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Dedicated to Professor Mircea Diudea on the Occasion of His 65th Anniversary

SYNTHESIS AND CHARACTERIZATION OF LEAD-FREE SODIUM NIOBATE POWDER

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ABSTRACT. Sodium niobate ($NaNbO_3$) fine powders were synthesized by hydrothermal method using ammonium niobate (V) oxalate hydrate ($C_4H_4NNbO_9$ x H_2O), sodium hydroxide (NaOH) and sodium citrate hydrate ($C_6H_9Na_3O_9$) as precursors. The samples were characterized by X-Ray diffraction (XRD), scanning electron microscopy (SEM), AFM (Atomic Force Microscopy), UV-VIS spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR).

X-ray diffraction for powder obtained by hydrothermal method revealed three phases mixture ($NaNbO_3$, Nb_2O5, $Na_2C_2O_4$). In order to obtain a material with perovskite structure, the powder was treated for 6 h at 600°C. After calcination, the X-ray powder diffraction (XRD) patterns shown reflections of a pure cubic structure (space group *Pm*-3*m*) with lattice parameters (a=b=c=3.909Å) comparable to those reported in the literature. The average particle sizes estimated by SEM image were 2-3 micrometers.

Keywords: *sodium niobate, hydrothermal method, X-ray diffraction, scanning electron microscopy*

INTRODUCTION

Photocatalysis is a promising technology with various applications, including water purification [1]. TiO_2 photocatalyst is the most commonly used, however, it is an effective material under UV light. Enormous efforts have been made to develop photocatalysts that have efficient photocatalytic activity in

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the visible range, either by modifying titanium dioxide or by developing semiconductors that show photocatalytic properties [2]. Semiconductors based on niobium oxide have received much attention in the recent years because of its photocatalytic promising characteristics, such as toxicity, chemical inertness and high stability under irradiation by the light. The most important material based on niobium oxide is probably $ANbO_3$, where A = K / Na / Li because it has a variety of interesting and useful properties, including the photocatalytic, piezoelectric, optical properties of ferroelectric, etc. [3]. $NaNbO_3$ has been prepared by various methods, such as hydrothermal synthesis [4], the sol-gel process [5], and solid-state method [6]. Among the methods of preparation, the hydrothermal synthesis, which involves the heating of Nb_2O_5 in different concentrations of KOH at 120-200˚C seems to be the most convenient and versatile. Depending on the reaction conditions, different sizes and shapes can be obtained, including micro- and nanoparticles, wires and blocks. Sodium niobate ($NaNbO_3$) have attracted considerable interest among scientists because of its ferroelectrics good property on high temperature, piezoelectric properties, thanks to excellent photorefractive properties and a moderate dielectric constant [7].

In general, the hydrothermal synthesis of nanocrystalline materials consists of introduction into a closed container (i.e., autoclave) of precursors and heating until the temperature and pressure generated by heating lead to the crystallization of the substances inside. Judicious control of temperature, pressure, duration of the process, the degree of filling of the autoclave, the concentration of the precursors allow to obtain nanocrystals with the size and type of crystal desired [8]. This method has many advantages, e.g., the product has a homogeneous crystallinity and it can be produced at a relatively low temperature (less than 150°C). The most important feature of the method is that it allows the reduction of the degree of particle agglomeration, small size distribution, and the control of morphology of the phase.

The crystal growth or material processing under hydrothermal conditions requires a pressure vessel capable of withstanding the high temperature and pressure and corrosive action of a solvent, as provided by the autoclave. Several Niobium combinations have been synthesized by hydrothermal method [9, 10].

The synthesis of nanotubes has become one of the most important research topics in nanotechnology and various materials have been produced in recent decades [11]. The successful titanium nanotubes synthesis is one of the examples of such intense research efforts. Kasuga et al. prepared TiO_2 nanotubes by hydrothermal method [12]. Zhang et al. reported preparation of potassium hexatitanate ($K_2Ti_6O_{13}$) using microwave activation [13]; this way is very attractive because of its short response time and low power consumption compared to conventional methods.

Ghamsari et al. reported the synthesis of potassium titanate by mixed method, sol-gel and hydrothermal [14]. Subohi et al. synthesized bismuth titanate with urea through combustion method; the product shows ferroelectric and dielectric properties [15].

RESULTS AND DISCUSSION

In our study we obtained sodium niobate ($NaNbO_3$) fine powders by hydrothermal method at 220°C and post annealing at 600°C in order to get a unique phase. Precursors used in this synthesis were ammonium niobate (V) oxalate hydrate ($C_4H_4NNbO_9$ xH_2O), sodium hydroxide (NaOH) and sodium citrate hydrate (C6H9Na3O9).

Structure of the sample phases were investigated by X-ray diffraction (XRD) using PANalytical X'Pert PRO MPD diffractometer with Cu Kα radiation, λ = 1.5406 Å, 2θ-step of 0.016° from 15° to 80°. In the prelevated samples, three mixed phases were observed: $NaNbO_3$, Nb_2O_5, and $Na_2C_2O_4$. (Figure 1 a). In order to obtain a material with perovskite structure, the powder was annealed for 6 h at 600°C. After calcination, the X-ray powder diffraction (XRD) patterns shown reflections of a pure cubic structure (space group *Pm*-3*m*) with lattice parameters a=b=c=3.909Å. Table 1 lists the extracted parameters of this structure.

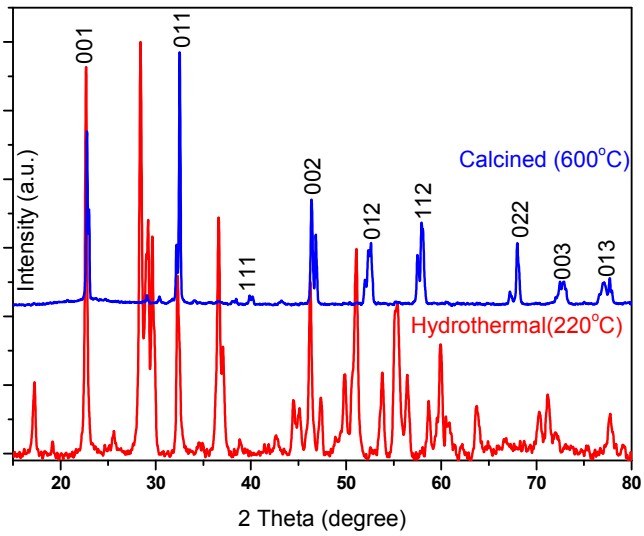

Figure 1 a). X-ray diffraction of $NaNbO_3$ obtained by hydrothermal method at 220°C and after thermal treatment at 600°C

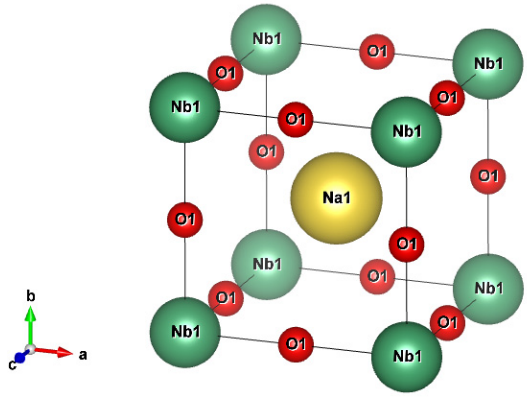

Figure 1 b). The structure of $NaNbO_3$ obtained by a hydrothermal method after thermal treatment

Table 1. The structure parameters of $NaNbO_3$ obtained by a hydrothermal method

Formula sum	$Na_{1.00}Nb_{1.00}O_{3.00}$
Formula mass/ g/mol	163.8944
Density (calculated)/ g/cm3	4.5569
Weight fraction/ %	100.000000
Space group (No.)	P m -3 m (221)
Lattice parameters	
a/ Å	3.909(2)
b/ Å	3.909(2)
c/ Å	3.909(2)
V/ 106 pm3	59.71494

In order to study the size and shape of particles we used SEM technique. Figure 2 shows the micrograph of $NaNbO_3$ powder obtained by hydrothermal method at 220°C.

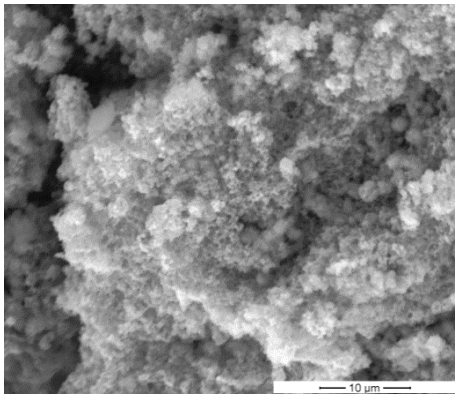

Figure 2. SEM images of mixed phases of $NaNbO_3$ powder obtained by hydrothermal method at 220°C

SEM images of the single phase of $NaNbO_3$ powder, as obtained after annealing treatment at 600°C, are illustrated in Figure 3. The average size of particles with a cubic shape was estimated around 2-3 micrometers. The EDX signal of this single phase is shown in Figure 4. The presence of all elements: Na, Nb and Oxygen have been confirmed.

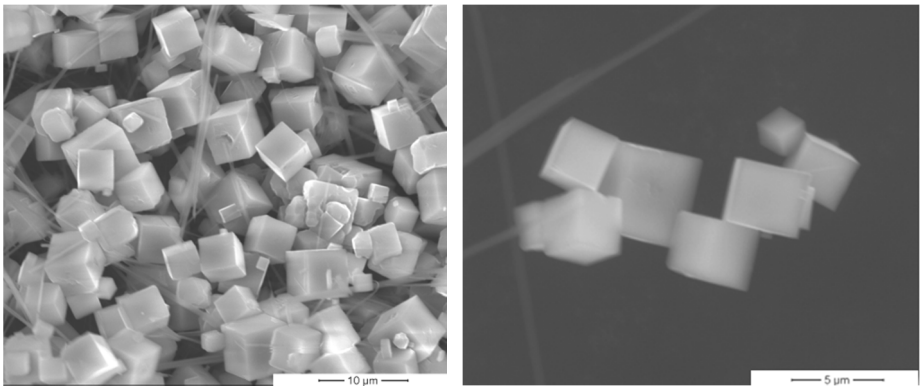

Figure 3. SEM images of single phase of $NaNbO_3$ powder as obtained and thermal treatment at 600°C

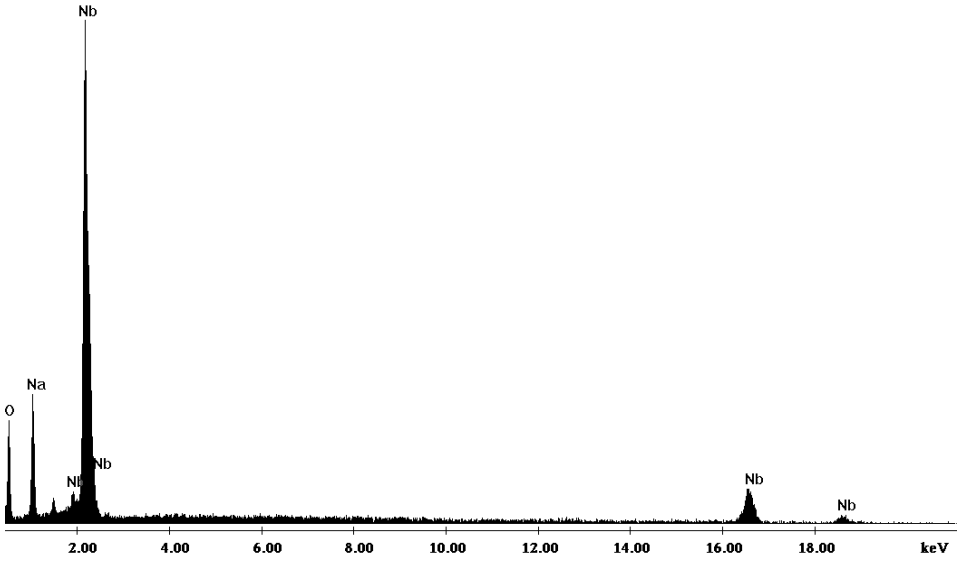

Figure 4. EDX images of single phase of $NaNbO_3$ powder as obtained after the thermal treatment at 600°C

The topography of $NaNbO_3$ was observed by Atomic force microscopy (Nanosurf® EasyScan 2 - Figure 5).

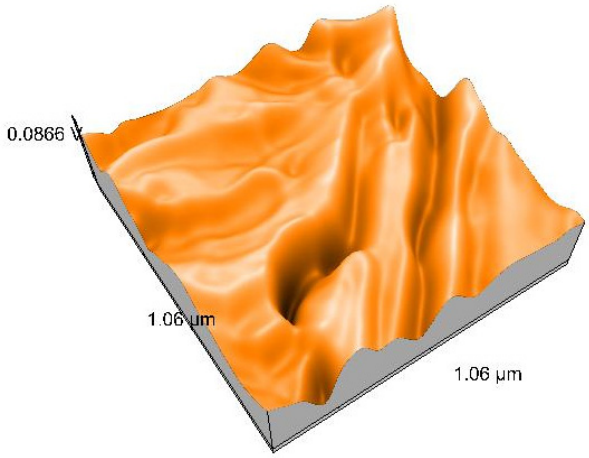

Figure 5. 3D topography of $NaNbO_3$ powder

The optical band gaps UV-VIS spectrometer was used in order to get the optical properties of $NaNbO_3$ powder. The pure $NaNbO_3$ sample shows only one intense absorption with steep edges in the UV region (Figure 6). The absorption and transmission spectra were recorded by LAMBDA 950 UV/Vis/NIR spectrophotometer.

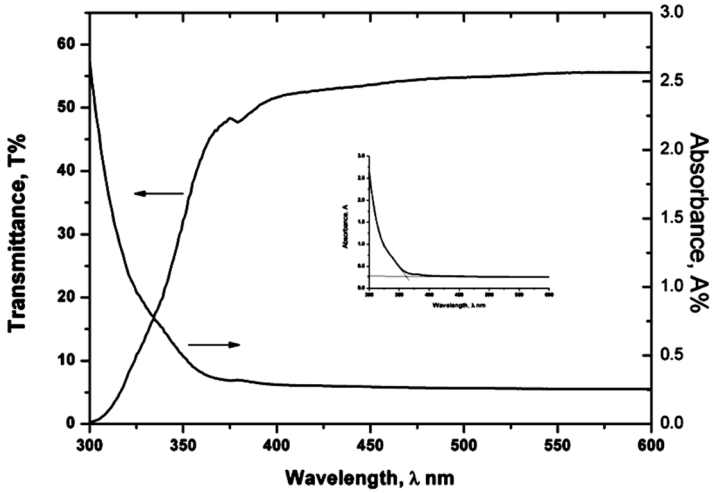

Figure 6. The absorption and transmission spectra of $NaNbO_3$, inset is represented the estimate band gap of $NaNbO_3$.

The band gap of $NaNbO_3$ is evaluated around 3.45 eV (inset of Figure 6), compared with those reported in literature [1].

IR spectrum was recorded on an FTIR spectrometer Shimadzu Prestige in the mid-IR range of 500-4000 wavenumbers operated in the transmittance mode, the KBr pellet technique.

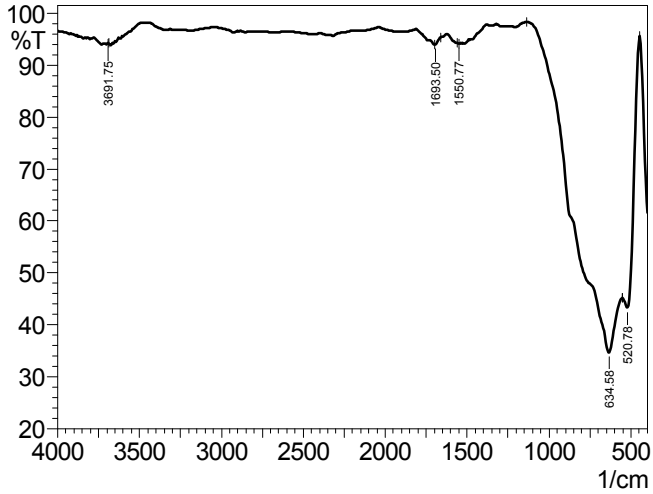

Figure 7. FT-IR spectra of the obtained $NaNbO_3$ powder after thermal treatment

Figure 7 shows the FT-IR spectrum of the obtained $NaNbO_3$ powder. The sharp peaks at 634 cm^{-1} and 520 cm^{-1} correspond to the vibrations of the Na-Niobate framework including Nb-O stretching, Nb-O-Nb bending and lattice vibrations. The spectrum also shows important signals such as: 3691 cm^{-1} (O–H stretching), 1693 cm^{-1} (C=O stretching vibrations), 1550 cm^{-1} [16]. The bands located at 1693 cm^{-1} and 1550 cm^{-1} can be assigned to the antisymmetric stretching and symmetric vibrations of carbon-oxygen bonds from COO- groups of the residual citric acid [17].

CONCLUSIONS

In this paper, we presented the synthesis of sodium niobate powder through hydrothermal method using ($C_4H_4NNbO_9$ x H_2O), sodium hydroxide (NaOH) and sodium citrate hydrate ($C_6H_9Na_3O_9$) as precursors. The particle size of sodium niobate was 2-3 micrometers with an estimated bandgap of 3.45 eV. The formation of $NaNbO_3$ phase is further confirmed by FT-IR analysis.

EXPERIMENTAL SECTION

Sodium niobate ($NaNO_3$) powder was synthesized by the hydrothermal method, followed by annealing at 600°C to achieve a perovskite phase structure. The precursors used for synthesis were $C_4H_4NNbO_9 \cdot H_2O$ (ammonium niobate (V) oxalate hydrate), $C_6H_5O_7Na_3 \cdot 2\ H_2O$ (sodium citrate) and NaOH (sodium hydroxide) 7M solution.

Niobate and citrate salts were dissolved in distilled water in a determined molar ratios and then were precipitated with 7M NaOH solution under strong stirring to obtain a homogeneous suspension. The suspension was introduced into the autoclave by teflon with steel jacketed to ensure a good seal. The autoclave was held at 220°C for 10 hours. After autoclaving, particle separation was made by decantation and filtration. The precipitate was washed on the filter paper with distilled water and ethyl alcohol before being dried in an oven at 80°C for 2 hours. Powder characterization was made by: X-ray diffraction (XRD), scanning electron microscopy (SEM). The mixture of phases of the primary powder was heated at 600° C for 6 hours. After calcination, the resulted single phase was characterized by XRD, SEM / EDAX, AFM, UV-VIS and FTIR.

Structure of the phases were investigated by X-ray diffraction (XRD) using PANalytical X'Pert PRO MPD diffractometer with Cu Kα radiation, λ = 1.5406 Å, 2θ-step of 0.016° from 15° to 80°.

The morphology and quantitative analysis of the powders were investigated by SEM / EDAX using an *Inspect S* PANalytical SEM / EDX.

The topography of NaNbO3 was studied by Atomic force microscopy type Nanosurf® EasyScan 2.

The absorption and transmission spectra was recorded with a LAMBDA 950 UV/Vis/NIR spectrophotometer.

IR spectra were recorded on an FTIR spectrometer Shimadzu Prestige in the mid-IR range of 500-4000 wavenumbers operated in the transmittance mode, the KBr pellet technique.

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