direct reaction between the two perovskites above 1200 °C, without the intermediate formation of Nd_2TiO_5 and $CaNdAl_3O_7$ at lower temperatures (Figure 5a). Similarly, the use of prereacted $NdAlO_3$ and stoichiometric amounts of $CaCO_3$ and TiO_2 results in the two perovskite phases (Figure 5b), which subsequently react into a solid solution as shown in Figure 5a. However, when $CaTiO_3$ is used in combination with stoichiometric amounts of Nd_2O_3 and Al_2O_3, the situation resembles the case when $CaCO_3$, TiO_2, Nd_2O_3, and Al_2O_3 are used as starting reagents. At 1000 °C (Figure 5c) the two intermediate phases Nd_2TiO_5 and $CaNdAl_3O_7$ form and subsequently react to give $CaTiO_3$ and $NdAlO_3$, which then react to form a solid solution at temperatures above 1200 °C, in accordance with Figure 4.

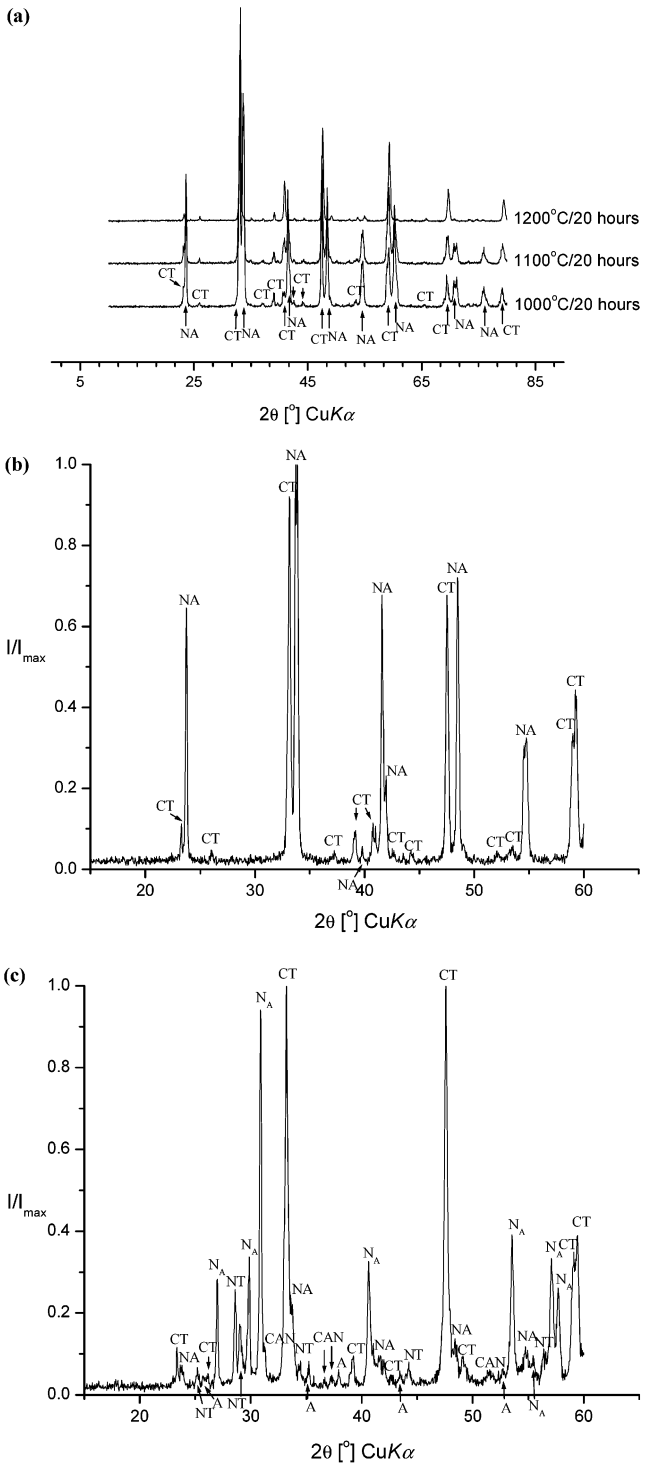


Figure 5. X-ray diffraction pattern of (a) a $CaTiO_3$ and $NdAlO_3$ mixture after firing at different temperatures, (b) a $CaCO_3$, TiO_2, and $NdAlO_3$ mixture after firing at 1000 °C/2 h, and (c) a $CaTiO_3$, Nd_2O_3, and Al_2O_3 mixture after firing at 1000 °C/2 h.

These findings suggest that the intermediate phases Nd_2TiO_5 and $CaNdAl_3O_7$ only form when free Nd_2O_3 and Al_2O_3 are present in the reaction mixture. In such a case several parallel reactions take place at temperatures between 1000 and 1200 °C. Apart from reacting with each other to form $NdAlO_3$, the two oxides Nd_2O_3 and Al_2O_3 react with either free CaO and TiO_2 or with $CaTiO_3$ to form Nd_2TiO_5 and $CaNdAl_3O_7$. Furthermore, Nd_2TiO_5 and $CaNdAl_3O_7$ react, forming the perovskites $CaTiO_3$ and $NdAlO_3$.

Inspection of the X-ray diffraction spectrum shown in Figure 4b reveals that in the early stages of the firing process the concentration of Nd_2TiO_5 and $CaNdAl_3O_7$ increases, whereas in the later stages it decreases. This confirms the transient nature of the two phases. With a high concentration of Nd_2O_3 and Al_2O_3, which is the case in the early stages of firing, the formation of Nd_2TiO_5 and $CaNdAl_3O_7$ proceeds faster than the reaction between them that leads to $CaTiO_3$ and $NdAlO_3$. However, the reverse is true for the later stages of the reaction when the majority of the Nd_2O_3 and Al_2O_3 is consumed.

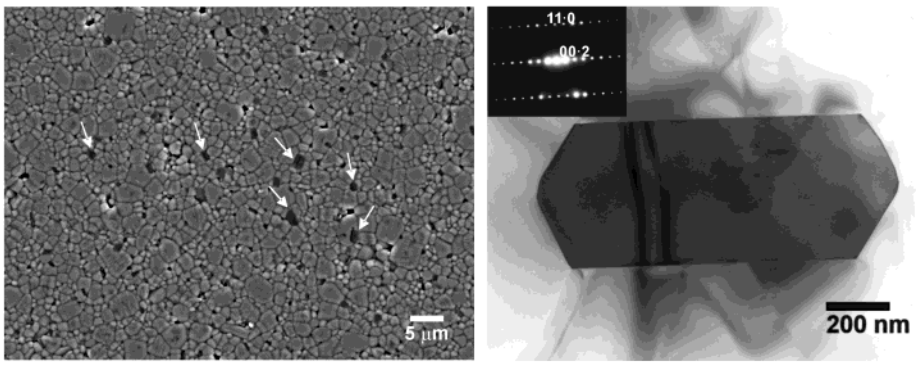
From these results, summarized in Table 1, we concluded that the reaction between $CaTiO_3$ and $NdAlO_3$ is common to all four alternatives of the reagent powders used for the synthesis of the $0.7CaTiO_3-0.3NdAlO_3$ solid solution.

Figure 6 shows the microstructrure of the sintered $0.7CaTiO_3-0.3NdAlO_3$ ceramics. Apart from the matrix-phase grains the secondary-phase inclusions with sizes ranging from 0.5 to 3 μm are clearly visible. In the course of our previous investigations it was determined that these inclusions are based on hexaluminate $CaAl_{12}O_{19}$.[5] Since the presence of these hexaluminate inclusions in the microstructure of the sintered ceramics seems to be unaffected by the choice of the reagent powders or the sintering conditions, we further concluded that their source must be the reaction between the two perovskites. To study this reaction in more detail, we prepared several diffusion couples.

According to the X-ray spectra shown in Figure 4b, a temperature of 1200 °C is sufficient for the reaction between $CaTiO_3$ and $NdAlO_3$ to occur. However, the kinetics of the reaction at this temperature is relatively slow. With the intention to follow the reaction on a more acceptable time scale, we fired the diffusion couples at 1350 °C. The interface area of the $CaTiO_3-NdAlO_3$ diffusion couple fired at 1350 °C for 6 h is shown in Figure 7. The reaction layer that forms between $CaTiO_3$ and $NdAlO_3$ consists of at least two phases: (1) a *continuous phase* filling the area between the $CaTiO_3$ and the $NdAlO_3$, and (2) *discrete particles*, segregated along the $NdAlO_3$ side. Semiquantitative EDS analysis shows that the discrete particles are rich in Al. Furthermore, EDS analysis reveals that in the continuous phase the concentration of Nd is higher than the concentration of Al, and the concentration of Ti is higher than the concentration of Ca. A clearer insight into the reaction between $CaTiO_3$ and $NdAlO_3$ is offered when the diffusion couple is fired for a longer period of time. Apart from the increase in the reaction-layer thickness associated with the nucleation of a higher concentration of Al-rich particles, the extended firing time results in the growth of the *discrete particles* (Figure 8). After a certain time the growing particles coalesce, thus forming Al-rich phase regions in the reaction layer. In the diffusion couple fired at 1350 °C for 100 h the average size of these phase regions exceeds 10 μm, which allows a more selective EDS analysis. The results of such an SEM/EDS analysis are comparable to the results of the TEM/EDS analysis performed on the $CaAl_{12}O_{19}$-based inclusions found in the $0.7CaTiO_3-0.3NdAlO_3$ ceramics. These findings and the similarity of the morphology lead us to a conclusion that the particles formed in the

Table 1. Solid-State Reactions Occurring during the Synthesis of the 0.7$CaTiO_3$−0.3$NdAlO_3$ Solid Solution

Reagent powders / *Temperature [°C]*	$CaCO_3$, TiO_2, Nd_2O_3, Al_2O_3	$NdAlO_3$ $CaCO_3$, TiO_2	$CaTiO_3$, Nd_2O_3, Al_2O_3	$CaTiO_3$, $NdAlO_3$
< 1000	$CaCO_3 \rightarrow CaO + CO_2$ $CaO + TiO_2 \rightarrow CaTiO_3$ *and/or* $CaCO_3 + TiO_2 \rightarrow CaTiO_3 + CO_2$			
1000 - 1200	$2CaO + 2TiO_2 + 3Nd_2O_3 + 3Al_2O_3 \rightarrow 2Nd_2TiO_5 + 2CaNdAl_3O_7$ *and/or* $2CaTiO_3 + 3Nd_2O_3 + 3Al_2O_3 \rightarrow 2Nd_2TiO_5 + 2CaNdAl_3O_7$ $Nd_2O_3 + Al_2O_3 \rightarrow NdAlO_3$ $Nd_2TiO_5 + CaNdAl_3O_7 \rightarrow CaTiO_3 + 3NdAlO_3$		$2CaTiO_3 + 3Nd_2O_3 + 3Al_2O_3 \rightarrow 2Nd_2TiO_5 + 2CaNdAl_3O_7$ $Nd_2O_3 + Al_2O_3 \rightarrow NdAlO_3$ $Nd_2TiO_5 + CaNdAl_3O_7 \rightarrow CaTiO_3 + 3NdAlO_3$	
>1200	$CaTiO_3 + NdAlO_3 \rightarrow (Ca,Nd)(Ti,Al)O_{3ss}$			



(a) **(b)**

Figure 6. (a) Microstructure of the 0.7$CaTiO_3$−0.3$NdAlO_3$ ceramics sintered at 1350 °C/10 h and thermally etched at 1270 °C/10 min. Arrows mark the hexaluminate inclusions. (b) Bright-field TEM image of the hexaluminate inclusion collected along [11·0] zone axis.

reaction layer of the diffusion couple are of the same type as those found in the microstructure of the 0.7$CaTiO_3$−0.3$NdAlO_3$ ceramics. Furthermore, Figure 8 reveals the enhanced growth rate of the $CaTiO_3$ grains in the vicinity of the reaction layer of the diffusion couple.

The analysis of the regions near the grain boundaries on both $CaTiO_3$ and $NdAlO_3$ sides of the diffusion couple are consistent with the results of the EDS analysis of the *continuous phase*. On the $CaTiO_3$ side the concentration of Nd in the reaction layer formed along the grain boundaries exceeds the concentration of Al. On the other hand, the grain boundaries on the $NdAlO_3$ side of the diffusion couple contain more Ti than Ca. These results suggest that during the interaction among the perovskites the diffusion of Al from the $NdAlO_3$ toward the $CaTiO_3$ is slower than the diffusion of Nd. Consequently, Al predominantly segregates in the form of Al-rich particles. Since these particles are based on hexalu-

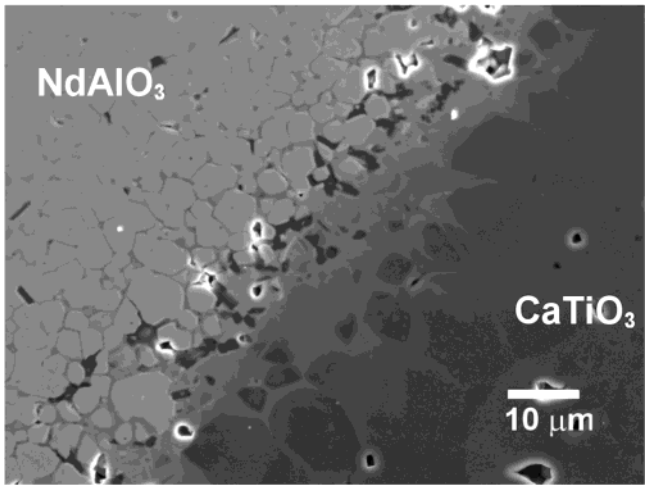


Figure 7. $CaTiO_3$−$NdAlO_3$ diffusion couple fired at 1350 °C/6 h.

minate-$CaAl_{12}O_{19}$, their formation also consumes some Ca, which is the reason for its lower concentration in the grain-boundary reaction layer formed on the $NdAlO_3$ side.

The diffusion couple simulates the situation that occurs at the interface area between $CaTiO_3$ and $NdAlO_3$ grains in the reaction mixture during the synthesis of the $0.7CaTiO_3$−$0.3NdAlO_3$ solid solution. The reaction between $CaTiO_3$ and $NdAlO_3$, apart from the formation of the perovskite solid solution, also results in the nucleation of the $CaAl_{12}O_{19}$-based inclusions. A relatively low concentration of these inclusions in the microstructure of the sintered $0.7CaTiO_3$−$0.3NdAlO_3$ ceramics suggests that they are a transient phase that forms due to kinetic rather than thermodynamic reasons. Thus, the last step in the reaction sequence, which leads to the stoichiometric solid solution, must be the reaction between the $CaAl_{12}O_{19}$-based inclusions and the newly formed perovskite phase. Therefore, the concentration of the inclusions in the microstructure of the sintered ceramics depends on the completeness of this solid-state reaction during the calcination process.

The consequence of the presence of the Al-rich $CaAl_{12}O_{19}$-based inclusions is the deficiency of Al in the perovskite matrix phase, which necessarily leads to the formation of defects. Since the $0.7CaTiO_3$−$0.3NdAlO_3$ solid solution is based on the equimolar substitution of Ca with Nd on the A-site and Ti with Al on the B-site, the deficiency of Al in the structure is, in terms of defect chemistry, equivalent to an excess of Nd. Theoretically, there are several different ways to accommodate the excess Nd in the perovskite structure (To satisfy electrical neutrality, the incorporation of Nd into the perovskite matrix must be accompanied by the incorporation of O):

(I) Nd can incorporate into the perovskite interstitially:

$$Nd_2O_3 \rightarrow 2Nd_i^{\bullet\bullet\bullet} + 3O_i'' \qquad (1)$$

(II) Nd can simultaneously occupy A and B sites in the perovskite structure:

$$Nd_2O_3 \rightarrow Nd_A^x + Nd_B^x + 3O_o^x \qquad (2)$$

(III) Nd can incorporate solely on the A-site, thus creating B-site and oxygen sublattice vacancies:

$$Nd_2O_3 \rightarrow 2Nd_A^x + 2V_B''' + 3O_o^x + 3V_o^{\bullet\bullet} \qquad (3)$$

Since the perovskite structure forms the cubic close-packing arrangement, the formation energies of Frenkel defects are considerably higher than the formation energies of Schottky defects.[13] The incorporation of excess Nd into the interstices according to eq 1 is thus unlikely to occur.

However, the mechanisms for the incorporation of an excess, large A cation, described by eqs 2 and 3, have both been reported in the literature.[14,15] The simultaneous incorporation of excess Nd on A- and B-sites, described by eq 2, would increase the ionic radii difference ($r_{Nd3+} = 0.983$ Å, $r_{Ti4+} = 0.605$ Å, $r_{Al3+} = 0.535$ Å, for the coordination number 6)[16] on the B-site and thus increase the distortion of the crystal lattice.

The mode of incorporation of excess Nd as described by the eq 3 leads to the formation of vacancies. Both mechanisms are thus possible sources of the extrinsic dielectric losses.

The mechanism of the accommodation of excess Nd in the perovskite matrix can be inferred from the diffusion couple shown in Figure 8. The micrograph of the etched surface reveals that the $CaTiO_3$ grains in the vicinity of the reaction layer grow faster than those in the bulk. The EDS analysis shows that the near-grain-boundary area of these grains contains some Nd. Such a situation implies that the incorporation of excess Nd creates high-diffusivity paths along the grain-boundary regions, which increase the grain-growth kinetics. The increase in diffusivity can be attributed to the creation of vacancies in the reaction layer formed along the grain boundaries. The effect of increased grain-growth kinetics due to the formation of oxygen vacancies in the perovskite lattice has already been reported for the case of Nd_2O_3-doped $BaCeO_3$ ceramics.[17,18]

Therefore, the most probable mechanism of accommodating excess Nd in the perovskite structure of the forming solid solution is that described by eq 3. Such a mechanism is further confirmed by the variation of the lattice parameter of the perovskite matrix as a consequence of a different concentration of hexaluminate inclusions, which is discussed in the following text.

In the scope of further experiments we explored the possibility of minimizing the concentration of inclusions by varying the calcination conditions. Figure 9 shows the microstructures of the sintered ceramics based on $0.7CaTiO_3$−$0.3NdAlO_3$ solid solutions that underwent different calcination procedures. The microstructure shown in Figure 9a belongs to a ceramic based on the $0.7CaTiO_3$−$0.3NdAlO_3$ solid solution, which was calcined in the form of pellets at 1300 °C/30 h with several intermediate crushings and repelletizings. Figure 9b,

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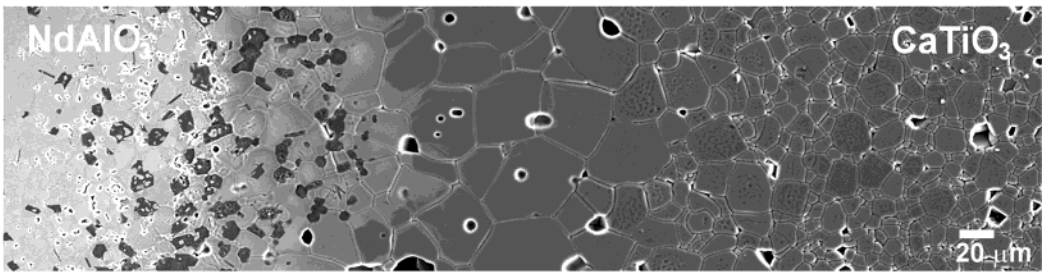

Figure 8. $CaTiO_3$−$NdAlO_3$ diffusion couple fired at 1350 °C/100 h, thermally etched at 1300 °C/10 min.

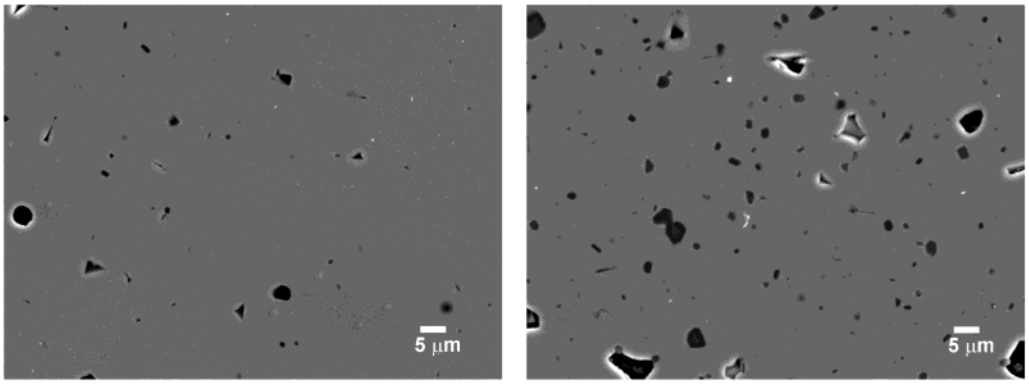

Figure 9. Microstructure of the $0.7CaTiO_3$−$0.3NdAlO_3$ ceramics sintered at 1350 °C/10 h, calcined at (a) 1300 °C/10 h and (b) 1300 °C/30 h with intermediate homogenization.

Table 2. Lattice Parameters of the Orthorhombic Perovskite $0.7CaTiO_3$−$0.3NdAlO_3$ Solid Solution vs Calcinations Conditions

lattice parameters	calcination conditions	
	1300 °C/10 h	1300 °C/30 h
a	5.4040(9)	5.4082(9)
b	7.6188(9)	7.6259(9)
c	5.3784(9)	5.3823(9)

on the other hand, shows the microstructure of a sintered ceramic based on a solid solution calcined at 1300 °C/10 h without intermediate crushing and repelletizing. As can be seen from Figure 9, such a difference in the calcination conditions results in a different amount of hexaluminate inclusions in the microstructure of the sintered ceramic. A less thorough, single-step calcination at 1300 °C/10 h yields a higher concentration of inclusions in the microstructure of the sintered ceramics.

The calculation of the lattice parameters shows that the increased concentration of the residual hexaluminate phase, which is a consequence of a less thorough calcination, results in a decrease of the unit-cell size of the orthorhombic perovskite solid solution (Table 2). In the case of the accommodation of excess Nd in the $CaTiO_3$−$NdAlO_3$ solid solution, such an effect can only be attributed to the formation of vacancies in the crystal structure, which confirms the mechanism described by eq 3.

Table 3 further reveals that a less thorough calcination results in ceramics with a lower Q-value. Such an adverse affect on the Q-value could theoretically be the consequence of either the lossy nature of the hexaluminate phase or the defects in the perovskite matrix associated with its formation. Since the Q-value we measured for the pure $CaAl_{12}O_{19}$ ceramics sintered at

Table 3. Microwave Dielectric Properties of the $0.7CaTiO_3$−$0.3NdAlO_3$ Ceramics Sintered at 1350 °C/10 Hours vs Calcinations Conditions

calcination conditions	ϵ_r	Qxf [GHz]	τ_f [ppm/K]
1300 °C/10 h	43	27.000	+3
1300 °C/30 h	43	34.000	+3

1600 °C/10 h is relatively high (Qxf = 17000 GHz), we concluded that the major effect arises from the defects formed in the perovskite matrix.

Annihilation of the defects proceeds via a relatively slow solid-state reaction between the hexalumante inclusions and the perovskite matrix phase. Therefore, to minimize their concentration, time-consuming calcination procedures need to be undertaken (Table 2), which is inconvenient for industrial applications. To shorten the calcination time required for the improvement of the Q-value, we considered adding excess Al_2O_3 for the synthesis of the $0.7CaTiO_3$−$0.3NdAlO_3$ solid solution. The excess Al_2O_3 results in a higher concentration of the hexaluminate inclusions, which increases the contact area between the inclusions and the matrix phase and thus speeds up the reaction. The addition of 3 wt % of Al_2O_3 prior to calcination at 1300 °C for 10 h results in an increase of the Q-value of the sintered ceramics to Qxf = 39000 GHz, despite a higher concentration of the hexaluminate inclusions in the microstructure.

Conclusion

The solid-state reaction mechanism that occurs during the synthesis of the $0.7CaTiO_3$−$0.3NdAlO_3$ solid solutions proceeds via the formation of the perovskite phases $CaTiO_3$ and $NdAlO_3$, regardless of the combination of the oxide powders used as reagents. The two

perovskites react above 1200 °C to form a solid solution. During this reaction the kinetics of the incorporation of Al into the forming perovskite solid solution is slower than the incorporation of Nd, which results in the formation of an Al-rich intermediate phase based on hexaluminate-$CaAl_{12}O_{19}$. The last solid-state reaction, which leads to the formation of the single-phase $CaTiO_3$−$NdAlO_3$ solid solution, takes place between the perovskite matrix and the inclusions of the hexaluminate phase. In the case of incomplete calcination some of the $CaAl_{12}O_{19}$-based inclusions remain present in the microstructure of the ceramics after sintering. Consequently, excess Nd needs to be accommodated in the perovskite matrix, which leads to the formation of B-site and oxygen sublattice vacancies. Such a defect structure increases the extrinsic dielectric losses (lowers the Q-value) of the $CaTiO_3$−$NdAlO_3$ ceramics. The minimization of the concentration of vacancies, which is necessary for an increase in the Q-value, can be achieved either by a thorough calcination process at temperatures above 1300 °C involving several intermediate homogenizations of the reaction mixture or by the addition of excess Al_2O_3 prior to a single-step calcination. A thorough calcination with intermediate homogenizations of stoichiometric amounts of reagent powders allows more time for the reaction between the inclusions and the matrix phase. It thus results in a lower concentration of hexaluminate inclusions in the micostructure and consequently a lower concentration of vacancies in the crystal structure of the perovskite matrix. The use of excess Al_2O_3 results in a higher concentration of hexaluminate inclusions, which provides an increased contact area between the matrix phase and the inclusions, and thus results in a faster annihilation of the defects in the perovskite. Since the $CaAl_{12}O_{19}$ is a low-loss phase, the increased concentration of the inclusions itself, as a result of the excess Al_2O_3, does not significantly affect the Q-value.

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