Study of Oxygen−Nitrogen Replacement in $BaTiO_3$ by ^{14}N Solid-State Nuclear Magnetic Resonance

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We here report about oxygen−nitrogen substitution in the anionic sublattice of $BaTiO_3$ by calcination in a NH_3 flow at 950 °C. The resulting oxynitride $BaTi(O,N)_3$ is shown to possess cubic structure by powder XRD and to contain 0.57 mass percent of nitrogen by hot gas extraction analysis. Solid-state ^{14}N-NMR is used to characterize the electronic surroundings of the N^{3-} anions in the oxynitride. Analysis of ^{14}N-NMR line shapes as well as comparison of line positions to those of TiN and $BaTaO_2N$ implies that the incorporated nitrogen anions do indeed occupy the oxygen sites in the $BaTi(O,N)_3$ lattice. The study illustrates the usefulness of solid-state NMR as a method for tracking ion substitution in highly symmetric environments, such as perovskite-structured oxynitrides, because of its high sensitivity to symmetry changes in the local electronic surroundings of nuclei.

Introduction

Recently, much attention has been focused on the modification of ionic compounds by applying selective substitutions to the anionic sublattice.[1−9] With such substitions, it is possible to specifically modify the electrical and optical properties of materials by changing the electronic band gap, using anions with varying electronegativity. Such systems are becoming increasingly important in material science and are being used for the production of sensors, solid electrolytes, ferroelectrics, and inorganic pigments.

Not much is known, however, about anion substitution in barium titanate, $BaTiO_3$, which in itself is a technologically important material. Although several studies exist about the $BaTiO_3/F^-$ system, it was doubted for a long time if the F^- anion is genuinely incorporated into the O^{2-} sublattice. Only recently, experimental evidence for this incorporation of F^- into the anion sublattice has been reported.[1−3] As for the substitution of oxygen by nitrogen in $BaTiO_3$, only scarce knowledge is available, even though the use of the general formula $AB(O,N)_3$ in the literature[4] suggests the possibility of such O/N exchange. Most publications, however, focus on perovskite-structured oxynitrides with A = Ba, Sr, Ca, La, and Nd, and B = Ta, Nb, and Zr. The oxynitrides with A = Ca, La and B = Ta are of interest as environmentally friendly pigments.[5] Structural investigations of these compounds have shown that the anionic sublattices are completely ordered.[6] For A = Ba and B = Ta, the oxynitride $BaTaO_2N$ has been described.[7] For B = Ti, nitrogen substitution has been investigated in detail only for systems with A = La, Nd.[8,9]

Here, we report about the first incorporation of nitrogen anions into the oxygen sublattice of $BaTiO_3$ by calcining a mixture of $BaCO_3$ and TiO_2 in a NH_3 flow. In the resulting oxynitride, $BaTi(O,N)_3$, a small number of oxygen anions are replaced by nitrogen, as shown schematically in Figure 1. The properties of the ^{14}N isotope are exploited to characterize the local environment of the nitrogen nuclei in the barium titanate matrix by solid-state nuclear magnetic resonance (NMR) spectroscopy. In this context, ^{14}N-NMR is shown to be a useful analytical tool for tracking O/N exchange in perovskite-structured oxynitrides.

Experimental Section

To produce $BaTi(O,N)_3$, ceramic powder with a nominal composition of $BaTiO_3 + 0.02\ TiO_2$ was prepared by the conventional mixed-oxide powder technique. After mixing (agate balls, water) of $BaCO_3$ (SOLVAY, VL600, <0.1 mol % Sr) and TiO_2 (MERCK, no. 808), the powder was calcined in NH_3 flow at 950 °C for 2 h in a tube furnace. The resulting bluish-green powder was then fine-milled (agate balls, 2-propanole) and densified to disks with a diameter of 6 mm and a height of nearly 3 mm. The

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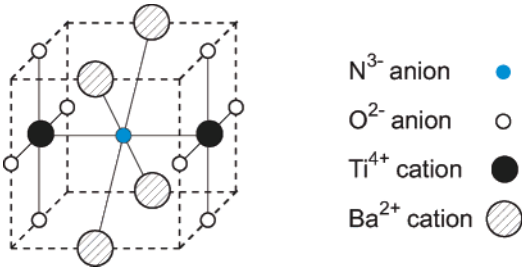

Figure 1. Schematic representation of the position of a substituted N^{3-} ion in the perovskite unit cell of $BaTiO_3$. Proper charge balance by lattice defects (oxygen vacancies) is not considered in this illustration.

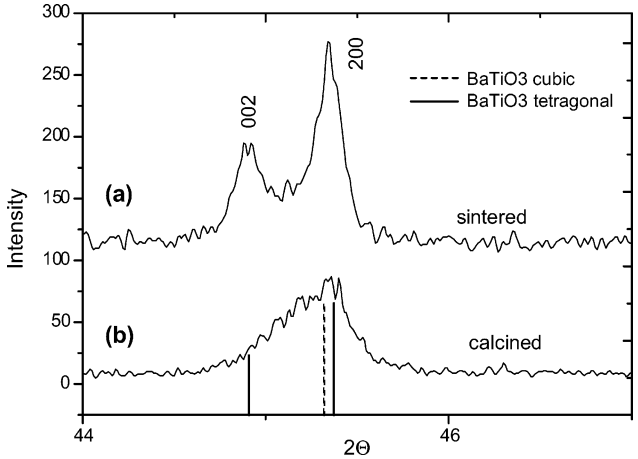

Figure 2. Powder XRD diagram of $BaTi(O,N)_3$ (a) sintered; (b) calcined. The stick diagram at the bottom indicates the relative amounts of tetragonal and cubic phase, derived from the intensities of the 002 and 200 reflections. It can be seen that the sintered samples consist mostly of the tetragonal phase, while the calcined samples contain predominantly the cubic phase (references: PDF2[73-1282]; PDF2[74-1962]).

samples were sintered in the tube furnace under flowing NH_3 with a heating rate of 15 K/min at 1300 °C for 4 h. To avoid interfering contamination, the samples were contained in ZrO_2 covered Al_2O_3 crucibles. For further analysis, the sintered samples were crushed again. Both calcined and sintered $BaTi(O,N)_3$ samples were analyzed by powder X-ray diffraction (XRD) on a STOE STADI MP diffractometer, using Cu Kα_1 radiation. The samples were mixtures of tetragonal and cubic phases without other crystalline compounds, with the calcined samples consisting mostly of the cubic phase (see Figure 2).

Analysis of nitrogen content was done using the method of hot gas extraction,[10] resulting in a nitrogen content of 0.57% (mass percent) for the calcined samples and 0.01% for the sintered samples (the latter value being well within the estimated measuring error). $BaTaO_2N$ was prepared as described in the literature,[7] and the cubic structure of the sample was confirmed by powder XRD analysis on the diffractometer mentioned above.

Both static and magic-angle spinning (MAS) ^{14}N-NMR spectra were recorded at 54.170 MHz on a BRUKER AVANCE 750 spectrometer with a nominal magnetic field of 17.6 T. A BRUKER MAS triple-resonance probe with 4-mm rotors was used, spinning at 5 kHz for the MAS spectra. The spectra were acquired with a $(\pi/2)$-τ-$(\pi/2)$-τ-acq quadrupole echo sequence, with the echo delay being equal to one rotor period, $\tau = 1/5000$ s. Relaxation delays between 1 and 15 s were used, and between 500 (MAS) and 5000 (static) transients were added. All spectra were referenced against the secondary standard of NH_4Cl, which produces a sharp and easily observable ^{14}N resonance, which was set to 0 ppm. This secondary reference is shifted by −342.4 ppm against the ^{14}N resonance in liquid nitromethane,[11] which is also cited as a reference compound in the literature. Because of their high electrical conductance, all samples were difficult to spin in the magnetic field (for TiN, this has been observed before by MacKenzie et al.)[12] and needed to be diluted with a non-nitrogen containing compound (zeolite NaY) to achieve stable sample spinning.

Results and Discussion

Incorporation of nitrogen into the O^{2-} sublattice of $BaTiO_3$ most likely occurs in the form of N^{3-} anions, and their additional negative charge needs to be compensated. Whereas in $BaTaO_2N$,[7] the presence of Ta^{5+} cations ensures that every third oxygen anion can be replaced by nitrogen, further oxidation of the Ti^{4+} cations is not possible in $BaTiO_3$. Therefore, the integration of N^{3-} into the anionic sublattice requires to balance charges according to the following defect equation:

$$3O_o^x + N_2 \rightleftharpoons 2N_o' + V_o^{\cdot\cdot} + \frac{3}{2}O_2 \qquad (1)$$

In the reducing conditions of the ammonia flow, additional oxygen vacancies can be created by the process

$$O_o^x \rightarrow V_o^{\cdot\cdot} + 2e' + \frac{1}{2}O_2 \qquad (2)$$

The total number of defects that can exist in the lattice is nevertheless limited, and thus it is expected that only a small number of O^{2-} anions can be replaced by nitrogen. As described by equation 1, for two N^{3-} anions built into the anionic sublattice, site balance requires the removal of two oxygens, whereas charge balance demands the creation of one additional oxygen vacancy. A general formula for the stoichiometry of a barium titanate oxynitride may hence be written as $BaTiO_{(3-1.5x-y)}N_x$, where y designates the number of excess oxygen vacancies (created, among others, by the process of equation 2). From the results of the hot gas extraction analysis, we find $x \approx 0.1$ for the calcined samples, which thus can be labeled as $BaTiO_{(2.85-y)}N_{0.1}$. However, although the hot gas analysis proves the presence of nitrogen in the samples, it is not clear whether the N^{3-} ions do indeed occupy the oxygen sites in the lattice, as suggested by the drawing in Figure 1.

Another possibility is to probe the nitrogen nuclei directly by solid-state NMR spectroscopy. The nitrogen isotope ^{15}N has a nuclear spin of $I = 1/2$ (thus making it amenable to all existing NMR methods for spin-1/2), however, it occurs with only 0.37% natural abundance, precluding NMR measurements on our samples without expensive isotopic labeling. The ^{14}N isotope occurs with 99.63% abundance and has a spin of $I = 1$, which means it possesses a nuclear quadrupole moment. The coupling of this quadrupole moment to the electronic surroundings dominates the appearance of solid-state ^{14}N-NMR spectra, broadening the resonance

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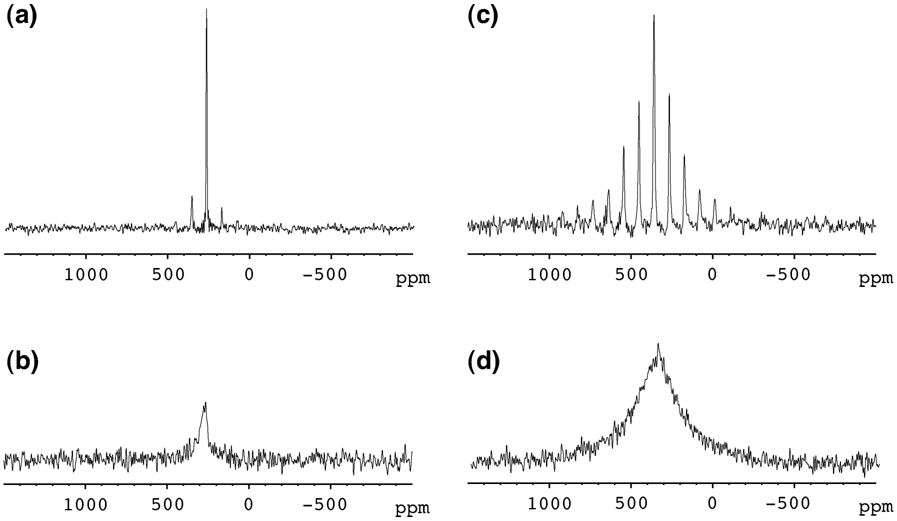

Figure 3. ^{14}N-NMR spectra of a representative calcined BaTi(O,N)$_3$ sample, (a) 5 kHz MAS (center band at 271.0 ppm), (b) static; and titanium nitride, TiN, (c) 5 kHz MAS (center band at 359.3 ppm), (d) static.

lines for compounds where the nitrogen nuclei experience a low-symmetry environment. Only for substances where the quadrupolar coupling constant $\chi = (e^2qQ/h)$ is relatively small can ^{14}N-NMR spectra be easily recorded.[11−16] For a highly symmetric environment (e.g., the unit cells of cubic barium titanate), the quadrupolar coupling vanishes altogether, and only a single sharp line is expected in the spectrum. This allows to evaluate the symmetry of the N^{3-} surroundings by acquisition of ^{14}N-NMR spectra. However, in binary nitrides such as AlN[13,14] or TiN,[12] the nitrogen also occupies sites of sufficiently high symmetry to give rise to sharp lines in the ^{14}N-NMR spectrum. (TiN is a likely side product of the oxynitride synthesis because of the formation process: $6TiO_2 + 8NH_3 \rightarrow 6TiN + 12H_2O + N_2$.) In such cases, the frequency shift of the resonance line is another parameter that can be used to characterize and distinguish nitrogen nuclei in different electronic environments.

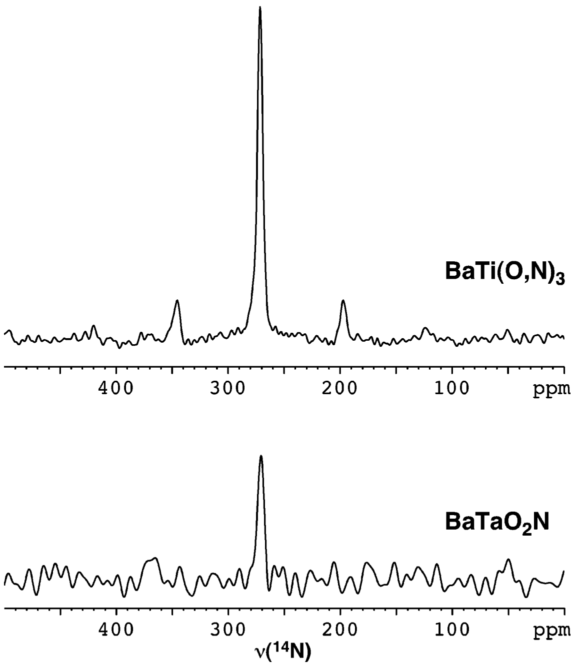

Figure 4. ^{14}N-NMR spectra of a representative calcined BaTi(O,N)$_3$ sample at 5 kHz MAS (center band at 271.0 ppm) (top); and BaTaO$_2$N at 5 kHz MAS (center band at 270.4 ppm) (bottom).

We therefore recorded ^{14}N-NMR spectra of TiN, BaTaO$_2$N, and the BaTiO$_{(2.85-y)}$N$_{0.1}$ samples, as described in the Experimental section. In Figure 3b, it can be seen that even for a static sample, the ^{14}N resonance line of the barium titanate oxynitride is fairly narrow, indicating a high (near isotropic) symmetry of the electronic surroundings. The static spectrum of TiN (Figure 3d) shows a broad line shape, the origin of which is most likely a distribution of NMR interaction parameters because of the inherently varying stoichiometry of titanium nitride.[17] Application of the magic-angle spinning (MAS) technique[18] has the effect of breaking up the line shape caused by first-order quadrupolar interaction and chemical shift anisotropy (CSA) into narrow spinning sidebands. The resulting spectra show a very sharp line for the barium titanate oxynitride at 271.0 ppm (Figure 3a). We also measured the ^{14}N-NMR spectrum of BaTaO$_2$N, where the N^{3-} anions are known to occupy the oxygen positions in the cubic structure.[7] As can be seen from Figure 4, the observed resonance line at 270.4 ppm is practically identical in shape and position to the line of the BaTiO$_{(2.85-y)}$N$_{0.1}$ sample. In contrast, the broad static line shape of TiN breaks down into a pattern of spinning sidebands (Figure 3c), with the center band appearing at 359.3 ppm, in good agreement with the previously reported value of 359.5 ppm.[13] The position of the TiN line is determined not only by the well-known chemical shift but also by a change of resonance frequency induced by the presence of electrons in the conduction band known as "Knight shift".[19] However, both shift contributions reflect changes in the electronic environment, so that by comparison of line positions and line shapes

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it can be concluded that the ^{14}N nuclei detected in the calcined oxynitride do not reside in TiN domains. Furthermore, the very narrow lines obtained for both static and MAS spectra of $BaTiO_{(2.85-y)}N_{0.1}$ as well as the matching line position of $BaTaO_2N$ imply that the incorporated nitrogen anions occupy the oxygen sites in the lattice. This is consistent with the fact that the calcined samples contain predominantly the cubic phase (Figure 2b). However, the ideal cubic perovskite structure (with space group $Pm\bar{3}m$) of $BaTiO_3$ is stable only above 130 °C, with a phase transition to tetragonal symmetry ($P4mm$) taking place at this temperature. Nevertheless, the existence of cubic $BaTiO_3$ at room temperature (i.e., well below the phase transition) is not unusual and has been explained by structural stress induced by lattice defects[20] or by reduced particle size.[21] In the case of $BaTiO_{(2.85-y)}N_{0.1}$, the presence of a relatively high number of oxygen vacancies caused by the nitrogen substitution seems to stabilize the cubic phase at room temperature.

Sintering our oxynitride samples at high temperatures, on the other hand, results in a predominantly tetragonal structure (Figure 2a). The tetragonal phase is characterized by a slight displacement of the Ti ions along the *c*-axis and by a corresponding small distortion of the oxygen octahedra. Because of this distortion, two distinct oxygen sites exist in the tetragonal structure, and nuclei occupying these sites should differ in their NMR parameters. Indeed, two closely overlapping CSA patterns were claimed to be found in the static ^{17}O spectrum of tetragonal $BaTiO_3$, whereas only one narrow symmetrical peak was observed in the MAS spectrum of cubic $BaTiO_3$.[22] The existence of only one ^{14}N line in the MAS spectra of our calcined oxynitrides hence further confirms that the nitrogen anions occupy lattice sites with high symmetry. We were not successful, however, with recording ^{14}N-MAS spectra of the sintered samples, even with signal averaging for more than 24 h. To exclude saturation effects caused by long relaxation times T_1, an attempt was made to acquire a spectrum with a recycle delay of 600 s but without success. Besides, the T_1's of the sintered samples are expected to be short, because of their relatively high conductivity.[13] This expectation is confirmed by the T_1 relaxation time of the calcined sample shown in Figures 3 and 4, which we estimated to be smaller than 50 ms by an inversion−recovery experiment. The absence of a ^{14}N-NMR signal is therefore most likely due to loss of nitrogen during the sintering process, as also the hot gas extraction analysis was not able to detect nitrogen in the sintered samples within experimental certainty. The fact that we were able to record reasonably good ^{14}N-NMR spectra of the calcined samples (where hot gas extraction found only 0.57% nitrogen) demonstrates that for oxynitride samples with high intrinsic symmetry, solid-state NMR is a sensitive analytical tool. The sharp lines produced by ^{14}N nuclei in cubic surroundings show up in the MAS spectrum within less than an hour, so that even smaller concentrations of nitrogen in the sintered samples should have been detected.

Conclusions

By calcination in a NH_3 flow at 950 °C, a small percentage of O^{2-} anions can be substituted by N^{3-} in $BaTiO_3$, producing an oxynitride, $BaTiO_{(2.85-y)}N_{0.1}$, with cubic structure. The nitrogen content of the samples was analyzed by hot gas extraction, and ^{14}N-NMR was employed to characterize the electronic surroundings of the N^{3-} anions. The ^{14}N-NMR results indicate that the nitrogen nuclei occupy sites of high symmetry, suggesting incorporation of the N^{3-} anions into the O^{2-} sublattice. Because of its sensitivity to symmetry changes in the local electronic surroundings of nuclei, solid-state NMR is a very useful method for tracking ion substitution in highly symmetric environments, such as perovskite-structured oxynitrides.

Further work is in progress to find new and efficient strategies for synthesizing mixed systems of the $BaTiO_{(3-1.5x-y)}N_x$ type, followed by comprehensive characterization of their composition and properties

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