Research Article

Top-Down Processing of NaNbO₃ Nanopowder

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We report the processing of NaNbO₃ nanopowder by combining the solid-state synthesis and subsequent milling in the agitator bead mill. The effect of different rotation speeds of the agitator shaft on the comminution process was followed by laser granulometry. The morphology and specific surface area of the powders were investigated by scanning electron microscopy and the N₂ adsorption method, respectively. With the optimized milling parameters, we obtained NaNbO₃ nanoparticles with an average size of 25 nm and a narrow particle size distribution. The result is comparable to other processing techniques, such as solution-based chemical routes or mechanochemical synthesis; however, the presented method does not require any complicated processing and it can be easily upscaled to yield large quantities of the NaNbO₃ nanopowder. Furthermore, the compaction behaviour of the obtained nanopowder was investigated, and a compaction-response diagram was constructed revealing good compactability of the powder. The green compacts, isostatically pressed at 740 MPa, had a relative density of 70% and a narrow pore size distribution with an average pore radius of 4 nm.

1. Introduction

Antiferroelectric materials have gained increased attention due to their large energy storage capacity, required for high-performance capacitors [1], and a large volume change accompanying the field-induced phase transition, which can be used in high-strain actuator and transducer applications [2]. Lead zirconate (PbZrO₃) is a prototype antiferroelectric [3, 4]; however, due to increased environmental concerns [5], lead-free antiferroelectrics, such as sodium niobate (NaNbO₃), are considered [6]. The phase transition behaviour of NaNbO₃ is quite complicated [7]. Beside the temperature and electric-field-induced phase transitions, size-induced phase transition phenomena have been recently observed [8, 9]. In order to investigate the effect of the particle/grain sizes on the polymorphism, and consequently on the functional properties, dense NaNbO₃ ceramics with a wide grain size range should be prepared. A necessary condition for the preparation of ultrafine-grained ceramics is the NaNbO₃ nanopowder.

Nobre et al. prepared NaNbO₃ nanoparticles by the Pechini route and calcination of the precursor at 700°C for 5 h. The powder had the particle size of around 60 nm, as determined by the Brunauer-Emmet-Teller (BET) method [10]. Lanfredi et al. prepared the NaNbO₃ nanoparticles from the solution of an oxalatoniobium complex, sodium nitrate, oxalic acid, and ammonium hydroxide. The particle size of the powder, obtained by calcining the precursor at 900°C for 5 h, was 85 nm, as calculated from the X-ray diffraction (XRD) data by the Sherrer equation. However, some impurities could be observed in the XRD pattern [11]. In both studies, dense NaNbO₃ ceramics were obtained after sintering at lower temperatures than usually needed for the solid-state synthesized powder, which was connected to the small particle size and to a high concentration of defects, such as oxygen vacancies. The latter were presumably created due to the incomplete oxidation of organic precursors. In 2005, Pithan et al. introduced a microemulsion-mediated hydrolytic decomposition of a mixed-alkoxide solution, followed by Soxhlet extraction, and subsequent calcining at
400°C to prepare the nanopowder with the particle size of a few 10 nm as observed by scanning electron microscopy (SEM) and the BET size of a few 100 nm [12].

Solution-based chemical routes, applied to prepare NaNbO₃ nanopowders, suffer various deficiencies, such as complicated processing, small product yield, difficult upscaling, and sometimes difficulties in a complete removal of residual carbon. In addition, they typically require additional calcination steps to obtain the crystalline product.

An alternative approach was introduced by Rojac et al. who prepared the NaNbO₃ nanopowder by mechanochemical synthesis [13]. After 40 h of high-energy milling of Na₂CO₃ and Nb₂O₅ in a planetary mill, the product consisted of agglomerates of 100–300 nm in size, while the crystallites were in the range of 10–20 nm, as determined from the transmission electron microscope images. The process however introduced impurities in the powder due to wear of the ZrO₂ milling vial and balls.

The aim of the present work was to establish a simple and effective processing route for the preparation of NaNbO₃ nanopowder by combining conventional and well established ceramic processing techniques, such as the solid-state synthesis of submicron-sized powder [9] and subsequent efficient milling to nanorange in an agitator bead mill. The influences of the milling time and different rotation speeds of the agitator shaft were followed by measurements of the particle size and size distribution and specific surface area. The optimization of the process resulted in a successful preparation of NaNbO₃ nanopowder. Furthermore, the nanopowder was isostatically pressed between 250 MPa and 740 MPa and its compaction-response diagram was constructed.

2. Experimental Work

The NaNbO₃ powder was prepared by solid-state synthesis from the high-purity Nb₂O₅ (99.9%, Sigma-Aldrich, Taufkirchen, Germany) and mechanically activated Na₂CO₃ (anhydrous 99.9+%, Chempur, Karlsruhe, Germany). The submicron-sized starting powders were mixed in a stoichiometric ratio and homogenized in a planetary mill (Fritsch Pulverisette 4 Vario-Mill, Fritsch GmbH, Idar-Oberstein, Germany) for 4 h, using a zirconia vial and balls, and acetone as the liquid medium (p. A., AppliChem, Darmstadt, Germany). After drying, the powder mixture was pressed into pellets and calcined twice in a closed alumina crucible at 700°C for 4 h with intermediate milling. The product was crushed in an agate mortar and milled in a planetary mill for 4 h, as described above. The particle size distributions of the powders were determined from the area distribution, measured by a static light-scattering granulometer (Microtrac S3500 Particle Size Analyzer, Montgomeryville, PA, USA). The phase purity of the obtained powder was analysed by XRD (a PANalytical X’Pert PRO MPD diffractometer equipped with a graphite monochromator (Almelo, The Netherlands), and the material was found to be single phase, since all the peaks could be described with the crystallographic card of the orthorhombic NaNbO₃ (Figure 1) [14]. A detailed description of the synthesis and phase analysis can be found elsewhere [9].

![Figure 1: XRD pattern of the solid-state synthesis prepared NaNbO₃ (blue line). All the peaks could be described with the crystallographic card of the orthorhombic NaNbO₃ (red tick marks).](image-url)

For milling the NaNbO₃ to nanorange, we used the Mini-Cer agitator bead mill (Netzsch Feinmahltechnik GmbH, Selb, Germany), where the grinding medium is accelerated in the chamber by an agitator shaft. Prior milling the as-synthesized powder was dispersed in isopropyl alcohol (p. A., AppliChem, Darmstadt, Germany) in an ultrasonic bath. The suspension was fed through the grinding chamber by a peristaltic hose pump (Verderlab, Haan, Germany), and zirconia beads with a diameter of 0.5 mm (Tosoh Corporation, Tokyo, Japan) were used as the grinding medium. The milling process was followed by the granulometer. The particle size distributions are described with the 90% particle size limit (d₉₀), 50% particle size limit (d₅₀), median value), and 10% particle size limit (d₁₀).

The powder morphology was investigated by a field emission scanning electron microscope (FE-SEM JSM-7600F, Jeol, Tokyo, Japan) with an operating voltage of 5 kV, while the specific surface area was analysed using the N₂ adsorption BET method (NOVA 2200E, Quantachrome Instruments, Boynton Beach, FL, USA). The BET equivalent particle diameters were calculated by the following equation:

\[
d_{\text{BET}} = \frac{\psi_A/\psi_V}{S_M \cdot \rho_t}
\]

where \(S_M\) is the specific surface area, \(\rho_t\) is the theoretical density of NaNbO₃ (4.55 g/cm³ [14]), and \(\psi_A/\psi_V\) is the shape factor ratio, for which a value of 6 was assumed [15].

The compaction behaviour of the powders was studied by uniaxial pressing the pellets with a pressure of 100 MPa and subsequently isostatically with pressures ranging from 250 MPa to 740 MPa. The relative densities were calculated from the dimensions and mass of the sample.

The pore size measurements of the compacted pellets were performed using the N₂ sorption equipment described above. The samples were dried at 250°C for 4 h and subsequently degassed at 200°C for 2 h prior to the measurement. The pore size distributions were calculated from the desorption curves using the method proposed by Barrett, Joyner, and Halenda (BJH) [16].
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(a)

100 nm

1 μm

Figure 2: The reference-NN powder prepared by the solid-state synthesis and milled in a planetary mill for 4 h: (a) FE-SEM images and (b) particle size distribution, as measured by laser granulometry.

3. Results and Discussion

The FE-SEM images of the NaNbO₃ powder, obtained after the solid-state synthesis and subsequent milling in a planetary mill, are presented in Figure 2(a). This powder is further denoted as “reference-NN.” The estimated primary particle size was around 200–300 nm; however, some agglomerates of around 400–700 nm could be observed. This was confirmed by the granulometric measurement (Figure 2(b)), with two maxima at around 150–200 nm and 400–500 nm, attributed to the primary particles and to the agglomerates, respectively. The milling in the planetary mill after the calcination obviously failed to break strong agglomerates, created during the calcination process.

In order to prepare the NaNbO₃ nanopowder, we milled the reference-NN powder in the agitator bead mill. Different rotation speeds of the agitator shaft, that is, 1000 rpm, 1500 rpm, and 2000 rpm, were applied. The milled powders are denoted as “nano-NN-1000,” “nano-NN-1500,” and “nano-NN-2000,” respectively. The milling process was followed by measuring the particle size distributions by laser granulometry which allowed a quick evaluation of the milling process, since the samples could be rapidly transported in the form of a suspension directly from the mill to the granulometer. The results of the milling process with different rotation speeds of the agitator shaft for times up to 75 min are presented in Figure 3. We observed a considerable narrowing of the size distributions and a major decrease of the d-values during the first 30 min of the milling process, while the size reduction was much smaller with further increase of the milling time. The milling process was stopped after 75 min, since a further increase of the time did not considerably reduce the particle size or in some cases even resulted in increasing the d-values due to increased particle agglomeration. This is partially observed for the nano-NN-1000 in Figure 3. In addition, long milling times could cause the wear of the zirconia beads and subsequent contamination of the powder and should therefore be avoided. The optimal conditions for the milling were identified to be the rotation speed of 2000 rpm and the milling time of around 75 min.

The NaNbO₃ nanopowders, milled for 75 min, were investigated by FE-SEM (Figure 4). The primary particle size was below 100 nm in all samples, and the images confirm the decrease of the particle size with increased rotation speed. In addition, some larger particles of around 200–400 nm could be observed; however, it was not clear, if they were agglomerates or particles. The amount of large particles decreased with increasing rotation speed.
The specific surface areas of the powders, milled for 75 min at different rotation speeds, were measured by the N₂ adsorption method. The results are summarized in Figure 5. The reference-NN powder had the specific surface area of 5.81 m²/g. After the 1000 rpm milling, the specific surface area increased for about 6 times, while the milling with 2000 rpm resulted in nanopowder with an almost 10 times larger specific surface area. In addition, the \( d_{\text{BET}} \) primary particle sizes, calculated by (1), are added to Figure 5. The primary particle sizes decrease from 41 nm to 25 nm with increasing rotation speed, which is in agreement with the FE-SEM observations (Figure 4). The particle size of the obtained nano-NN powders is within the ranges reported for solution methods [10–12] and mechanochemical synthesis [13].

The compaction behaviour of the reference-NN and the nano-NN-2000 powders is presented in Figure 6 in the form of a compaction-response diagram [17]. The curve of the reference-NN has a constant slope throughout the whole investigated isostatic pressure range between 250 MPa and 740 MPa, where the highest relative density of about 69% was obtained. A different compaction behaviour was observed in the case of the nano-NN-2000 powder, where lower relative densities were obtained in the lower pressure region up to about 550 MPa; however, a steeper slope, revealing a better compactability of this powder, resulted in higher relative densities at pressures above 550 MPa, as compared to the reference-NN powder. The interpolated value of around 64% relative density at 450 MPa for the nano-NN-2000 powder is comparable to the value reported for the compaction of the solution-derived NaNbO₃ nanopowder by Lanfredi et al., that is, 65% at a uniaxial pressure of 450 MPa [11]. However, the authors reported that this relative density was the limiting value, since the compaction rate at pressures above 320 MPa
was very small. In our case, the limiting value seems to be at higher pressures, since a considerable increase of the relative density was observed with increasing the pressure up to about 650 MPa, where a relative density of around 69.2% was measured. The highest relative density of about 70.2% was achieved at the pressure of 740 MPa.

The pore size and size distribution within the green body are important parameters of the sintering process.

Figure 4: FE-SEM images of the nano-NN-1000 (a), nano-NN-1500 (b), and nano-NN-2000 (c) powders.
Figure 5: Specific surface areas of the obtained nano-NN-1000, nano-NN-1500, and nano-NN-2000 powders, as measured by the BET method. The calculated $d_{BET}$ values are included in the corresponding columns. The specific surface area of the reference-NN powder is added for comparison.

Figure 6: The compaction-response diagram of the reference-NN and nano-NN-2000 powders. Note that the dotted lines are a guide for the eye only.

Figure 7: Pore size distribution of the reference-NN and nano-NN-2000 green samples, compacted with an isostatic pressure of 740 MPa. The numbers above the distributions represent the average pore radius.

4. Summary

NaNbO$_3$ nanopowder was prepared by simple top-down processing, combining the solid-state synthesis and subsequent bead milling. The milling process was optimized to yield nanoparticles with the average size of around 25 nm, which is comparable to the particle sizes obtained by solution-based chemical routes or mechanochemical synthesis. The proposed approach does not require any expensive reactants or high-energy milling and, as it is easily upscaled, it could yield a large quantity of the NaNbO$_3$ nanopowder. The compaction behaviour of the nanopowder was investigated in order to establish a suitable starting point for further research of the sintering process. The NaNbO$_3$ nanopowder exhibited a better compactability than the submicron NaNbO$_3$ powder, with an about six times lower average pore radius, and a narrower pore size distribution in the green samples.

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