

Water Soluble $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ as a New Molecular Precursor for Synthesis of Sodium Niobate

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A water-soluble tetraperoxo niobate $[\text{Nb}(\text{O}_2)_4]^{3-}$ was prepared by reaction of niobic acid with H_2O_2 at pH = 11 in aqueous ammonia solution. The corresponding ammonium salt, $(\text{NH}_4)_3[\text{Nb}(\text{O}_2)_4]$, was grown as a single crystal, and its crystal structure was solved. A white precipitate has been obtained from the solution containing $(\text{NH}_4)_3[\text{Nb}(\text{O}_2)_4]$ and Na_2CO_3 . Based on the elemental, TG, redox titration and Raman spectroscopic analyses, we have concluded that the obtained compound was $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$. This compound has been demonstrated to be a convenient precursor for synthesis of NaNbO_3 by simple calcinations in air at the reduced temperature of 400–500°C.

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1. Introduction

NaNbO_3 is known to form a solid solution with KNbO_3 , which has found important applications for nonvolatile memory devices, actuators and microsenors.^{1),2)} The conventional solid-state reaction method for synthesis of NaNbO_3 , which uses Nb_2O_5 and Na_2CO_3 as starting materials, often leads to poor compositional homogeneity of the ceramic powder as sodium components tend to volatilize at high temperature required for the synthesis. To overcome this difficulty inherent to the solid-state reaction method, several solution-based methods have been applied for synthesis of NaNbO_3 at lower temperatures, where the severe loss of sodium components can be avoided. These include (i) the amorphous complex method using either oxalate-niobium complex³⁾ or malate-niobium complex,⁴⁾ (ii) the polymerizable complex method⁵⁾ and (iii) the sol-gel method based mainly on the hydrolysis/condensation of metal alkoxides.⁶⁾ One of the serious drawbacks in these solution-based routes is connected with the fact that a huge amount of organic compounds are required sometimes reaching almost 80% of the total weight and making it difficult for the complete removal of residual carbon. In contrast, the aqueous peroxide-based route as well as the hydrothermal method⁷⁾ can overcome this specific problem of the above mentioned methods because of the total absence of organics throughout the process.

The aqueous peroxide-based method^{8)–11)} has been applied for synthesis of lead titanate, alkaline earth titanates, stannates, zirconates and hafnate. In particular, the method has become increasingly important after chloride-free peroxide based techniques have been developed by Camargo et al.,^{12)–15)} since possible degradation of electronic properties due to a small concentration of residual chloride¹⁶⁾ and generation of corrosive HCl gas during the processing can be avoided. To date, little attention has been paid to the potential of the aqueous peroxide-based route for synthesis of niobates. In this paper, the synthesis of sodium triperoxo niobium compound ($\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$) from a chloride-free aqueous solution is reported. $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ was used as a precursor for the low-temperature synthesis of pure crystalline NaNbO_3 without use of a dry and inert atmosphere usually needed for

alkoxide-based sol-gel synthesis of niobates.^{6),17)–20)}

2. Experimental

2.1 Synthesis, elemental analysis and single crystal XRD experiment

The flow chart for synthesis of our new precursor compound of $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ for conversion to NaNbO_3 is shown in Fig. 1. In a typical synthesis, 2 g (6.25 mmol) of $\text{Nb}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ powder (so-called one of forms of niobic acids) was dissolved in 40 cm³ of 30 mass% H_2O_2 and 5 cm³ of 28 mass% aqueous ammonia to obtain a clear colorless solution having a pH of 11. This solution is called “Solution A”, and it contains tetraperoxo niobium complex ($[\text{Nb}(\text{O}_2)_4]^{3-}$). Thereafter, Na_2CO_3 in the molar ratio of $[\text{Nb}] : [\text{Na}] = 1 : 1$, was added into the “Solution A”. Intensive effervescence was observed owing to decomposition of sodium carbonate. The

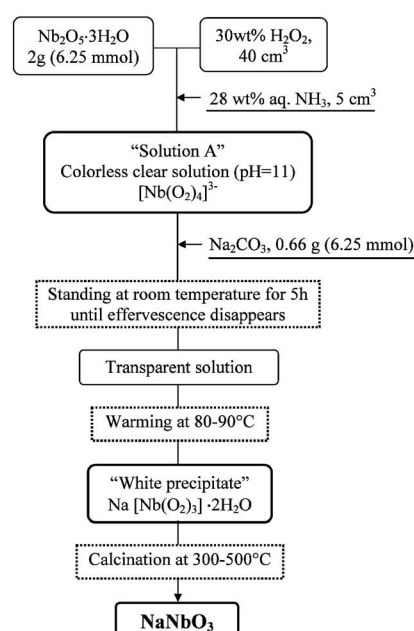


Fig. 1. Flow chart showing the synthesis of a new precursor of $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ for conversion to NaNbO_3 .

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Table 1. Details of Data Collection and Structure Refinement using $(\text{NH}_4)_3[\text{Nb}(\text{O}_2)_4]$ Single Crystal

Diffractometer	Rigaku AFC5
Radiation	MoK α , $\lambda=0.071073$ nm
Monochromator	graphite
Temperature	293 K
Formula	$\text{H}_{12}\text{O}_8\text{N}_3\text{Nb}$
Mol. wt	275.02
Crystal System	Tetragonal
Space Group	I-4 2 m (No. 121)
<i>a</i> /nm	0.7048(2)
<i>c</i> /nm	0.8574(2)
Volume/ nm ³	0.4259(2)
Z	2
ρ /g cm ⁻³	2.144
Crystal size/ mm ³	0.11 $\times$ 0.11 $\times$ 0.22
θ limit/ °	38.497
Reflections, parameters	1012 (403 unique), 19
R(int)	0.0743
Final R1 (<i>I</i> > 2 σ (<i>I</i>))	0.0535
wR2 (<i>I</i> > 2 σ (<i>I</i>)), goodness of fit	0.1412, 0.8905

reaction mixture was allowed to stand at room temperature for 5 h until the end of effervescence. On warming this solution at 80–90°C, the induced reaction became exothermic with the precipitation of a white compound. The precipitate was soluble in water at pH=7 and it had white color. The precipitate, with a formula of $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ (as has been discussed in 3–2), was calcined at 300–500°C to convert it into the target compound of NaNbO_3 .

Single crystals with a formula of $(\text{NH}_4)_3[\text{Nb}(\text{O}_2)_4]$ were grown from the “Solution A” depicted in Fig. 1. White shiny crystals were obtained just after complete decomposition of hydrogen peroxide involved in the “Solution A”. For structural analysis the prismatic crystals were picked up directly from the solution, and one of them was mounted on the glass capillary. The diffraction data were collected by a Rigaku AFC5 diffractometer. The details of data collection and structure refinement are summarized in **Table 1**. The crystal structure was solved by direct method using Sir97²¹⁾ after correcting of the diffraction data for the absorption. The guided refinement was carried out by CRYSTALS²²⁾ software. After the isotropic refinement of thermal parameters, hydrogen atoms in the NH_4^+ groups were placed on nitrogen by symmetry. Their positions and thermal parameters were kept constant. After that we carried out refinement of the anisotropic thermal parameters of non-hydrogen atoms.

The elemental analysis of the prepared single crystals gave H, 4.2%; C, 0%; N, 15.2%; and O, 45.4%, which leads to the conclusion that the most likely chemical formula of the crystal is $(\text{NH}_4)_3[\text{Nb}(\text{O}_2)_4]$ containing H, 4.2%; C, 0%; N, 15.2%; and O, 46.5%. On the other hand, the elemental analysis of the precipitate gave H, 1.9%; C, 0%; N, 0%; O, 32.4%; ash (percentage from TG), 65.1%. The most probable chemical formula was determined to be $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ by judging from the elemental analysis and taking into account the results of redox titration and Raman spectroscopy as discussed later in 3–2.

2.2 Characterization

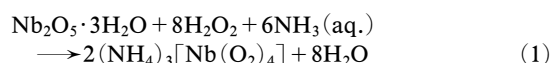
The thermo gravimetric and differential analyses were performed from room temperature to 820°C with heating rate of

1°C/min using MAC Science TG-DTA 2000 apparatus. α - Al_2O_3 was used as a reference. The phase composition of the $(\text{NH}_4)_3[\text{Nb}(\text{O}_2)_4]$ and powders after calcination of $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ at different temperatures were characterized by X-ray diffraction in a 2θ range from 10 to 90°, using Cu K α radiation (MXP^{3va}, MAC-Science, Japan) at room temperature. A model T-64000, Jobin Yvon/Atago Bussan, France/Japan Raman Spectrometer with a liquid nitrogen cooled CCD detector was used for recording Raman spectra with a 514.5 nm line of Ar laser for excitation (10 mW and 10 s acquisition time). The specific surface area of the samples was measured by the conventional three-point BET method using nitrogen gas as absorbent (Model SA9601, Horiba). The powder morphology of the samples was studied using scanning electron microscopy (FE-SEM) (Hitachi S-4500 scanning microscope).

3. Results and Discussion

3.1 Formation of a water-soluble Nb compound: $(\text{NH}_4)_3[\text{Nb}(\text{O}_2)_4]$

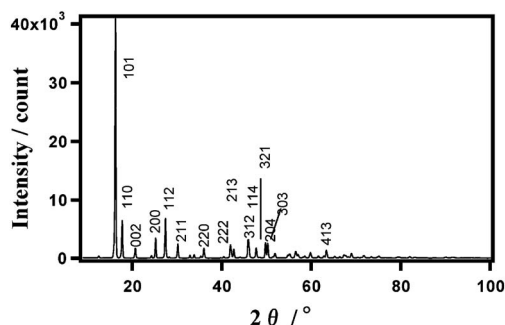
The reaction of niobic acid ($\text{Nb}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$) with hydrogen peroxide in the presence of ammonia gives a clear colorless solution having the composition $[\text{Nb}(\text{O}_2)_4]^{3-}$.²³⁾ Though the mechanism for the formation of peroxo niobium compound is quite complicated, the reaction at pH = 11 can be summarized by Eq. (1)



The excess of hydrogen peroxide and high pH help in increasing the number of peroxide groups coordinating to metal center²³⁾ and also help in stabilizing the solution of tetraperoxo niobium. The excess of H_2O_2 decomposes slowly with evolution of oxygen gas. When most of the H_2O_2 is consumed, white shiny crystals having composition $(\text{NH}_4)_3[\text{Nb}(\text{O}_2)_4]$ are obtained. The powder XRD pattern for the $(\text{NH}_4)_3[\text{Nb}(\text{O}_2)_4]$ is shown in **Fig. 2**. The XRD peaks can be indexed assuming the tetragonal crystal system and lattice parameters of $a=0.704$ nm and $c=0.856$ nm. The interplanar spacings obtained for this compound agree with the parameters obtained for a potassium salt $\text{K}_3[\text{Nb}(\text{O}_2)_4]$ reported by Guerchais and Rohner.²⁴⁾ The final refined atomic parameters from the single crystal diffraction data are summarized in **Table 2**. The corresponding picture of the unit cell of $(\text{NH}_4)_3[\text{Nb}(\text{O}_2)_4]$ is presented in **Fig. 3**. One may notice that isolated anions $[\text{Nb}(\text{O}_2)_4]^{3-}$ form body centered tetragonal lattice. The atomic positions of hydrogen have not been refined therefore discussion about possible hydrogen bonding would not be reliable. The metal–oxygen (Nb–O) distances are slightly different for each oxygen atom in the peroxo group and the values of 0.1970(11) nm and 0.2012(8) nm are rather common for Nb–O bonds. The O(1)–O(2) bond of 0.132(2) nm in the peroxo group is relatively small compared to 0.145–0.149 nm for most of the peroxo complexes, however it is not outstanding since it is comparable with oxygen–oxygen distance of 0.1327 nm in the isostructural $\text{K}_3[\text{Cr}(\text{O}_2)_4]$ compound. The space between anions is filled with the ammonium counter ion.

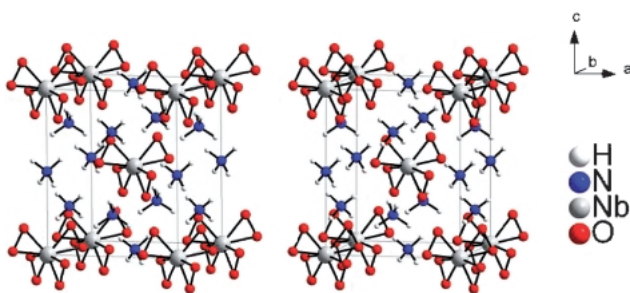
3.2 Preparation of $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ as a novel precursor for NaNbO_3

When sodium carbonate was added to the tetraperoxonioium solution, lots of effervescence come out from the solution, and after 5 h a colorless transparent solution was obtained. On warming the reaction mixture on a water bath at 80–90°C, an exothermic reaction sets in with precipitation of a white

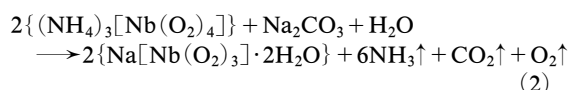
Fig. 2. Powder XRD pattern of $(\text{NH}_4)_3[\text{Nb}(\text{O}_2)_4]$.Table 2. Final Atomic Coordinates and Anisotropic Thermal Parameters of $(\text{NH}_4)_3[\text{Nb}(\text{O}_2)_4]$

Atom	Site	x	y	z
Nb	2a	0	0	0
O(1)	8i	0.1998(8)	0.1998(8)	0.0331(11)
O(2)	8i	0.135(2)	0.135(2)	0.168(2)
N(1)	4d	0	1/2	1/4
N(2)	2b	1/2	1/2	0
H(1)	16j	-0.1072	0.5528	0.3156
H(2)	8i	0.5800	0.5800	0.0700

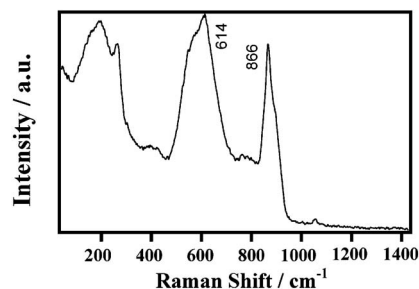
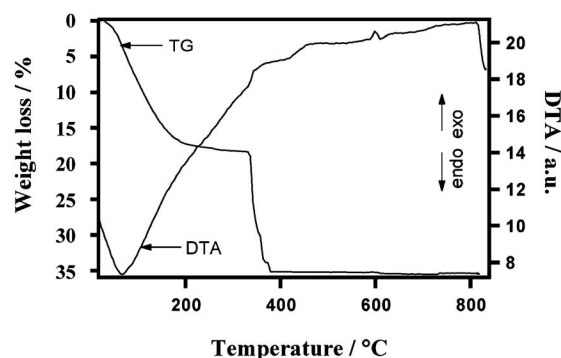
Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Nb	0.0243(3)	0.0243(3)	0.0220(4)	0	0	0
O(1)	0.043(2)	0.043(2)	0.116(7)	-	-	-
				0.023(3)	0.023(3)	0.009(3)
O(2)	0.115(8)	0.115(8)	0.105(11)	-	-	0.046(8)
				0.073(8)	0.073(8)	
N(1)	0.0312(18)	0.0312(18)	0.049(4)	0	0	0
N(2)	0.042(4)	0.042(4)	0.049(5)	0	0	0

Fig. 3. Setero view of the crystal lattice of $(\text{NH}_4)_3[\text{Nb}(\text{O}_2)_4]$. Isolated anions $[\text{Nb}(\text{O}_2)_4]^{3-}$ form body centered tetragonal lattice and the space between them is filled with ammonium counter ions.

compound containing sodium and niobium. The exothermic nature of the reaction can be ascertained to the evolution of oxygen and ammonia. The reaction can be described by Eq. (2)



The elevated temperature is essential to shift the equilibrium to the right side of Eq. (2) due to the hydrolysis of $(\text{NH}_4)_2$

Fig. 4. Raman Spectrum of the precipitate powder of $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$.Fig. 5. TG-DTA curve for the precipitate powder of $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$.

CO_3 and elimination of gas products. The elemental analysis (carbon, hydrogen and nitrogen) for the precipitate shows presence of hydrogen, suggesting that the precipitate contains hydrate water. The determination of peroxide in the precipitate powder, accomplished by redox titration involving potassium permanganate,²⁵⁾ indicated the occurrence of three peroxide groups per Nb^{5+} center. The presence of peroxoniobium species was probed by Raman spectroscopy after drying of the fresh precipitate in vacuum over conc. H_2SO_4 (Fig. 4). A sharp stretching Raman mode at 866 cm^{-1} from $\nu(\text{O}-\text{O})$ has been observed as reported²⁶⁾ to appear around this area together with a strong peak at 614 cm^{-1} of $\nu(\text{Nb}-\text{O}_2)$ which also appeared in the spectrum. The TG profile (Fig. 5) of the precipitate shows two-step weight loss in the region $40\text{--}200^\circ\text{C}$ and $200\text{--}380^\circ\text{C}$. The first weight loss can be substantiated with the dehydration as well as evaporation of small amounts of adsorbed water molecules, and the second step of weight loss can be assigned to decomposition of the peroxo moiety leading to the formation of NaNbO_3 as the final product. The weight loss of 34.9% detected over the temperature range of $40\text{--}800^\circ\text{C}$ on the TG curve of the precipitate is close to the calculated value of 33.9%. Thus, based upon the elemental, TG, redox titration and Raman spectroscopic analyses, the precipitate can be formulated as $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$.

It should be mentioned here that in the case where the reaction pH is extremely high, Lindquist ion, $[\text{Nb}_6\text{O}_{19}]^{8-}$, could be salted out as $\text{Na}_8[\text{Nb}_6\text{O}_{19}]$.²⁷⁾ But the present reaction condition at $\text{pH}=11$ is such that it favors the formation of sodium salt of niobium peroxide and dispel the formation of $\text{Na}_8[\text{Nb}_6\text{O}_{19}]$. Thus the present chemical scheme may allow the precipitate to be an exclusive precursor for the formation of NaNbO_3 .

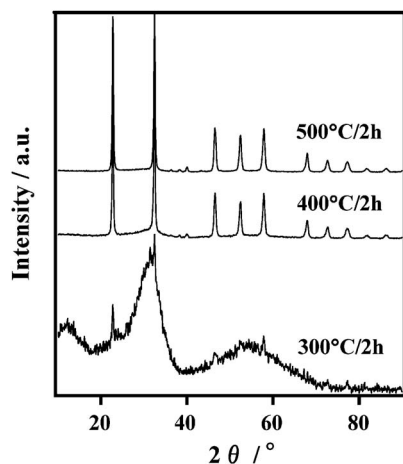


Fig. 6. XRD patterns of powders obtained upon decomposition of $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ at (a) 300, (b) 400, and (c) 500°C for 2 h.

3.3 Conversion of $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ to NaNbO_3

X-ray diffractograms for the precipitated $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ powder calcined at different temperatures are shown in Fig. 6. The powder formed by calcination at 300°C was primarily amorphous in structure, as shown by broad reflections with very weak reflections characteristic to an early stage of sodium niobate formation. A nearly single-phase NaNbO_3 powder was obtained after calcination at 400°C for 2 h. By products or other phases such as Nb_2O_5 , Na_2CO_3 and $\text{Na}_8[\text{Nb}_6\text{O}_{19}]$ were not detected, although there still exists the parasitic amorphous component as indicated by the presence of a weak broad feature between 30° and 40°. It is worth mentioning that crystalline NaNbO_3 powder free from residual reactant or undesired by-products could be obtained at relatively low temperature in comparison to the other solution-based methods.²⁸⁾

Usually, when the so-called amorphous complex (AC) method is used, even though the crystalline phase can be attained at 450°C, complete elimination of residual carbon requires temperature higher than 550°C.⁴⁾ In addition, the sample obtained at 400°C by the AC method is amorphous whereas the sample obtained by this method at 400°C shows almost complete crystallization and free from other crystalline impurities. Further the purity of NaNbO_3 obtained by our method was ascertained by Raman spectroscopy, a technique that is complimentary to X-ray diffraction in finding small amounts of a secondary phase or impurity. The Raman spectra (Fig. 7) of the NaNbO_3 powders calcined at 400 and 500°C reproduce the well-known perovskite phase,²⁹⁾ and show no peaks due to any impurities. Thus, it has been proved that NaNbO_3 can be obtained at reduced temperature and free from crystalline impurities. The complete absence of organics as well as the stoichiometrically ($\text{Na}/\text{Nb}=1$) hetero-metallic nature of the precursor compound can be the strong reasons that helped in obtaining NaNbO_3 powder at reduced temperature.

Figure 8 shows the SEM images of the precipitated $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ (Fig. 8A) and crystalline NaNbO_3 (Fig. 8B) obtained by calcination of $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ at 400°C. The $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ powder shows a uniform particle size with average diameter (D_{SEM}) of 90 nm. On the other hand the SEM image of the NaNbO_3 powder shows the presence of particle growth, resulting in two classes of particles, one with average particle size $D_{\text{SEM}} \sim 150$ nm and the

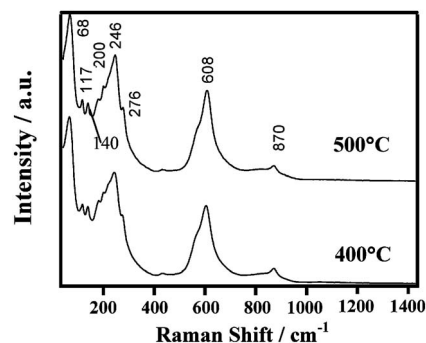


Fig. 7. Raman spectra for NaNbO_3 powders obtained upon decomposition of $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ at 400 and 500°C for 2 h.

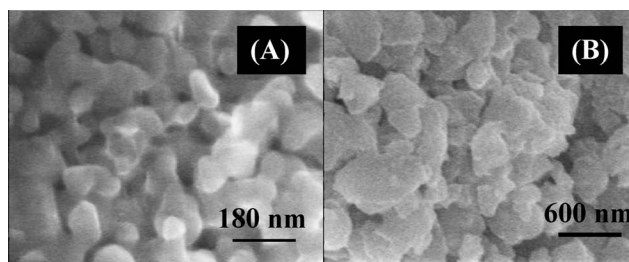


Fig. 8. SEM images of (A) the precipitate powder of $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ and (B) its decomposed product (NaNbO_3) at 400°C.

other with $D_{\text{SEM}} \sim 300$ nm. The size of particles can also be estimated by the equivalent mean diameter (D_{BET}) calculated by eq. (3), wherein ρ_t is the theoretical density of NaNbO_3 ($\rho_t = 4.50 \text{ g/cm}^3$) and S_{BET} is the specific surface area of NaNbO_3 .

$$D_{\text{BET}} = 6 / (\rho_t \times S_{\text{BET}}) \quad (3)$$

Substituting the measured value of $S_{\text{BET}} = 24.6 \text{ m}^2 \text{ g}^{-1}$ into eq. (3) yields $D_{\text{BET}} = 54 \text{ nm}$, which is much smaller than the figures of D_{SEM} (150–300 nm) suggesting the presence of either loose agglomerates or porous particles.³⁰⁾

4. Conclusion

We have developed the new precursor for synthesis of NaNbO_3 based on a chemical reaction between tetraperoxo niobium complex and sodium carbonate in an aqueous ammonia solution. Elemental, TG, redox titration and Raman spectroscopic analyses established the molecular composition of the precursor as $\text{Na}[\text{Nb}(\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$. The decomposition of this compound upon heating at temperatures higher than 400°C produced crystalline NaNbO_3 free from any crystalline impurities. The use of the present hetero-metallic compound with $\text{Na}/\text{Nb}=1$, that is actually a sodium salt of triperoxo niobium complex, derived from the newly developed aqueous solution route permits the preparation of pure and homogeneous NaNbO_3 at reduced temperature.

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