Polymorphism in Micro-, Submicro-, and Nanocrystalline NaNbO₃

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NaNbO₃ powders with various particle sizes (ranging from 30 nm to several microns) and well-controlled stoichiometry were obtained through microemulsion-mediated synthesis. The effect of particle size on the phase transformation of the prepared NaNbO₃ powders was studied using X-ray powder diffraction, Raman spectroscopy, and nuclear site group analysis based on these spectroscopic data. Coarsened particles exhibit an orthorhombic *Pbcm* (D_{2h}^{11} , no. 57) structure corresponding to the bulk structure, as observed for single crystals or powders prepared by conventional solid-state reaction. The crystal symmetry of submicron powders was refined with the space group $Pmc2_1$ ($C_{2\nu}^2$, no. 26). The reduced perovskite cell volumes of these submicron powders were most expanded compared to all the other structures. Fine particles with a diameter of less than 70 nm as measured from SEM observations showed an orthorhombic Pmma (D_{2h}^{5} , no. 51) crystal symmetry. The perovskite formula cell of this structure was pseudocubic and was the most compact one. A possible mechanism of the phase transformation is suggested.

1. Introduction

Lead-free and environmentally friendly NaNbO₃-based solid solutions such as (K_x , Na_{1-x})NbO₃ or (Li_x, Na_{1-x})NbO₃ have presently been drawing interest as piezoelectric materials.¹⁻⁴ Sodium niobate (NaNbO₃), being one of the end members of such solid solutions, is known as an antiferroelectric perovskitetype compound, which may transform into a ferroelectric one by chemical doping^{5,6} or by an imposed bias electrical dc field.⁶ Some of the NaNbO₃-based solid solutions serve as relaxortype dielectric materials,⁷ and also, NaNbO₃ itself indicates a relaxor-like dielectric behavior.⁸ Recently, nanosized powders of NaNbO₃-based lead-free oxides are believed to potentially gain importance to meet the demand of improved sinterability.^{9–11}

An in-depth understanding of the crystallographic structure of nanosized crystallites is fundamental in order to maintain or even improve material functions such as piezoelectric and dielectric response. The study of size-induced phase transformations is an essential topic within the establishment of the next generation of nanotechnology. Recently, (K_{0.5}, Na_{0.5})NbO₃ was found to exhibit a phase transformation driven by particle size reduction.¹⁰ The transformation was successfully monitored by X-ray powder diffraction (XRPD) combined with Raman scattering spectroscopy. The latter is at present the most powerful method to detect local distortions in a crystal lattice and eventually phase transitions.^{12–17} Actually, $(K_{0.5}, Na_{0.5})$ -NbO3 transforms from a monoclinic structure with a space group of either *Pm* or *P*2 to a triclinic one with *P*1 or *P*-1 symmetry at a critical Brunauer-Emmett-Teller (BET) equivalent particle size of about 200 nm with decreasing particle size.¹⁰ This feature

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is believed to be related to the cationic ordering of K^+ and Na^+ in the lattice.¹⁸ In this study, we investigated one of the end members of such a solid solution, NaNbO₃, containing only one of the alkaline cations, in order to describe the influence of the particle size by excluding that of atomic distribution.

Bulk NaNbO₃ materials (single crystals and ceramics) reveal a much more complex phase-transition behavior^{5,6,15,17} than the macroscopic KNbO3 system. KNbO3 undergoes several structural phase transitions, ^{5,6,12} which are typical for many perovskite-type phases such as BaTiO₃,¹⁹ from cubic to tetragonal at 435 °C, and then to orthorhombic and rhombohedral at 225 and -10 °C,⁵ respectively. At room temperature, NaNbO₃ is antiferroelectric. Darlington et al.20 described the crystallographic structure as a monoclinic one. Later, Xu et al.²¹ reported the stable NaNbO3 modification at room temperature as an orthorhombic one with the space group *Pbcm* (D_{2h}^{11} , no. 57). The structure of NaNbO₃ has 8 perovskite formulas per unit cell at room temperature, and consequently, 117 optical phonons exist. Raman scattering studies successfully reflected the phase-transition behavior of NaNbO3 associated with the tilts of NbO₆ octahedra, dependent on the thermodynamical variables temperature^{15,17} and pressure.¹⁶ Softening of the librational modes of NbO₆ octahedra on cooling from room temperature was found to be a result of octahedra reorientation.¹⁵ Pressure-induced spectral changes at 7 GPa have been discussed as a result of a first-order phase transition and a major structural change accompanying a transformation of the crystallographic symmetry.¹⁶ Dielectric properties and Raman scatterings of NaNbO₃ ceramics, which were prepared from powders obtained through the thermal decomposition of a precursor derived from a complex niobium salt and sodium nitrate, were also reported, and it has been concluded that the orientation of NbO₆ groups is a dominant phase-transformation mechanism at temperatures below room temperature.²²

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Polymorphism in Crystalline NaNbO3

Particle size, which influences the surface energy and the internal pressure of a particle,^{13,23,24} is another important thermodynamical parameter. Chemical aspects such as homogeneity and lattice defects, depending on the synthesis route, may also play a role. In the present study, we focused on NaNbO₃ powders produced by a microemulsion-mediated approach allowing control of nucleation and growth during the formation of ultrafine nanosized particles.^{11,25} Particle size induced polymorphism of the prepared NaNbO₃ powders has been investigated by XRPD and Raman scattering spectroscopy.

2. Experimental Section

2.1. Powder Preparation. Stoichiometric NaNbO3 powders were prepared through the hydrolysis of mixed ethanolic solutions of sodium and niobium ethoxides using a water in oil microemulsion as the reaction medium. The synthesis process has already been described in detail elsewhere.¹¹ As the precursor, an ethanolic solution of sodium-niobium ethoxide was prepared from pure niobium ethoxide mixed with pure sodium ethoxide (ABCR). Niobium ethoxide was obtained from NbCl₅ (Alfa Aesar) suspended in toluene (Merck, analytical grade) by the addition of ethanol and ammonia (Linde), filtering off ammonium chloride, and subsequent vacuum distillation (158 °C, 0.1 mbar). After the preparation of the precursor solutions, a stoichiometric amount of the microemulsion was added in order to form the nanosized powders. Raw powders were annealed in air for 1 h at various temperatures between 200 and 1000 °C. After cooling to room temperature, a part of all these powders was heat-treated for 12 h at the same temperatures in air again.

2.2. Characterization. The stoichiometry of all powders was evaluated from the results of inductively coupled plasma with optical emission spectroscopy (ICP-OES) for the metallic ions and of infrared spectroscopy for oxygen extracted by heating under helium gas flow. Samples for ICP-OES were prepared as solutions in H₂SO₄, which were diluted to a total volume of 50 mL by dissolving 10 mg of the respective powders in 3 mL of heated H₂SO₄. The carbon content was measured by detecting the CO₂ amount evolving from the samples burnt in flowing oxygen using infrared spectroscopy. The morphologies and particle sizes of all powders were studied by scanning electron microscopy (SEM, Hitachi S-4100). The average particle size of the powders was also evaluated from their specific surface areas measured by means of N2 adsorption BET method using a surface area analyzer (Micromeritics, Gemini 2360). XRPD patterns and Raman spectra were collected at room temperature using a Philips X'Pert diffractometer (Cu Ka radiation) and a Jobin Yvon T64000 spectrometer (Ar⁺ laser excitation with 514.5 nm wavelength and <50 mW power at the sample), respectively. Refinement of the XRPD patterns was performed according to the Rietveld method by using the Fullprof software package.²⁶ A program in the Grams/AI software package (Thermo Galactic) was used to analyze the Raman scattering profiles.

3. Results and Discussion

3.1. Chemical Analysis of the Prepared Powders. Figure 1 represents the SEM images of the as-synthesized powder used as raw material for further annealing and of the powders annealed for 12 h. We will use the terms NN @ T-1 and NN @ T-12 when the raw powder is annealed for 1 h or for 12 h, respectively, at the temperature T in Celsius. Particles of the raw powder (see Figure 1a) are connected by surfactant residues and form loose agglomerates. The average diameter of the



Figure 1. SEM images of (a) the raw NN powder and the powders annealed for 12 h at (b) 400, (c) 500, (d) 600, (e) 700, (f) 800, (g) 900, and (h) 1000 °C.

individual particles is around 30 nm, and the particle shape is spherical. The powders were coarsened up to the micron order (see Figure 1h). Figure 2 shows some selected XRPD patterns measured for the raw and annealed powders. Figure 2a reveals that the as-synthesized particles are amorphous. The XRPD patterns for NN @ 500-1 and NN @ 400-12 showed sharp and intense diffraction patterns (see Figure 2b and c) reflecting the crystallization of single-phase NaNbO3. This was also monitored by Raman spectroscopy (see Figure 3). The Raman spectrum of the raw powder (see Figure 3a) and those for the samples annealed for 1 h at temperatures up to 400 °C are mainly composed of carbon chain deformation modes (200- 300 cm^{-1}), C–O and C–C stretching modes (around 900 cm⁻¹), which are ascribed to the surfactant molecules, and their decomposition products.¹¹ However, upon annealing for 1 h above 500 °C or for 12 h above 400 °C, these specific bands disappeared (see Figure 3b and c), and typical perovskite-type spectra with intense peaks in the $50-300 \text{ cm}^{-1}$ and 500-700cm⁻¹ regions¹⁰⁻¹⁷ have been obtained for these powders. The contents of organic and inorganic carbon, such as carbonates, in these powders were less than 0.1 wt %, respectively. Figure 4 shows the molar percentages of the elements dependent on annealing temperature for the prepared powders as a result of ICP-OES and infrared spectroscopy. As shown, the stoichiometry of Na/Nb/O = 1:1:3 was achieved for the powders



Figure 2. XRPD patterns recorded for (a) the raw NN powder, (b) NN @ 500-1, (c) NN @ 400-12, (d) NN @ 500-12, (e) NN @ 800-12, and (f) NN @ 1000-12.



Figure 3. Raman spectra collected for (a) the raw NN powder, (b) NN @ 500-1, and (c) NN @ 400-12.

annealed at temperatures above 400 °C. In summary, powders, annealed at temperatures above (i) 400 °C for 12 h or (ii) 500 °C for 1 h, contain particles without residual surfactant. XRPD combined with Raman scattering confirm that the samples are single-phase NaNbO₃.

3.2. Particle Size Determination. To evaluate the average particle size, the BET method²⁷ was applied in combination with direct observation of the morphology and the particle dimensions by SEM.

In the case of unimolecuar adsorption, the relationship between the adsorption equilibrium pressure p and the volume of gas adsorbed at p (BET equation²⁷) is

$$\frac{p}{v(p_0 - p)} = \frac{c - 1}{v_{\rm m}c} \cdot \frac{p}{p_0} + \frac{1}{v_{\rm m}c}$$

under an adsorption equilibrium state at a constant temperature, where p_0 , v_m , and c are the saturation pressure, the volume



Figure 4. Annealing temperature dependence of the molar percentages of Na (\bigcirc), Nb (\triangle) and O (\square) in the NaNbO₃ powders annealed for (a) 1 h and (b) 12 h.



Figure 5. BET plots obtained for (a) the raw NN powder and the powders annealed for 12 h at (b) 400, (c) 500, (d) 600, (e) 700, (f) 800, (g) 900, and (h) 1000 $^{\circ}$ C.

adsorbed in a unimolecular layer, and the BET constant. Therefore, in the case of unimolecular adsorption, the plots of p/p_0 and $p/v(p_0 - p)$ should give a linear correlation (in the range of p/p_0 from 0.05 to 0.35 ²⁷). BET plots for the powders annealed for 12 h are shown in Figure 5. All powders except for NN @ 1000-12 (see Figure 5h) showed excellent linear correlations of $p/v(p_0 - p)$ as a function of p/p_0 from which v_m values were obtained. The poor linear correlation for NN @ 1000-12 is probably due to a very small surface area of the sample. The specific surface areas (SSA) were calculated, their errors being less than 5% except for NN @ 1000-12. Subsequently, BET equivalent particle diameters (d_{BET}) were calculated by the relationship

$$d_{\rm BET} = \frac{6}{\rm SSA \times \rho}$$

where ρ is the theoretical density of NaNbO₃, for which the



Figure 6. Annealing temperature dependence of (a) specific surface area (SSA: \triangle , 1 h treatment; \blacktriangle , 12 h treatment) and BET equivalent particle diameters (d_{BET} : \bigcirc , 1 h treatment; \blacklozenge , 12 h treatment) and (b) particle sizes determined by the line intercept method averaged for about 100 particles, which were randomly selected (d_{SEM} : \bigcirc , 1 h treatment; \blacklozenge , 12 h treatment). The vertical bars in the graphs (a) and (b) indicate the errors evaluated from linear regressions for the BET results and the standard deviations obtained from the quantitative evaluation of SEM images, respectively.

theoretical value for single crystals (4.575 g/cm³)⁹ was used, since the changes of density evaluated from the representative XRPD refinements and the corresponding deviations of d_{BET} were less than 0.3%. Figure 6 shows the resulting dependence of SSA, d_{BET} , and d_{SEM} on the annealing temperatures, where d_{SEM} is the average particle size determined through SEM analysis. It could be concluded from the BET results and direct SEM observations that particles in the powders annealed at temperatures below 500 °C are smaller than 200 nm in d_{BET} and 100 nm in d_{SEM} , respectively, and that particles coarsen to a size of >1.2 μ m in $d_{\rm BET}$ ($d_{\rm SEM} \approx 1 \ \mu$ m) by an annealing treatment at 1000 °C. The values of d_{BET} include the effect of loose agglomeration of particles, and the d_{SEM} values represent the intrinsic particle sizes. Figure 6a indicates that agglomeration of particles starts during removal of surfactant at 400 °C and agglomeration is promoted at 600 °C. In the following part of this report, we basically use d_{SEM} values to indicate particle sizes.

3.3. Size-Induced Phase Transformation. 3.3.1. X-ray Powder Diffraction. On annealing raw powders above 400 °C for 12 h, several structural changes have been observed (see Figure 2). The lattice constants could be refined by applying an orthorhombic symmetry for all samples. The evolution of the primitive volume V/Z (V and Z are the volume of the lattice and the number of formula per unit cell, respectively) and the dimension of a perovskite formula are plotted as a function of the annealing temperature, i.e., particle size (see Figure 7). Two discontinuities separating three different temperature ranges, and thus particle size regions, can be distinguished.

The lattice parameters refined for NN @ 1000-12 were close to those refined for bulk material.²¹ The structure is described



Figure 7. Annealing temperature dependence of (a) the reduced perovskite cell volume and (b) the lattice parameters obtained for the powders annealed for 12 h. The average d_{SEM} values are indicated in parentheses in graph (a).

as *Pbcm* $(D_{2h}^{11}$, no. 57) space group with a = 5.5071(1) Å, b = 5.5698(1) Å, and c = 15.5245(4) Å (hereafter referred to as O_1 structure).

For intermediate annealing temperatures 700 °C < T < 900°C, the *hkl* reflections with odd *l* values, indexed in the O_1 symmetry, vanish. This indicates that the unit cell now only contains two instead of four octahedral units along the c axis. NaNbO₃ exhibits a new structure (hereafter referred to as O_2 structure) with $Pmc2_1$ space group ($C_{2\nu}^2$, no. 26) and lattice constants corresponding to a = 7.7673(3) Å, b = 5.5150(2) Å, and c = 5.5651(2) Å (determined for NN @ 800-12). In comparison with the O_1 structure, the primitive volume is expanded by up to 0.2%, while particle size is reduced from 1.1 μ m to 580 nm through the O_1 to O_2 transition (NN @ 1000- $12 \rightarrow NN @ 900-12$). Such a behavior is not expected, since a reduction of the particle size should induce an increase of the internal pressure resulting from an increase of surface curvature, which should lead to a reduction of the unit cell volume or a transformation to a more symmetrical structure.¹³ On the other hand, the effect of reduced cell volume with decreasing particle size is clearly observed for the O₂ structures: NN @ 900-12 $(580 \text{ nm}) \rightarrow \text{NN} @ 700-12 (180 \text{ nm}).$

For lower temperatures 400 °C < T < 500 °C, a third polymorph, the O_3 structure, was described in the *Pmma* space group (D_{2h}^5 , no. 51) with unit cell constants differing from the ones of the O₂ structure (a = 5.5211(7) Å, b = 7.7951(6) Å, and c = 5.5235(5) Å). The symmetry increased and the lattice volume shrunk compared to O_2 , which could be attributed to the increase of the internal pressure in the particles. The three perovskite formula parameters become closer for the O_3 structure, which can be considered as a pseudocubic structure. Nevertheless, the primitive volume of the O_3 structure, again, interestingly expands in the case of smaller particles annealed at temperatures below 600 °C down to 400 °C.

Moreover, one should note that, for the NN @ 600-12 sample, the refinement of the XRPD pattern was performed by considering a mixture of two phases. Both O_2 and O_3 structures

 TABLE 1: Results of the Rietveld Refinements and the Nuclear Site Group Analysis Performed for the NaNbO3 Coarse

 Powder (NN @ 1000-12), Intermediate Powder (NN @ 800-12), and Fine Powder (NN @ 500-12)

atom	х	у	z	biso (Å ²)	Wyck	site sym.	irreducible representations
NN @ 1000–12, O_1 , $Pbcm$ (D_{2h}^{-11} , no. 57)							
Nb	0.2429(4)	0.2627(4)	0.1252(5)	0.3(1)	8e	C_1	$3A_{g} + 3A_{u} + 3B_{1g} + 3B_{1u} + 3B_{2g} + 3B_{2u} + 3B_{3g} + 3B_{3u}$
Na1	0.262(2)	0.75	0	0.7(1)	4c	C_2^x	$A_{\rm g} + A_{\rm u} + 2B_{1\rm g} + 2B_{1\rm u} + 2B_{2\rm g} + 2B_{2\rm u} + B_{3\rm g} + B_{3\rm u}$
Na2	0.258(3)	0.777(2)	0.25	0.7(1)	4d	$C_{\rm s}^{xy}$	$2A_{\rm g} + A_{\rm u} + 2B_{1\rm g} + B_{1\rm u} + B_{2\rm g} + 2B_{2\rm u} + B_{3\rm g} + 2B_{3\rm u}$
01	0.301(3)	0.25	0	0.3(1)	4c	C_2^x	$A_{\rm g} + A_{\rm u} + 2B_{1\rm g} + 2B_{1\rm u} + 2B_{2\rm g} + 2B_{2\rm u} + B_{3\rm g} + B_{3\rm u}$
O2	0.174(4)	0.242(4)	0.25	0.3(1)	4d	$C_{\rm s}^{xy}$	$2A_{g} + A_{u} + 2B_{1g} + B_{1u} + B_{2g} + 2B_{2u} + B_{3g} + 2B_{3u}$
03	0.516(2)	0.019(4)	0.140(1)	0.3(1)	8e	C_1	$3A_{\rm g} + 3A_{\rm u} + 3B_{\rm 1g} + 3B_{\rm 1u} + 3B_{\rm 2g} + 3B_{\rm 2u} + 3B_{\rm 3g} + 3B_{\rm 3u}$
O4	0.967(2)	0.466(3)	0.113(1)	0.3(1)	8e	C_1	$3A_{\rm g} + 3A_{\rm u} + 3B_{\rm 1g} + 3B_{\rm 1u} + 3B_{\rm 2g} + 3B_{\rm 2u} + 3B_{\rm 3g} + 3B_{\rm 3u}$
presence of an inversion center						Γ_{Total}	$15A_{g} + 13A_{u} + 17B_{1g} + 15B_{1u} + 15B_{2g} + 17B_{2u} + 13B_{3g} + 15B_{3u}$ B. + B. + B.
lattice	lattice constants (Å) reliability factors					T Acoustic	$15A_{2} + 13A_{3} + 17B_{12} + 14B_{13} + 15B_{22} + 16B_{23} + 13B_{22} + 14B_{23}$
a	5.5071(1)	$R_{\rm p} = 15.0$	$R_{\rm b} = 5.7$			Гтр	$14B_{10} + 16B_{20} + 14B_{30}$
b	5.5698(1)	$R_{\rm wn} = 18.6$	$R_{\rm f} = 9.5$			Γ _{silent}	$13A_{\rm p}$
с	15.5245(4)	$R_{\rm exp} = 14.0$				Γ_{Raman}	$15A_{\rm g} + 17B_{1\rm g} + 15B_{2\rm g} + 13B_{3\rm g}$
NN @ 800-12, O ₂ , F					$D_2, Pmc2_1$ (C	$C_{2\nu}^{2}$, no. 26)	
Nb	0.751(1)	0.7541(9)	0.779(3)	0.5(1)	4c	C_1	$3A_1 + 3A_2 + 3B_1 + 3B_2$
Na1	0	0.257(4)	0.75	1.2(1)	2a	C_s^{yz}	$2A_1 + A_2 + B_1 + 2B_2$
Na2	0.5	0.263(4)	0.777(4)	1.2(1)	2b	C_s^{yz}	$2A_1 + A_2 + B_1 + 2B_2$
01	0	0.191(7)	0.317(5)	0.8(1)	2a	C_s^{yz}	$2A_1 + A_2 + B_1 + 2B_2$
O2	0.5	0.317(6)	0.315(5)	0.8(1)	2b	C_s^{yz}	$2A_1 + A_2 + B_1 + 2B_2$
03	0.221(4)	0.508(3)	0.082(4)	0.8(1)	4c	C_1	$3A_1 + 3A_2 + 3B_1 + 3B_2$
O4	0.271(4)	0.942(3)	0.513(5)	0.8(1)	4c	C_1	$3A_1 + 3A_2 + 3B_1 + 3B_2$
absence of an inversion center						Γ_{Total}	$17A_1 + 13A_2 + 13B_1 + 17B_2$
0						Γ_{Acoustic}	$A_1 + B_1 + B_2$
lattice	constants (A)	reliability	y factors			Γ_{Optical}	$16A_1 + 13A_2 + 12B_1 + 16B_2$
а	7.7673(3)	$R_{\rm p} = 14.7$	$R_{\rm b} = 4.7$			Γ_{IR}	$16A_1 + 12B_1 + 16B_2$
b	5.5150(2)	$R_{\rm wp} = 17.8$	$R_{\rm f} = 7.4$			Γ_{Raman}	$16A_1 + 13A_2 + 12B_1 + 16B_2$
С	5.5651(2)	$R_{\rm exp} = 14.4$					
	NN @ 500-12, O					D ₃ , Pmma (L	D_{2h}^{5} , no. 51)
Nb	0.75	0.750(2)	0.7511(2)	0.3(1)	4k	C_{s}^{yz}	$2A_{g} + A_{u} + B_{1g} + 2B_{1u} + B_{2g} + 2B_{2u} + 2B_{3g} + B_{3u}$
Na1	0.75	0	0.254(4)	1.4(1)	2e	C_{2v}^{z}	$A_{\rm g} + B_{1\rm u} + B_{2\rm g} + B_{2\rm u} + B_{3\rm g} + B_{3\rm u}$
Na2	0.75	0.5	0.261(3)	1.4(1)	2f	C_{2v}^{z}	$A_{\rm g} + B_{1\rm u} + B_{2\rm g} + B_{2\rm u} + B_{3\rm g} + B_{3\rm u}$
01	0.25	0	0.153(6)	0.7(1)	2e	C_{2v}^{z}	$A_{\rm g} + B_{1\rm u} + B_{2\rm g} + B_{2\rm u} + B_{3\rm g} + B_{3\rm u}$
02	0.25	0.5	0.178(5)	0.7(1)	2f	$C_{2v}{}^z$	$A_{\rm g} + B_{1\rm u} + B_{2\rm g} + B_{2\rm u} + B_{3\rm g} + B_{3\rm u}$
03	0	0.209(2)	0.5	0.7(1)	4h	C_2^y	$A_{\rm g} + A_{\rm u} + 2B_{1\rm g} + 2B_{1\rm u} + B_{2\rm g} + B_{2\rm u} + 2B_{3\rm g} + 2B_{3\rm u}$
O4	0.5	0.280(2)	0	0.7(1)	4g	C_2^y	$A_{\rm g} + A_{\rm u} + 2B_{1\rm g} + 2B_{1\rm u} + B_{2\rm g} + B_{2\rm u} + 2B_{3\rm g} + 2B_{3\rm u}$
presence of an inversion center						Γ_{Total}	$8A_{\rm g} + 3A_{\rm u} + 5B_{1\rm g} + 10B_{1\rm u} + 7B_{2\rm g} + 8B_{2\rm u} + 10B_{3\rm g} + 9B_{3\rm u}$
						$\Gamma_{Acoustic}$	$B_{1u} + B_{2u} + B_{3u}$
lattice	constants (A)	reliability	y factors			I Optical	$8A_g + 3A_u + 5B_{1g} + 9B_{1u} + 7B_{2g} + 7B_{2u} + 10B_{3g} + 8B_{3u}$
a	5.5211(7)	$\kappa_{\rm p} = 13.4$	$K_{\rm b} = 4.9$				$9B_{1u} + /B_{2u} + 8B_{3u}$
b	7.7951(6)	$K_{\rm wp} = 17.9$	$K_{\rm f} = 5.9$			I Silent	$3A_{\rm u}$
С	5.5235(5)	$R_{\rm exp} = 13.7$				I Raman	$8A_{\rm g} + 5B_{1\rm g} + 7B_{2\rm g} + 10B_{3\rm g}$

are present, which indicates that the particle size within this powder is not homogeneous.

Table 1 represents the data obtained from the Rietveld refinement of NN @ 1000–12, NN @ 800–12, and NN @ 500–12 structures as typical representatives of the O_1 , O_2 , and O_3 structures, respectively. No drastic changes have been observed in the bond lengths. The average Na–O (1.79(2) nm) interatomic distance is close to the value in the literature, while the length of the octahedral Nb–O edges (1.98(2) nm) is compressed by about 3%.²⁸

Sketches of all these structures O_1 , O_2 , and O_3 are shown in Figure 8 with the three particle size ranges identified for the powders annealed for 12 h from the results of XRPD and Raman spectroscopy, which will be discussed in section 3.3.2. The phase transitions, on particle size reduction, occur largely on the modification of the octahedral framework. Major differences in these structures can be recognized along the stacking axis (defined as the axis perpendicular to the equatorial plane of the octahedrons (i.e., c, a, and b axes for the O_1 , O_2 , and O_3 structures, respectively). The zigzag chains of octahedra, running along the apical direction, are unchanged through both phase transitions ($O_1 \rightarrow O_2$ and $O_2 \rightarrow O_3$). According to the space group and the lattice constants, the O_1 structure can be seen as a stacking of two different kinds of crystallographic layers. Although they are built from identical NbO₆ octahedrons, the difference arises from a different rotation angle between two following layers. Even if the level of distortion of the equatorial plane of the octahedron is higher within the O_2 structure compared to O_1 , one can consider that the O_2 structure distortion is lower. The different orientations between neighboring layers are no longer present in the O_2 structure symmetry. The symmetry of NaNbO₃ at a particle size below 70 nm (O_3 structure) is closer to the ideal cubic perovskite structure: the rotation between octahedrons within one crystallographic layer vanished, resulting in a more cubic like structure.

3.3.2. Raman Spectroscopy. Figure 9 shows the Raman spectra and their fit traces obtained for NN @ 1000-12, NN @ 800-12, and NN @ 500-12. The Raman scattering pattern measured for the highly coarsened powder (NN @ 1000-12) could be modeled by a combination of 36 Lorentzian functions (see Figure 9a). The spectrum profiles and the positions of the bands for the main components indicated excellent agreement with the assignments reported for pure bulk materials.^{15-17,22} Two strong bands at 61.0 and 74.5 cm⁻¹ can be assigned to the Na⁺ translational modes against the NbO₆ octahedrons. The bands at 92.2, 120.3, 123.5, 142.8, and 154.0 cm⁻¹ are assigned

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Figure 8. Illustrations of the differences between (a) NN @ 1000–12, (b) NN @ 800–12, and (c) NN @ 500–12 structures. Particle size ranges obtained from XRPD and Raman spectroscopy are also indicated.



Figure 9. Fit traces of the Raman spectra obtained for (a) NN @ 1000-12, (b) NN @ 800-12, and (c) NN @ 500-12. The average d_{SEM} values are indicated in parentheses.

to the librational modes of the NbO₆ octahedra. All bands above 160 up to 900 cm⁻¹ are generated by the internal vibrations of the NbO₆ octahedra. Strictly speaking, the ν_1 to ν_6 modes are defined for the equilateral shape approximation of the free NbO₆ octahedron; however, we apply these descriptions following the literature for the NbO₆ octahedron in the perovskite lattice

structures.^{15,16,22} Triply degenerated $\nu_6 (F_{2u})$ and $\nu_5 (F_{2g})$ modes showed a splitting of the scattered intensities composed by a complicated band profile in the region from 170 to 300 cm⁻¹. Weak $\nu_4 (F_{1u})$ bands appeared at 377.3 and 433.1 cm⁻¹. The ν_2 (E_g) , $\nu_1 (A_{1g})$, and $\nu_3 (F_{1u})$ modes form the second most intense band region. The $\nu_2 (E_g)$ and $\nu_1 (A_{1g})$ bands were fitted by two Lorentzian functions at 556.4, 569.4, and 599.4, 613.3 cm⁻¹, respectively, since their band shapes are asymmetric. The ν_3 (F_{1u}) mode appeared as a shoulder at 670.3 cm⁻¹ with a symmetric peak profile. The final weak band at 870.6 cm⁻¹ is assigned to the $\nu_1 + \nu_5$ combination mode, which has F_{2g} as an irreducible representation.

The Raman spectrum for NN @ 800-12 was fitted by 31 functions (see Figure 9b). A remarkable difference with respect to the spectrum for NN @ 1000-12 was observed in the external vibrational modes below 165 cm⁻¹. The Raman spectrum registered for NN @ 500-12 (see Figure 9c) could be fitted by only 22 Lorentzian functions compared to the spectra for NN @ 1000-12 and NN @ 800-12. This indicates that the crystal symmetry was drastically modified by the annealing temperature, i.e., particle size. The evolution of Raman spectra with the annealing temperature is represented in Figure 10.

Figure 11 shows that the wavenumbers and the full widths at half-maximum (fwhm) of specific librational and internal (v_5 and v_3) modes of the NbO₆ octahedra change with annealing temperature, d_{BET} and d_{SEM} , respectively. The wavenumber and fwhm values are influenced by surrounding lattice defects, Coulomb interactions, and vibrational relaxation.^{22,29} The annealing temperature characteristics of the wavenumbers and the fwhm values were shifted toward lower temperatures by longer annealing time (see upper graphs in Figure 11). This indicates that the annealing time promotes the transformations of the vibrational motions. On the other hand, it seems, according to the plots of the wavenumber and fwhm versus d_{BFT} (see middle graphs in Figure 11), that a shorter annealing time promotes the vibrational transformation. In the cases of the d_{SEM} -wavenumber and -fwhm plots, both curves obtained for the shorter and longer annealing times superimposed each other (see lower graphs in Figure 11). Therefore, a correlation between particle size of the powders and lattice dynamics such as NbO₆ tilting and internal vibrations is believed to exist. The corresponding bands were located at around 136, 275, and 652 cm⁻¹ up to 100 nm in d_{SEM} (see lower graphs in Figure 11) and abruptly shifted toward higher wavenumber above this particle size. Figure 12 shows the plots of the wavenumbers versus averaged d_{SEM} values for all the respective phonons. In the region below 160 cm⁻¹, which includes the Na⁺ translational modes and the NbO₆ librational modes, several bands, which have been observed for the well-coarsened powders, disappeared below $d_{\text{SEM}} = 500$ nm. The remaining three Na⁺ translational modes finally converged to only one band below $d_{\text{SEM}} = 70$ nm. Below 70 nm, one of the NbO₆ librational modes at 154 cm⁻¹ disappeared, a final convergence of the v_5 and v_6 bands could be confirmed, one of the v_4 modes completely disappeared, and the splitting of the ν_1 mode converged. Consequently, it can be concluded from our Raman spectroscopic results that there are three different types of structures for coarse ($d_{\text{SEM}} > 600$ nm: O_1), intermediate (200 nm < d_{SEM} < 400 nm: O_2), and fine powders ($d_{\text{SEM}} < 70 \text{ nm}$: O_3). These size ranges obtained from Raman spectroscopy are indicated in Figure 8.

The results of nuclear site group analysis³⁰ for the O_1 , O_2 , and O_3 structures are also shown in Table 1. The analysis for O_1 with a *Pbcm* structure gave 60 Raman active and 44 IR active normal modes, which are mutually excluded. This large number



Figure 10. Evolution of the Raman spectra by annealing temperature for (a) 1 h and (b) 12 h treatments. The average d_{SEM} values are indicated in parentheses.



Figure 11. Annealing temperature, d_{BET} , and d_{SEM} dependence of the wavenumbers (O, 1 h treatment; \bullet , 12 h treatment) and the full widths at half-maximum (fwhm: \triangle , 1 h treatment; \blacktriangle , 12 h treatment) plotted for (a) the NbO₆ librational and (b) v_5 and (c) v_3 bands. The horizontal bars in the graphs (b) and (c) indicate the errors estimated from linear regressions for the BET plots and the standard deviations of the particle sizes, respectively.

of Raman modes expected from the theoretical point of view is a cause of the complicated scattering profile (see Figure 9a). Highly coarsened powders showed sharp splittings (61 and 74 cm^{-1}) of the Na⁺ translational mode (see Figure 10). This reflects 2 major contributions among the different interactions between Na^+ and NbO_6^- ions in the *Pbcm* structure. With decreasing annealing temperature, i.e., particle size, these split bands shifted to higher wavenumbers, and their separation



Figure 12. d_{SEM} dependence of the wavenumbers plotted for all observed vibrational modes.

became smaller. This behavior is quite similar to that observed for Li-doped compositions, as reported for $\text{Li}_x \text{Na}_{1-x} \text{NbO}_3$ studied by Raman spectroscopy.³¹

The assigned symmetry $Pmc2_1$ for the O_2 structure is not centrosymmetric, and therefore, the Raman-IR mutual exclusion is absent (see Table 1). For this structure, 57 Raman active and 44 IR active normal modes can be derived. If molecular dipole-electrostatic field interactions are taken into consideration for the IR active motions, 101 Raman bands are estimated to exist for the $Pmc2_1$ structure due to the LO–TO splittings. In the present case, only 31 functions instead of the theoretical number of 57 or 101 bands were necessary in order to model the Raman spectra for the intermediate powders due to overlapping of many bands, which could not be resolved in the complicated scattering profile. In fact, although the $Pc2_1b$ (C_{2 ν}⁵, no. 29) structure of Li_{0.02}Na_{0.98}NbO₃ induces LO-TO splitting, no remarkable band broadening or splitting have been registered.³¹ Therefore, long-range static forces are assumed to be weak in the NaNbO3-based materials.³² The spectra obtained for NN @ 950-1 downward to NN @ 750-1 and NN @ 900-12 downward to NN @ 700-12, which have submicron particle sizes (approximately 600-200 nm), indicated a similar evolution of Raman spectra compared to the case of the Licontent dependency ($x \le 0.3$) of the scattering profiles for $Li_xNa_{1-x}NbO_3$.³¹

Finally, for the O_3 structure, the splitting of the Na⁺ translational band could not be resolved by the curve analysis, and consequently, only one broad band at 61 cm⁻¹ was observed. This could be caused by a higher crystallographic symmetry and almost only one type of Na⁺–NbO₆⁻ ionic interaction in the fine particles. This consideration is consistent with the pseudocubic structure for the O_3 structure (see Figure 7b). The O_3 structure assigned to the fine powders is centrosymmetric with 30 Raman active and 24 IR active normal modes (see Table 1). This lower number of normal modes yields more simple scattering profiles in comparison with the O_2 and O_3 structures.

3.3.3. Hypothetical Mechanisms. The enhancement of the internal pressure within fine particles, known as Gibbs-Thomson effect, is the most extensively assumed mechanism for the stabilization of more symmetric structures than the thermodynamically stable ones at ambient temperature and pressure (accompanied with shrinkage of the lattice).13,23,24 However, (K_{0.5}, Na_{0.5})NbO₃ presents a different behavior. This compound undergoes a phase transformation from a monoclinic symmetry (*M*-type) to a triclinic one (*T*-type) accompanied by an expansion of the lattice below a critical d_{BET} value of 200 nm.¹⁰ According to the atomic positions, the unique Na/K position of the *M*-type structure is discriminated into two different ones in the T-type structure, allowing an ordering of the A-site cations. Such an ordering within Na/K distribution could occur resulting from possible chemical gradients arising during the preparation, which could remain in the particle of the raw powder. The low diffusion rate of Na or K ions due to low annealing temperature impedes further homogenization. For NaNbO₃ containing only one alkali metal on the A-site of the perovskite structure, such a phenomenon is not possible. The distortion related to the rotation of octahedra on different crystallographic layers is reduced through both phase transitions with decreasing particle size, i.e., increasing internal pressure. The expansion observed for the lattice as the particle size is reduced is not in agreement with the Gibbs-Thomson effect and not yet elucidated.

4. Conclusions

A phase transformation induced by reduced particle size was investigated for NaNbO₃ powders prepared through microemulsion-mediated synthesis and subsequent annealing treatment. X-ray diffraction and Raman spectroscopy demonstrated that the orthorhombic *Pbcm* structure (O_1) of coarsened powders in micron order transforms via the orthorhombic *Pmc*2₁ structure (O_2) to the *Pmma* symmetry (O_3) with decreasing particle size in submicron (200–400 nm) and nano (<70 nm) orders, respectively. The $O_1 \rightarrow O_2$ transition causes the disappearance of the inversion center of the unit cell. The distortion of the structure is lowered as the particle size is reduced according to Gibbs—Thompson effect. Nevertheless, the complex lattice volume evolution of NaNbO₃ has not been elucidated yet.

The comparison between NaNbO₃ and (K_{0.5}, Na_{0.5})NbO₃ behavior versus particle size lowering indicates that the transition from monoclinic to triclinic symmetry for (K_{0.5}, Na_{0.5})NbO₃ could originate from the ordering of K and Na cations in the structure.

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