

Structural and Optical Properties of Perovskite-Type Compounds Obtained by Ultrasonic Method

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Abstract. Perovskite-type NaTaO_3 (NaT) and NaNbO_3 (NaN) materials have been successfully obtained by ultrasonic method with immersed sonotrode in the reaction medium followed by annealing at 600°C , for 6 h. The influence of thermal treatment on phase composition, particle size, and morphology of the obtained materials have been investigated by X-ray diffraction (XRD), Diffuse reflectance ultraviolet-visible spectroscopy (UV-Vis), Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy (SEM), and semiquantitative elemental analysis – EDX. The average size of the crystallites of NaT materials was found to be 37.7 nm while that of NaN materials was found to be 30.5 nm. The optical band gap was determined using Kubelka–Munk equation from UV-Vis spectroscopic measurements and is estimated to be 4.05 eV for NaTaO_3 and 3.87 eV for NaNbO_3 perovskite-type samples. EDX semiquantitative analysis has highlighted the purity of the obtained materials, and quantification confirmed the stoichiometry of the compounds (ABO_3).

1. Introduction

In recent years, continuous efforts are being made worldwide to improve the performance characteristics of ABO_3 -type materials suitable for practical applications [1]. Ceramics with ABO_3 type structure have been widely used in various electronic and microelectronic devices such as capacitors, piezoelectric transducers, pyroelectric detectors/sensors, memory devices, microwave tunable devices, etc, NaNbO_3 and NaTaO_3 being well-known perovskite oxides which possess attractive physical properties [2].

It has been shown that the preparation method has a great influence on the morpho - structural properties of the perovskite materials [3-5]. The conventional techniques for synthesizing tantalates and niobates powders are based on the solid state reaction, which requires long periods of heating (800°C) and that leads to inhomogeneity in composition [6-8].

Sol–gel using alkoxides, hydrothermal and colloid emulsions are time consuming and involve highly unstable alkoxides and difficult to maintain in reaction conditions [9]. The soft-chemical route allows a better control of physico-chemical properties through manipulation of synthesis parameters. However, this method implies long reaction times and thermal treatment [5]. In this context, the use of new techniques



working at room temperature, capable to reduce the reaction time, as well as to manipulate the final product properties must be taken into account.

The aim of this study was to prepare nanoparticles of NaTaO₃ and NaNbO₃ using the ultrasonic method with immersed sonotrode in the reaction medium and to investigate their properties. Physico-chemical properties were investigated using X-ray diffraction (XRD), ultraviolet (UV) diffuse spectroscopy, FT-IR studies, scanning electron microscopy (SEM), and semiquantitative elemental analysis - EDX.

2. Experimental procedure

The synthesis of the materials with perovskite structure by ultrasonic method with immersed sonotrode in the reaction medium was performed. All chemicals were of analytical grade and used without further purification. In order to obtain NaTaO₃ and NaNbO₃ materials, tantalum (V) ethoxide (Ta(OC₂H₅)₅), ammonium niobate (V) oxalate (C₄H₄NNbO₉ · x H₂O), sodium citrate (C₆H₅Na₃O₇ · x H₂O) and sodium hydroxide (NaOH) were used.

In a first time, the solution for obtaining NaT material was prepared as follows: tantalum ethoxide was added dropwise in 50 mL bidistilled water and the precipitation with 7 M NaOH solution up to pH 11 was achieved afterwards. In case of NaN material, ammonium niobate oxalate in 5 × 10⁻³ M concentration was dissolved in 50 mL bidistilled water, to which 5 × 10⁻³ M sodium citrate solution was added. For better precipitation 7 M NaOH solution was added until the pH 9. The solutions were subjected to ultrasonic process with an ultrasonic processor Sonics Vibra Cell type at 80 °C, 60 min, with 80% amplitude and pulsations 10 seconds On / Off 5 seconds.

The obtained precipitates were filtered and washed with bidistilled water and alcohol for the removal of soluble products, and then were dried at 110 °C, for 2 hours. The resultant powders were a mixture of phases and to obtain single phase perovskite structure, they were thermally treated for 6 hours at 600 °C, at a heating rate of 5 °C/min.

The structural properties of the as-obtained materials were determined by X-ray diffraction (PANalytical X'Pert PRO MPD Diffractometer with Cu tube). The light absorption properties of the materials were studied by UV-Vis diffuse reflectance spectroscopy (UV-VIS) using a Lambda 950 Perkin Elmer device and FT-IR studies were performed with a Shimadzu Prestige FT-IR spectrometer, in KBr pellets, in the range 500 - 4000 cm⁻¹. The morphology and quantitative analysis of the powders were investigated by SEM using an Inspect S PANalytical SEM / EDX.

3. Results and discussions

X-ray diffraction patterns and crystalline structures of NaT and NaN materials are presented in Figure 1, Figure 2 respectively. The XRD patterns were recorded from 20° to 80° (2θ) using CuKα radiation with λ=1.54060 Å. From Figure 1, it can be seen that the materials are well crystallized, the diffraction peaks being all indexed by the perovskite structure. Also, the diffraction patterns were refined with X'Pert HighScore Plus program, using CIF 1521386 (for NaT) and CIF 5910011 (for NaN). Following the Rietveld refinement analysis of diffraction data (for NaT material) the following crystallographic data were obtained: tetragonal symmetry, space group P4/mbm, unit cell parameters a=b=5.5552 and c=3.9338 Å, α = β = γ = 90 °, V=121.40 Å³ (according to JCPDS No. 01-073-0881). For the NaN sample the following parameters are obtained: cubic symmetry, space group Pm-3m, unit cell parameters a=b=c= 3.9 (2) Å, α = β = γ = 90 °, V= 59.48 Å³ (according to JCPDS No. 00-019-1221).

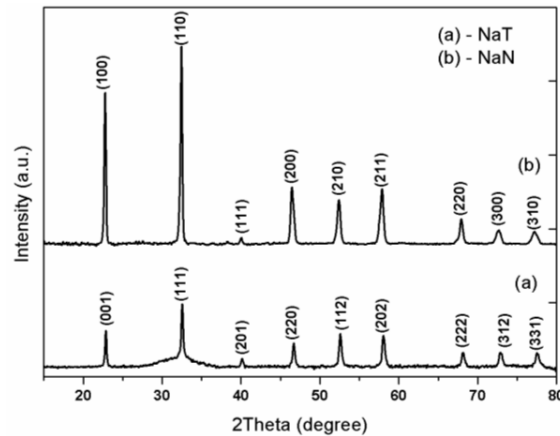


Figure 1. XRD patterns for NaT (a) and NaN (b) samples.

The crystallite size was estimated from the XRD patterns (with Scherrer's equation) and the average size of the crystallites was 37.7 nm for NaT sample and 30.5 nm for NaN sample.

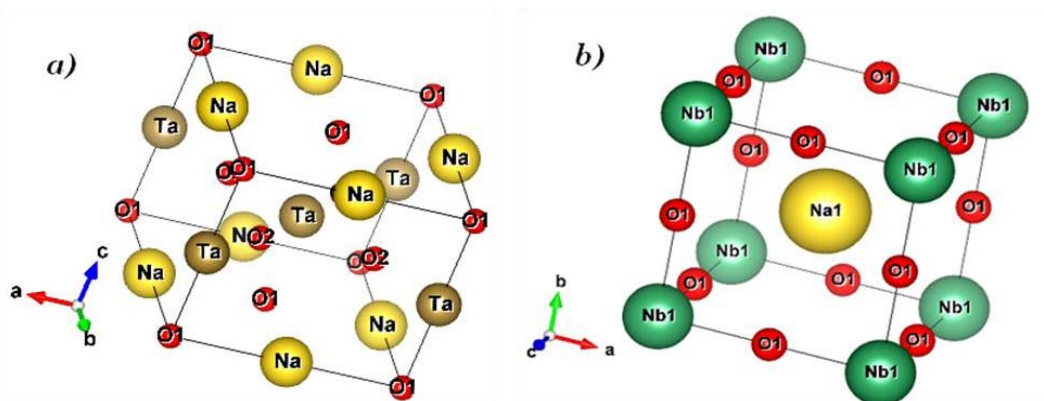


Figure 2. Crystalline structures of NaT (a) - space group P4/mbm and NaN (b) - space group Pm-3m materials.

Figure 3 shows the absorption spectra of tantalates and niobates materials recorded between 300 and 800 nm using diffuse reflectance module. The optical band gap was determined using Kubelka–Munk equation and is estimated to be 4.05 eV for NaTaO₃ perovskite-type sample and 3.87 eV for NaNbO₃. As already shown in [10], the band gap of niobate is smaller than those of tantalate and this can be due to the levels of the conduction bands consisting of Nb 4d that are more positive than those of Ta 5d [10].

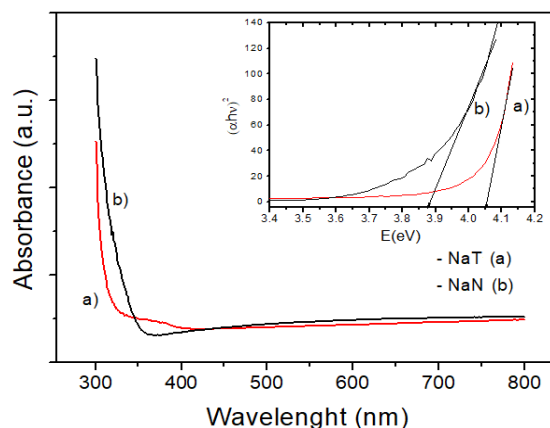


Figure 3. Diffuse reflectance spectra of the NaT (a) and NaN (b) materials. Insert: optical band gap calculated from the UV-Vis spectroscopic measurements by using the Tauc plots of $(\alpha h\nu)^{1/2}$ versus $E(\text{eV})$.

On the other hand, it should be mentioned that different values are reported in the literature for the NaTaO_3 samples obtained by different synthesis methods (sol-gel, hydrothermal and/or solid state) [5, 11] and this can be related to the deviation from 180° of the Ta-O-Ta bond angle in the perovskite type structure [12, 13].

FT-IR studies of the tantalate and niobate (NaT and NaN) synthesized by ultrasonic method with immersed sonotrode in the reaction medium are presented in Figure 4. The FT-IR spectrum of the NaT powder exhibits beside the wide band in the range $400\text{--}1000\text{ cm}^{-1}$, with maximum around 600 cm^{-1} characteristic to the vibrations of Ta – O bonds [1], some bands characteristic to alkoxide groups (1352 and 1438 cm^{-1} corresponding to the $\delta(\text{C—H})$ bending vibrations [14]. More, a large band at 3385 cm^{-1} together with a weak band located at 1631 cm^{-1} , characteristic to $\nu(\text{OH})$ and $\delta(\text{HOH})$ vibrations of water molecules associated by hydrogen bonds [15] are observed for NaT material.

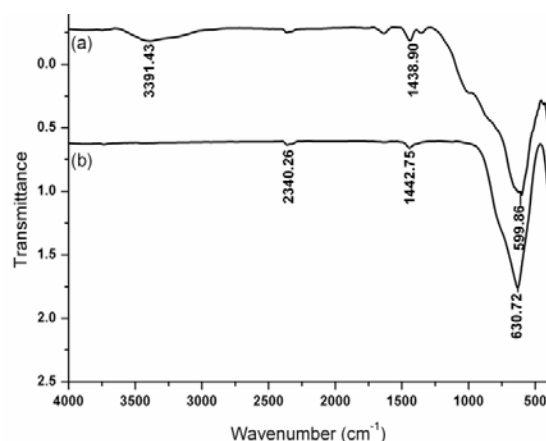


Figure 4. FT-IR spectra of NaT (a) and NaN (b) materials.

The FT-IR spectrum of the NaN powder exhibits only the wide band with maximum located at 630 cm^{-1} , characteristic according to the literature to the stretching vibrations of Nb – O bonds [16] or to the vibration mode of niobium - dioxo bridge [17].

The morphology of the NaT and NaN samples synthesized by ultrasonic method with immersed sonotrode in the reaction medium and annealed at 600°C was studied by scanning electron microscopy (SEM) as shown in Figure 5. From Figure 5.a) agglomerated particles can be observed. It is important to mention that the observed morphology is quite different to that reported by other authors. Using the hydrothermal method, it was observed the formation of cubic particles, with the grain size about 100 nm [18]. Regarding NaN sample (Figure 5.b), it can be observed that the particles are agglomerated in rod-like formations with various sizes (a few micrometers), due to the ultrafine nature of the sample. To highlight the purity of the obtained materials, the semiquantitative analysis EDX was performed (Figure 6).

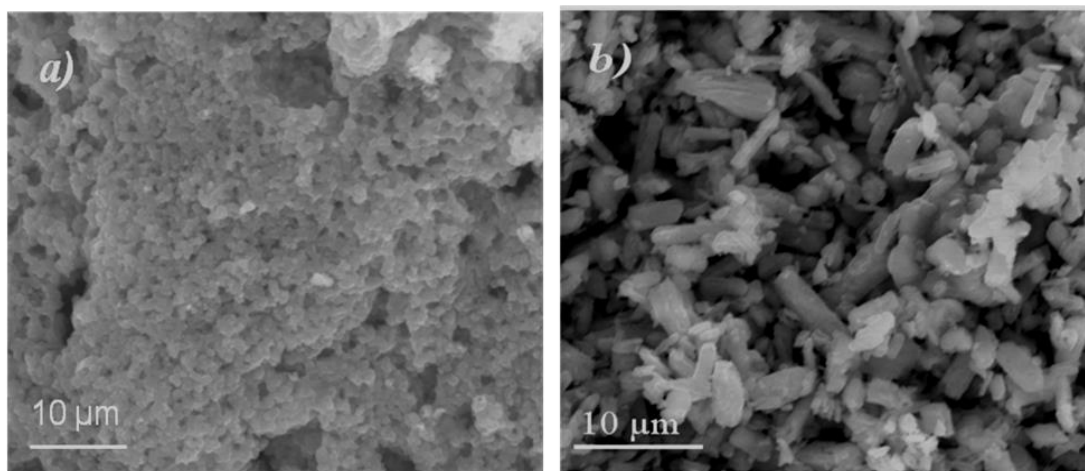


Figure 5 . SEM morphology for NaT (a) and NaN (b) materials.

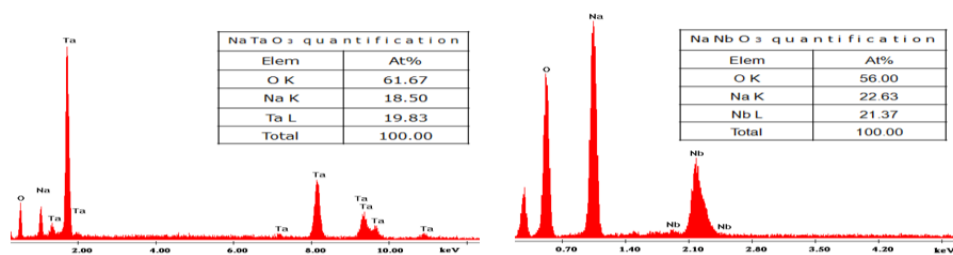


Figure 6. EDX analysis and element quantification.

Thus, one can observe the obtained materials are without any impurities, and quantification confirmed the stoichiometry of the compounds (ABO₃).

4. Conclusions

By ultrasonic method with immersed sonotrode in the reaction medium followed by thermal treatment at 600°C at, NaTaO₃ and NaNbO₃ materials with cubic symmetry has been successfully synthesized. The crystallite size of NaTaO₃ and NaNbO₃ was estimated to be 37.3 nm and 30.5 nm, respectively. The calculated value of optical band gap indicated that band gaps of niobates are smaller than those of tantalates. SEM images showed rod-like formations of NaNbO₃ comparative with agglomerated particles for NaTaO₃ with the expected stoichiometry. Therefore, one can conclude that the ultrasonic method with

immersed sonotrode in the reaction medium is a fast and effective technique to obtain single phase perovskite type materials of NaTaO₃ and NaNbO₃.

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