Chem. Mater. **2006,** *18,* 4227−4230

Articles

Synthesis of $MNbO_3$ Nanoparticles (M = Li, Na, K)

Sebastian Wohlrab,[†] Margarita Weiss,[‡] Hongchu Du,[†] and Stefan Kaskel*,[†]

Department of Inorganic Chemistry, Technical University Dresden, Mommsenstr. 6,
D-01069 Dresden, Germany, and Triebenberg Laboratory, Institute of Structure Physics, Technical
University Dresden, Zum Triebenberg 50, D-01328 Dresden - Zaschendorf, Germany

Received February 14, 2006. Revised Manuscript Received July 12, 2006

The alkali niobates $MNbO_3$ (M = Li, Na, K) were synthesized using a matrix-mediated synthesis strategy. Integration of the metal ions inside (a) a sugar−PVA (D-sucrose/polyvinylalkohol) matrix, (b) activated carbon, and (c) mesoporous cross-linked polystyrene is used for the space-confined formation and crystallization of the compounds. Calcination of the amorphous precursors causes crystallization of the niobates and disintegration of the matrix. The resulting nanopowders were investigated using wide-angle X-ray diffraction (WAXS), and pure phases were detected using the different matrixes. Scanning electron microscopy (SEM) reveals the uniform size and morphology of the particles. According to nitrogen physisorption isotherms of the powders, specific surface areas up to 188 $m^2\ g^{-1}$ can be obtained. The applicability of the three different methods is discussed.

Introduction

The synthesis of inorganic nanoparticles has attracted considerable attention in recent years. Materials with reduced domain size are of interest in ceramics for structural applications,[1] and new insights into material properties in the nanodimension are of fundamental interest.[2,3] Thus, size effects of materials with characteristic functional behavior such as magnetic,[4,5] electric,[6] or optical properties[7] are addressed. Here, we report the application of three matrix-mediated synthesis strategies for the preparation of the alkali niobates $LiNbO_3$, $NaNbO_3$, and $KNbO_3$. They are of interest due to their ferroelectric and piezoelectric properties.[8,9]

Several methods for the preparation of alkali niobates are known, but mainly with the focus on highly crystalline products, whereas the particle size is seldom addressed. Hydrothermal methods,[10,11] a glycothermal technique,[12] synthesis from metal alkoxides,[13,14] sol−gel processes,[15,16] and the use of polymeric precursors (the Pechini method)[17] have been described. A sol-gel method based on bimetallic alkoxide precursors was developed to produce $LiNbO_3$ below 10 nm in diameter.[18] Furthermore, a solvothermal method was found to produce nanoscale perowskite structures as a general soft-chemistry route.[19]

Recently, routes for the synthesis of complex oxides were reported. Nanoscale oxides were obtained by thermolysis of inorganic−organic precursors, and the particle size is adjusted with the use of different precursor types. The sugar−PVA matrix method[20] and the activated carbon route[21] have not yet been reported for alkali niobates. Here, both methods were applied to $MNbO_3$ (M = Li, Na, K) compounds for the first time. For the sugar−PVA matrix method, alkali nitrates and a water-soluble niobium complex were mixed with D-sucrose and poly(vinyl alcohol) (PVA) (Scheme 1, a). Infiltration of a metal salt solution into activated carbon also gives a precursor (Scheme 1, b). After calcination, phase pure oxide particles a few nanometers in diameter were

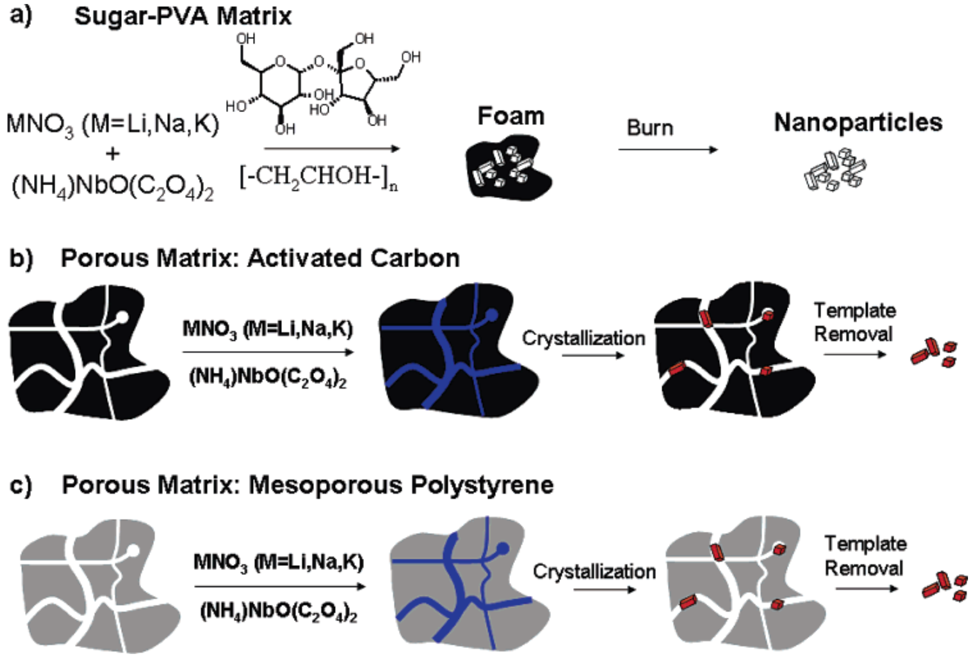
---

* To whom correspondence should be addressed. E-mail: stefan.kaskel@chemie.tu-dresden.de. Fax: 49 351 4633 7287. Tel.: 49 351 4633 4885.
[†] Department of Inorganic Chemistry.
[‡] Triebenberg Laboratory, Institute of Structure Physics.

(1) Cahn, R. W.; Haasen, P.; Cramer, E. J. *Materials Science and Technology, Vol. 11, Structure and Properties of Ceramics*; Wiley-VCH: Weinheim, 1998.
(2) Fendler, J. H. *Nanoparticles and Nanostructured Films*; Wiley-VCH: Weinheim, 2002.
(3) Schmid, G. *Nanoparticles*; Wiley-VCH: Weinheim, 2003.
(4) Drofenik, M.; Lisjak, D.; Makovec, D. *Mater. Sci. Forum* **2005**, *494*, 129.
(5) Lockwood, J. D. *Nanostructure Science and Technology, Surface Effects in Magnetic Nanoparticles*; Springer: New York, 2005.
(6) Rüdiger, A.; Schneller, T.; Roelofs, A.; Tiedke, S.; Schmitz, T.; Waser, R. *Appl. Phys. A* **2005**, *80*, 1247.
(7) Noguez, C. *Opt. Mater.* **2005**, *27*, 1204.
(8) Landolt, H.; Börnstein, R. *Numerical data and functional relationships in science and technology − Ferroelectrics and Related Substances, Volume 36*; Springer: Berlin, 2001.
(9) Jaffe, B.; Cook, W. R.; Jaffe, H. *Piezoelectric Ceramics*; Techbooks: Marietta, 1990.
(10) Goh, G. K. L.; Lange, F. F.; Haile, S. M.; Levi, C. G. *J. Mater. Res.* **2003**, *18*, 338.
(11) Lu, C. H.; Lo, S. Y.; Lin, H. C. *Mater. Lett.* **1998**, *34*, 172.
(12) Lu, C. H.; Lo, S. Y.; Wang, Y. L. *Mater. Lett.* **2002**, *55*, 121.
(13) Hirano, S. I.; Kato, K. *Adv. Ceram. Mater.* **1987**, *2*, 142.
(14) Amimi, M. M.; Sacks, M. D. *J. Am. Ceram. Soc.* **1991**, *74*, 53.
(15) Nazeri-Eshghi, A.; Kuang, A. X.; Mackenzie,J. D. *J. Mater. Sci*. **1990**, *25*, 3333.
(16) Nazeri, A.; Kahn, M. *J. Am. Ceram. Soc.* **1992**, *75*, 2125.
(17) Pribosic, I.; Makovec, D.; Drofenik, M. *Chem. Mater.* **2005**, *17*, 2953.
(18) Pooley, M. J.; Chadwick, A. V. *Radiat. Eff. Defects Solids* **2003**, *158*, 197.
(19) Niederberger, M.; Pinna, N.; Polleux, J.; Antonietti, M. *Angew. Chem.* **2004**, *116*, 2320,

10.1021/cm060367o CCC: $33.50

Scheme 1. Illustration of the Synthesis Methods Used for the Preparation of Nanoscale Niobates



obtained. Additionally, for a new method to generate nanoparticles, a porous cross-linked polystyrene was used as a matrix to generate a precursor for subsequent alkali niobate nanoparticle synthesis (Scheme 1, c).

Experimental Section

The inorganic salts $LiNO_3$, $NaNO_3$, and KNO_3 were purchased from Gruessing (purity >99%). Polyvinylalkohol (purity >98%, Merck, M_r =120000 g/mol), ammonium niobate oxalate ($(NH_4)NbO(C_2O_4)_2 \cdot xH_2O$ **ANO,** 99.99%, Aldrich), ethanol (>96%, Fluka), and D-sucrose (>98%, Fluka) were used without further purification. The activated carbon "Norit A" (NORIT Germany GmbH, S_g = 895 m^2 g^{-1}) was dried under vacuum for 2 h at 130 °C. The mesoporous cross-linked polystyrene (Purolite MN200MR/4627, S_g = 800 m^2 g^{-1}) was dried under vacuum at room temperature overnight.

Sugar−PVA Method. The alkali nitrates were mixed with ammonium niobate oxalate in a 1:1 molar ratio. After dissolution of 1 g of the mixture in 20 mL of bidistilled water, a mixture of PVA and D-sucrose in a mass ratio of 1:10 was added. For LN1, NN1, and KN1, 32 g of this mixture was used. After the mixture was heated to 90 °C for 1 h, all solid material was dissolved. The resulting solution was heated until the water amount was 20% of the starting value. From this highly viscous mixture, the precursors were produced by heating for 30 min at 220 °C in an oven. After calcination at 530 °C, white powders were obtained (yield: 100%).

Activated Carbon Method. The alkali nitrates were mixed with ammonium niobate oxalate in a 1:1 molar ratio. After dissolution of 1 g of the mixture in 5 mL of bidistilled water, 20 g of Norit A was added. The resulting precursor was dried at 120 °C overnight. Calcination of the dried product at 600 °C yielded in quantitative amounts the white products.

Crystallization Using Mesoporous Cross-linked Polystyrene. The alkali nitrates were mixed with ammonium niobate oxalate in a 1:1 molar ratio. After dissolution of 1 g of the mixture in 0.5 mL of a mixture of bidistilled water and ethanol (5:1), 0.5 g of the mesoporous cross-linked polystyrene was added. The resulting precursor was dried at 120 °C overnight. Calcination of the dried product at 580 °C yielded in quantitative amounts the white products.

Characterization. Powder X-ray diffraction patterns were recorded in transmission geometry using a STOE Stadi-P diffractometer and Cu Kα_1 radiation (wavelength, $\lambda = 0.15405$ nm). The average crystallite size was calculated from the Scherrer equation (STOE Size/Strain analysis[20]). TG measurements were performed on a Netzsch STA409 system with a coupled mass spectrometer. The morphologies of the products were observed on a Zeiss DMS 982 Gemini field emission scanning electron microscope (SEM). The samples were sputtered with Pd and measured at 2 kV. Nitrogen physisorption measurements were performed on a Quantachrome Autosorb 1C. Prior to the measurements, the samples were evacuated at 150 °C for 5 h. The specific surface areas were calculated from the Brunauer−Emmet−Teller (BET) equation (P/P_0 = 0.1−0.3).

Results and Discussion

The synthesis of complex nanocrystalline oxides is difficult because the reaction temperature required for the formation of the complex oxide and the crystallization is often above 600 °C, a treatment that, especially for high surface area materials, causes rapid sintering and densification of the particles, and thus small particles are only obtained in a highly aggregated form not suitable for further processing in solution. However, if the formation and crystallization is carried out inside a matrix (exo-templating[21]) remaining stable during the formation of oxidic compounds, agglomeration can be avoided and ideally separated nanoparticles can be obtained.[20,21] The application of the matrixes (a) sugar−PVA and (b) activated carbon to alkali niobates could also result in a narrow particle size distribution of the formed nanocrystals, due to the confinement inside the porous system. However, pores of the matrixes used in this work are predominately in the range below 2 nm, whereas the

---

(20) Panda, A. B.; Tarafdar, A.; Sen, S.; Pathak, A.; Pramanik, P.*J. Mater. Sci.* **2004**, *39*, 3739.

(21) Schwickardi, M.; Johann, T.; Schmidt, W.; Schüth, F. *Chem. Mater.* **2002**, *14*, 3913.

(22) STOE Size/Strain analysis (WinXPow) v.1.06, 1999.

Table 1. Synthesis Conditions and Properties of the Alkali Niobates Synthesized

sample	compound	matrix	synthesis temperature (°C)	phase purity[a]	d^b (nm)	$S_g{}^c$ (m^2/g)	$S_g{}^d$ (m^2/g)
LN1	$LiNbO_3$	sucrose/PVA	530	+	36	36	71
LN2	$LiNbO_3$	Norit A	600	0	54	24	10
LN3	$LiNbO_3$	mesoporous polystyrene	580	+	34	38	31
NN1	$NaNbO_3$	sucrose/PVA	530	+	68	18	44
NN2	$NaNbO_3$	Norit A	600	0	20	61	42
NN3	$NaNbO_3$	mesoporous polystyrene	580	0	29	42	132
KN1	$KNbO_3$	sucrose/PVA	530	+	31	42	188
KN2	$KNbO_3$	Norit A	600	−			
KN3	$KNbO_3$	mesoporous polystyrene	580	−			

[a] +, pure phase; 0, traces of impurities; −, other product. [b] Crystallite diameter from Scherrer equation. [c] Calculated from $S_g = 6/\rho d$. [d] Specific BET surface area after calcinations.

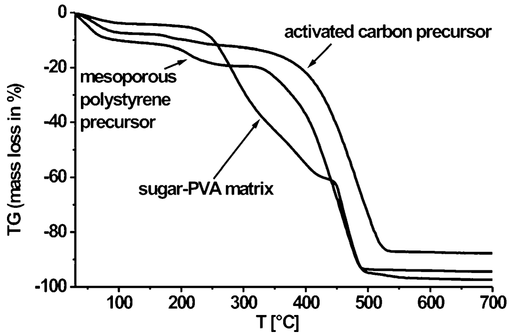


Figure 1. TG data from the calcination and decomposition of the different matrixes in the $LiNbO_3$ synthesis.

particles synthesized in this work are somewhat larger, since the matrix is removed in the course of the heat treatment (see below). To extend this matrix-mediated synthesis of nanoparticles at high temperatures, additionally, (c) a mesoporous cross-linked polystyrene ($S_g = 800$ m^2/g) was used to act as a matrix for the crystallization of the particles. These three matrixes were used to form the three alkali niobates: $LiNbO_3$, $NaNbO_3$, and $KNbO_3$, resulting in nine different precursors (Table 1).

These resulting products vary in composition, crystallinity, particle size, and specific surface area with respect to the synthesis conditions.

For example, to synthesize $LiNbO_3$ (LN1−LN3) three different precursors were prepared. For LN-1, a sugar−PVA matrix embedding the Li−Nb source was formed. Equimolar amounts of $LiNO_3$ and ammonium niobate oxalate (ANO) were dissolved in water and afterward D-sucrose and PVA were added. Evaporation and drying at 220 °C of the highly viscous solution give an amorphous fluffy precursor with a metallic black color (Scheme 1, a). To generate the precursors from activated carbon and the mesoporous cross-linked polystyrene, solutions of $LiNO_3$ and ammonium niobate oxalate were infiltrated in the porous materials (Scheme 1, b,c). Drying at 120 °C gave another two precursors for the synthesis of LN2 and LN3.

Thermogravimtric Analysis. The formation of the alkali niobate phases without using a matrix-assisted method typically occurs above 450 °C. With respect to the temperature needed for complex oxide formation, a critical point for the matrix-mediated particle synthesis is the combustion of the matrix. TG measurements were used to determine the weight loss associated with the matrix removal in order to achieve complete combustion without residual carbon impurities in the samples. The three precursors (LN1−LN3) were heated at a rate of 5 °C/min from 20 to 800 °C (Figure 1).

Both the sugar−PVA matrix and the mesoporous polystyrene precursor disintegrate to form $LiNbO_3$ at about 490 °C, whereas the activated carbon precursor (LN2) has a somewhat higher thermal stability and is oxidized at about 540 °C. However, the decomposition of the sugar−PVA matrix starts already at 250 °C due to the sugar decomposition. The following synthesis conditions were chosen on the basis of the TG data. A slightly higher temperature than those observed for template removal in TG/DTA measurements ensures quantitative yields. The temperatures used were 530 °C for the sugar−PVA matrix, 580 °C for the mesoporous polystyrene, and 600 °C for the activated carbon precursor.

X-ray Powder Diffraction. The resulting materials were characterized using wide-angle X-ray diffraction (Figure 2) to analyze the purity of the phases and calculate the particle sizes using the Scherrer equation.

In addition to the differences in the size of $LiNbO_3$ crystals obtained using different matrixes (LN1−3, Figure 2a), the products NN1−3 and KN1−3 were characterized (Figure 2b,c). For the $LiNbO_3$ and $NaNbO_3$ all three precursors give predominately the desired phase. However, for the activated

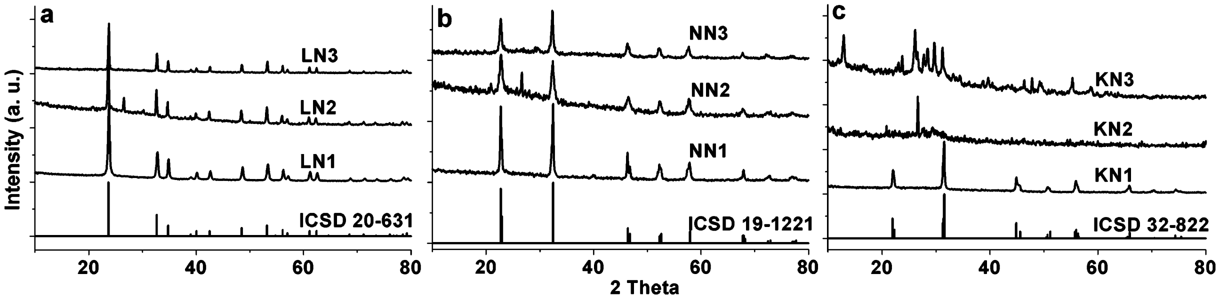


Figure 2. X-ray powder diffraction patterns of the niobate products resulting from the different synthesis strategies: (a) $LiNbO_3$; (b) $NaNbO_3$; (c) $KNbO_3$.

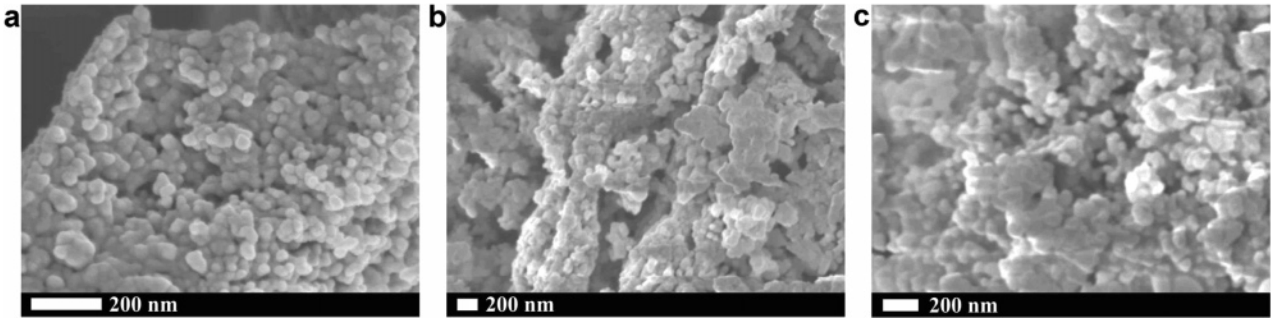


Figure 3. Scanning electron micrographs of $LiNbO_3$ obtained from (a) the sugar−PVA matrix (LN1), (b) activated carbon (LN2), and (c) the mesoporous cross-linked polystyrene (LN3).

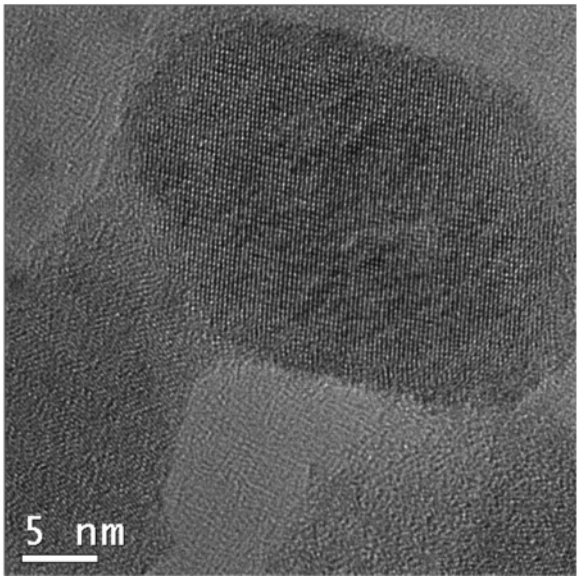


Figure 4. High-resolution electron micrograph of $LiNbO_3$ (LN1).

carbon precursor, an impurity at $2\Theta = 26.60°$ is detected, indicating graphite traces within the sample (ICSD 26-1076). $LiNbO_3$ crystallizes in the rhombohedral space group *R*3*c*. $NaNbO_3$ is orthorhombic (space group *Pbma*). The particle sizes estimated from the Scherrer equation vary between 20 and 68 nm. For $KNbO_3$, only the sugar−PVA matrix mediated method is suited to produce a pure product **(KN1)**. By this method $KNbO_3$ in the orthorhombic space group *Cm*2*m* is obtained.

Electron Microscopy. To characterize the size of the nanoparticles, high-resolution SEM images were taken. In Figure 3a−c the images for the three $LiNbO_3$ products (LN1−3) are shown.

For all methods one can see the granular shape of the particles, while the activated carbon precursor also produces platelike particles. The particle size estimated from the SEM images is in the same range as those calculated using the Scherrer equation. A high degree of crystallinity is also detected using high-resolution electron microscopy displaying particles from the product LN1 (Figure 4). The particles show some degree of connectivity in larger agglomerates. It is noteworthy that the particles of this sample always show rounded edges and no defined crystal faces.

BET Measurements. To determine the specific surface area of the powders, nitrogen physisorption measurements (3 point method) were carried out. The surface areas obtained from this method vary between 10 and 188 m^2/g (Table 1). The relatively high surface areas obtained for NN3 and KN1 may be attributed to amorphous carbon traces within the sample. For all the other samples, the surface area is more or less in agreement with the particle size determined from the Scherrer equation (Table 1).

Conclusion

Three matrix-mediated methods to produce nanoscopic alkali niobates $LiNbO_3$, $NaNbO_3$, and $KNbO_3$ were presented. TG measurements reveal different decomposition temperatures, the lowest being observed for the sugar−PVA matrix. The latter is suited to form pure phases for all three niobates, whereas for the porous carbon and the porous polymer impurities are observed especially for $KNbO_3$. The crystallite size of the products determined using the Scherrer equation is in a range of 20−68 nm and the specific surface area is between 10 and 188 m^2/g. Scanning electron micrographs of the samples confirm these results. Uniform spherical particles are obtained by the sugar−PVA matrix approach; this method seems quite promising also in the synthesis of other complex nanoscale oxides such as $CaBi_2Nb_2O_9$.

Acknowledgment. The generous support of the Federal Ministry of Education and Research (Young Scientist Nanotechnology Initiative, BMBF: FK 03X5502) is gratefully acknowledged.

CM060367O