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journal homepage: [www.elsevier.com/locate/matlet](http://www.elsevier.com/locate/matlet)Photoluminescence in  $\text{NaNbO}_3$  particles and films

Guilhermina Ferreira Teixeira\*, Thiago Rago Wright, Daniela Cristina Manfroi, Elson Longo, José Arana Varela, Maria Aparecida Zaghete

Biochemistry and Chemistry Technology, Chemistry Institute-UNESP, 55, Professor Francisco Degni Street, Araraquara, Brazil

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## ABSTRACT

In this work, we report the photoluminescence properties of  $\text{NaNbO}_3$  particles and films. The crystallization of  $\text{NaNbO}_3$  particles produced  $\text{Na}_2\text{Nb}_2\text{O}_6 \cdot n\text{H}_2\text{O}$  intermediate phase which was then converted to  $\text{NaNbO}_3$  following thermal treatment. The particles were obtained from the reaction between  $\text{Nb}_2\text{O}_5$  and  $\text{NaOH}$  by microwave hydrothermal synthesis at varying range of the reaction time. Films were obtained from the  $\text{NaNbO}_3$  particles by electrophoretic deposition. Both the  $\text{NaNbO}_3$  particles and films presented photoluminescence properties around the same emission region (450 nm).

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## 1. Introduction

Owing to the ongoing technological development and the increasing need for the development of new ceramic, several studies are being carried out in order to combine electrical properties with photoluminescence properties. For example, the combination of piezoelectric property with photoluminescence property is known to be the basis of piezophotonic devices. Furthermore, the combination of a photon-excited semiconductor with piezoelectric properties leads to the development of piezo-phototronic devices. These devices are potentially applied in light emitting diode, photocell and solar cell, and photon detector [1].

$\text{NaNbO}_3$  is a lead-free perovskite semiconductor [2] with piezoelectric property [3], which has attracted increasing attention among researchers because of its capacity to form the basis of the class of environmentally friendly materials, and the efficiency of these materials is directly related to their crystalline and morphological structures.

In particular, structural order-disorder is always present in real materials and may play an important role in technological applications by altering their electronic and optical properties.

Although  $\text{NaNbO}_3$  electrical properties are widely explored, there are few studies about their photoluminescence properties, whereas most of the studies are about the photoluminescent properties of lanthanides doped  $\text{NaNbO}_3$  [4–8]. This work seeks to therefore explore the photoluminescence properties of pure  $\text{NaNbO}_3$  powder and films aiming to check their possible application in piezophotonics as well as in piezo-phototronics devices.

## 2. Experimental procedure

The microwave hydrothermal synthesis of  $\text{NaNbO}_3$  powders was performed beginning with  $\text{NaOH}$  (p. a. Quemis) and  $\text{Nb}_2\text{O}_5$  (Alfa Aesar, 99%). In this case, the  $\text{NaOH}$  acts as a mineralizer agent and sodium source. The reaction was carried out in a Teflon vessel model XP-1500 (CEM Corp.), in a MARS-5 (CEM Corp.) microwave digestion. For the preparation of the suspensions precursor, 0.696 g of  $\text{Nb}_2\text{O}_5$  was added to 30 mL of a  $8 \text{ mol.L}^{-1}$   $\text{NaOH}$  water solution. This resultant suspension was then transferred into Teflon vessels and placed inside a microwave furnace. The synthesis was carried out at  $180^\circ\text{C}$  for different time periods (30 and 60 min.). The obtained powders were thoroughly washed with water by centrifugation and finally dried at room temperature. After that the product of 30-minute synthesis time was calcined at  $550^\circ\text{C}/4$  hours. The obtained particles were characterized by X-ray powder diffraction (XRD) using a (Rigaku-DMAX/2500PC, Japan) with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the  $2\theta$  range from  $20^\circ$  to  $75^\circ$  with  $0.2^\circ/\text{min}$ . Raman spectra were collected (Bruker RFS-100/S Raman spectrometer with Fourier transform). A 1064 nm YAG laser was used as the excitation source, and its power was kept at 150 mW. The morphology of as-prepared samples was observed using a high resolution field-emission gun scanning electron microscopy FE-SEM (Carl Zeiss, model Supra 35-VP, Germany). Photoluminescence (PL) spectra were collected with a Thermal Jarrel-Ash Monospec 27 monochromator and a Hamamatsu R446 photomultiplier. A krypton ion laser (Coherent Innova) with an exciting wavelength of 350 nm was used, with the nominal output power of the laser kept at 550 mW. All measurements were performed at room temperature.

For the preparation of the material as film by means of electrophoretic deposition (EDP), a 2 kV of voltage was applied for 10 minutes in a stable ethylic suspension containing 0.00675 g

\* Corresponding author. Tel.: +55 16 3301 9712; fax: +55 16 3301 9707.

E-mail address: [mina.guilher@gmail.com](mailto:mina.guilher@gmail.com) (G.F. Teixeira).

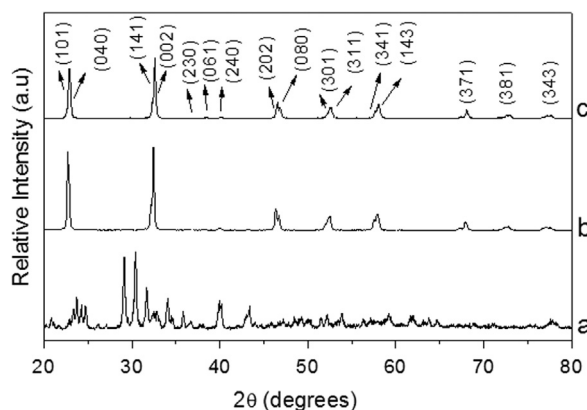


Fig. 1. XRD patterns of particles obtained by microwave hydrothermal synthesis at 180 °C: (a) 30 minutes prior to thermal treatment; (b) 30 minutes after thermal treatment; (c) 60 minutes.

of  $\text{NaNbO}_3$  particles, promoting a uniform and rapid deposition in Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Si substrate. In the following deposition, the films were heated using microwave radiation at 800 °C for 10 minutes. They were subsequently characterized by PL analysis and FE-SEM.

### 3. Results and discussions

NbO<sub>7</sub> decahedra and NbO<sub>6</sub> octahedra derived from the breakage of the Nb<sub>2</sub>O<sub>5</sub> reagent that are connected by vertices forming Nb<sub>6</sub>O<sub>19</sub><sup>8-</sup> ions denoted as the Lindqvist ion are known to give rise to the different niobates structures and compositions that are directly related to the processing conditions of the material [9,10]. Nb<sub>6</sub>O<sub>19</sub><sup>8-</sup> ions present in the solution incorporate with Na<sup>+</sup> ions forming Na<sub>2</sub>Nb<sub>2</sub>O<sub>6</sub>·nH<sub>2</sub>O structures, followed by structural rearrangement and release of water molecules, resulting in NaNbO<sub>3</sub>.

The X-ray diffractogram, Fig. 1, shows the diffraction pattern of the powders obtained by microwave hydrothermal synthesis. Based on the results, it is observed that a pure orthorhombic crystal structure of NaNbO<sub>3</sub> is favored by an increase of the synthesis time period, which is in accordance with the JCPDS file no. 33.1270. For the 30-minute synthesis time, the obtained product consists of Na<sub>2</sub>Nb<sub>2</sub>O<sub>6</sub>·nH<sub>2</sub>O, while after undergoing thermal treatment it was converted into NaNbO<sub>3</sub> with an orthorhombic crystal structure similar to that obtained for the 60-minute synthesis time. The present work likewise that of Song et al. observed the favoring of the formation of the NaNbO<sub>3</sub> crystalline phase given by an increase in the synthesis time [11], but we present the advantage of obtaining particles in less synthesis time due to the use of microwave in the synthesis which allows to synthesize nanomaterials in shorter synthesis time due to the fast crystallization kinetic [12]. Another study worth mentioning is that of Paula et al. where they obtained cubic particles of NaNbO<sub>3</sub> free of secondary phase at a temperature of 200 °C for 1 h time period [9].

FEG-SEM micrographs of as-prepared particles are shown in Fig. 2. Regarding the images, it can be seen that the sample obtained after 30 min (Na<sub>2</sub>Nb<sub>2</sub>O<sub>6</sub>·nH<sub>2</sub>O) consists of fiber-like particles (Fig. 2a), and the fiber-like shape was found to endure following thermal treatment (Fig. 2b). This observation suggests that the thermal treatment induced phase transformation though it did not change the particle morphology. For the 60-minute synthesis time, the micrographies show NaNbO<sub>3</sub> cubic particles with well-defined edges (Fig. 2c).

Similar results were obtained by Yu et al. suggesting that the formation process of NaNbO<sub>3</sub> cubic particles starts with the niobium

dissolution whereby a metastable phase (Na<sub>2</sub>Nb<sub>2</sub>O<sub>6</sub>·nH<sub>2</sub>O) is formed in the niobium particle surface growing until all the niobium is consumed, which is considered to be a very sensitive process to the synthesis conditions [13]. According to Zhu et al., during the hydrothermal treatment for the formation of NaNbO<sub>3</sub> particles, fiber-like or wheel-like intermediary structures are found to form NbO<sub>6</sub> octahedra suggesting that the cube-like NaNbO<sub>3</sub> structures are formed through the dissolution of fibers under hydrothermal conditions [14], which is said to be the consequence of a coarsening process referred to as Ostwald ripening. Ostwald ripening is described by the growth of a determined particle through the dissolution of smaller ones and their subsequent deposition over the surface of the greater particles spontaneously in an attempt to decrease the total surface energy which takes place shortly after nucleation [15].

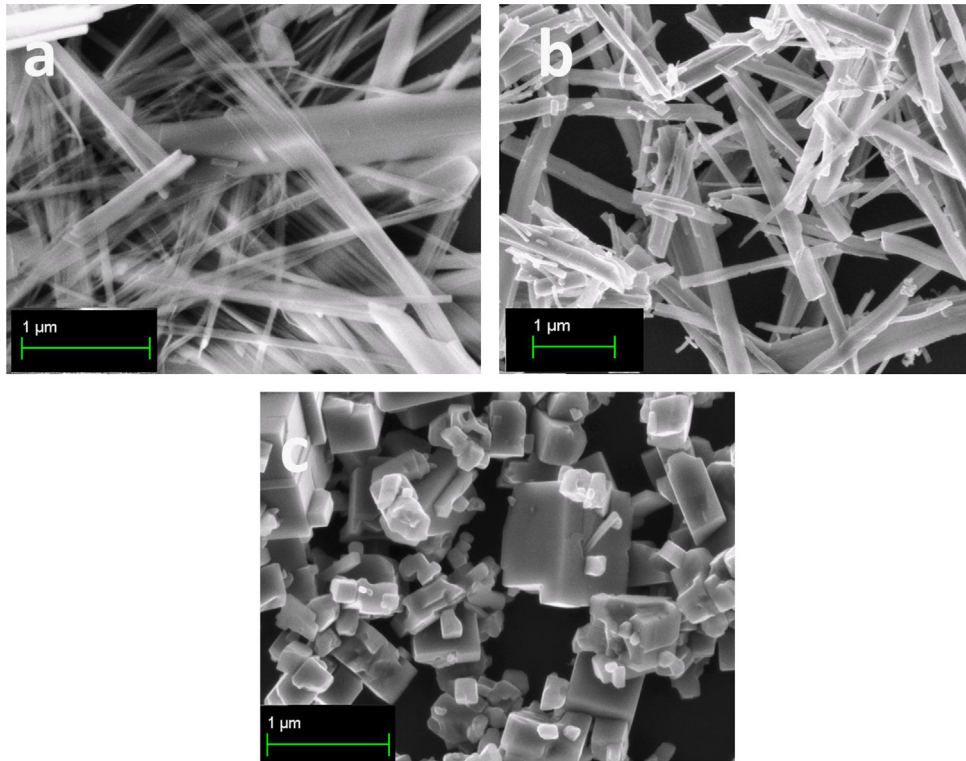
The images of NaNbO<sub>3</sub> films surface are represented in Fig. 3. From the images, it can be observed that the films exhibit homogeneous yet porous covering, as can be seen in images zoom of Fig. 3a and b. This was due to the sintering time which was not enough for the densification of the material.

Fig. 4 shows the PL spectra under room condition (at room temperature) of as-prepared particles. Observing the spectra (Fig. 4), it can be seen that the major intensity of PL is for Na<sub>2</sub>Nb<sub>2</sub>O<sub>6</sub>·nH<sub>2</sub>O fibers prior to thermal treatment and the smaller PL emission is presented by NaNbO<sub>3</sub> fiber-like particles. Prior to thermal treatment, the fibers are found to exhibit emission around 550 nm, while the PL emission is found to be decreased by the following thermal treatment where the band is shifted towards a higher energy region of electromagnetic spectrum, such as the sample with cubic-like particles (450 nm). At low temperature, Almeida et al. obtained two PL bands centered at approximately 430 nm and 540 nm in glass-ceramic containing NaNbO<sub>3</sub> crystal. This result is due to the presence of NaNbO<sub>3</sub> nanocrystals in the material. The emission in 430 nm was attributed to direct exciton recombination, and the low quantum efficiency can indicate that the emission at 540 nm is originated from trap states. At room temperature, the PL band is centered only in region around 430 nm, next to NaNbO<sub>3</sub> PL emission region reported by us [16].

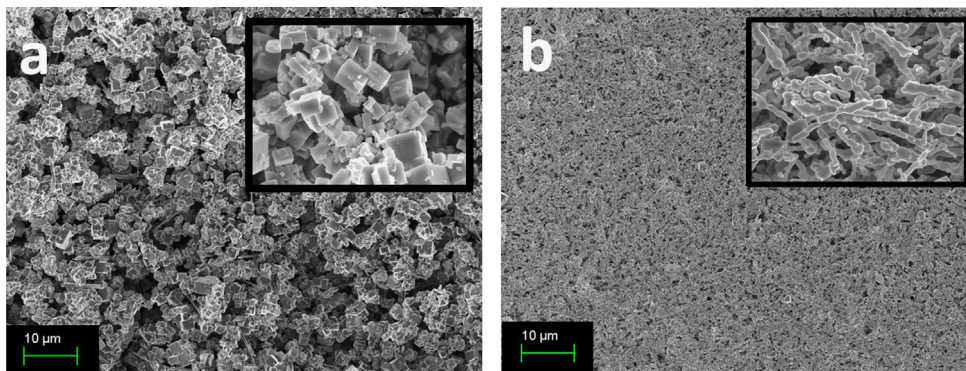
In the work reported here, the PL bands can be attributed to bulk energy levels which is said to be consistent with their attribution to transitions between O<sup>2-</sup> and Nb<sup>5+</sup> and based on the local structure of NbO<sub>6</sub> octahedra. By similar structure analyses, NbO<sub>6</sub> assumes the form of a regular octahedron, which emanates from the strong covalent bonding due to the orbital hybridization between Nb d and O 2p. This crystalline structure is characterized by a high degree of symmetry, without the presence of structural defects (oxygen vacancies or distortions) which are capable of changing the clusters organization. However, the order-disordered NaNbO<sub>3</sub> presents a symmetry rupture along the O–Nb–O bonds, resulting in complex clusters with different coordination numbers ([NbO<sub>6</sub>]<sub>6</sub>–[NbO<sub>5</sub>]) or distortions in the [NbO<sub>6</sub>]<sub>6</sub>–[NbO<sub>6</sub>] octahedral clusters. The wide-band visible emission observed in this work is a characteristic property of practically all self-activated ABO<sub>3</sub> perovskites [17,18].

Also, the result of the PL emission can be attributed to the different products formed under hydrothermal conditions due to increasing synthesis time, and thermal treatment of Na<sub>2</sub>Nb<sub>2</sub>O<sub>6</sub>·nH<sub>2</sub>O to form orthorhombic NaNbO<sub>3</sub> structure, which promotes the displacement of PL band to the blue region (450 nm) observed in the spectra. In addition, this displacement to a more energetic electromagnetic spectrum region and the decrease of PL emission indicates that NaNbO<sub>3</sub> crystalline structure is more stable than Na<sub>2</sub>Nb<sub>2</sub>O<sub>6</sub>·nH<sub>2</sub>O.

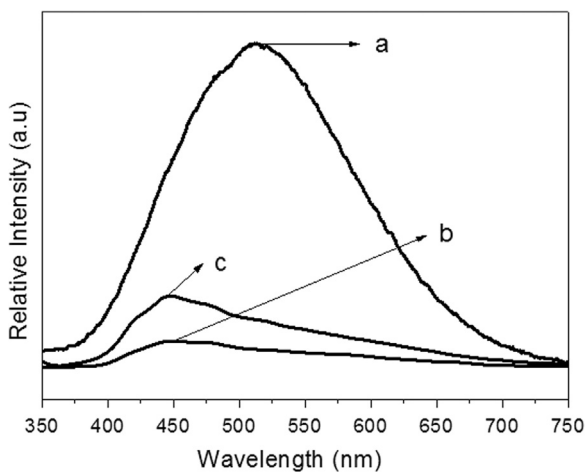
The NaNbO<sub>3</sub> film obtained from fiber particles exhibits smaller PL emission compared to the film obtained from cubic particles, and both PL emission regions are found to be around 450 nm (Fig. 5). These results corroborate to PL emission of the particles,



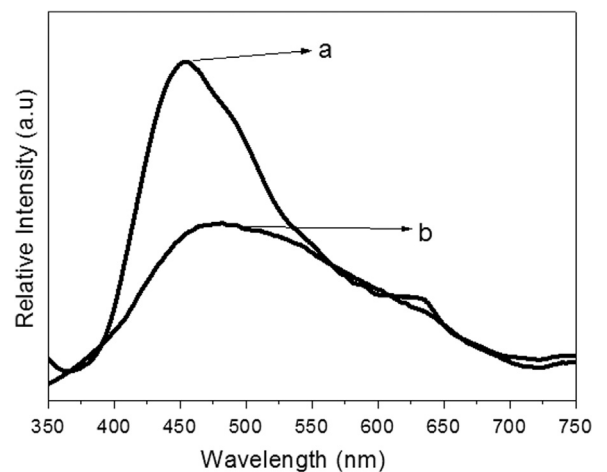
**Fig. 2.** Images obtained by FE-SEM: (a) 30 min prior to thermal treatment; (b) 30 min following thermal treatment; (c) 60 min.



**Fig. 3.** Images obtained by FE-SEM: (a) film obtained with cubic particles; (b) film obtained with fiber particles.



**Fig. 4.** PL spectra of particles: (a) 30 minutes prior to thermal treatment; (b) 30 minutes following thermal treatment; (c) 60 minutes.



**Fig. 5.** PL spectra (a) film obtained with cubic particles; (b) film obtained with fiber-like particles.

since the PL emission of  $\text{NaNbO}_3$  cubic-like particles (Fig. 4c) is higher than  $\text{NaNbO}_3$  fiber-like particles (Fig. 4d).

By researching on PZT, a material with similar structure to the  $\text{NaNbO}_3$ , we verified that PL characteristics can change according to the morphology of the material [19]. However, the PL results shown in this present study indicate that the PL emission region is not related to the morphology of the materials but to the products obtained and the organization of their respective crystalline structure. Since orthorhombic  $\text{NaNbO}_3$  shown here presents two different morphologies (fiber-like particles and cubic-like particles), and both have PL emission in the same region, this region is not the same PL emission region of  $\text{Na}_2\text{Nb}_2\text{O}_6 \cdot n\text{H}_2\text{O}$  which also presents fiber-like particles.

The fast crystallization of  $\text{NaNbO}_3$  obtained from 60-minute synthesis time promoted by microwave can produce a more disorganized structure when compared to  $\text{NaNbO}_3$  obtained by thermal treatment of  $\text{Na}_2\text{Nb}_2\text{O}_6 \cdot n\text{H}_2\text{O}$ . The heating of  $\text{Na}_2\text{Nb}_2\text{O}_6 \cdot n\text{H}_2\text{O}$  at  $500^\circ\text{C}$  to yield orthorhombic  $\text{NaNbO}_3$  promotes a better self-assembly of crystalline structure in fiber-like particles than cube-like particles, decreasing structural defects and the intermediary levels within the band gap, resulting in a decreasing PL emission.

#### 4. Conclusions

$\text{Na}_2\text{Nb}_2\text{O}_6 \cdot n\text{H}_2\text{O}$  fiber-like particles and  $\text{NaNbO}_3$  cubic-like particles were produced by microwave hydrothermal synthesis.  $\text{Na}_2\text{Nb}_2\text{O}_6 \cdot n\text{H}_2\text{O}$  can be used as a precursor to obtain  $\text{NaNbO}_3$  fiber-like particles. The  $\text{NaNbO}_3$  particles are used in the processing of films by means of electrophoretic deposition. In addition to the well-known electrical properties,  $\text{NaNbO}_3$  powders and films are found to present photoluminescence, which is undoubtedly a required property for piezophotonic and piezo-phototronic applications. The emission region of the  $\text{NaNbO}_3$  powders and films is the same (around 450 nm) and is found to be related to the

crystalline structure organization of the powders by means of charge transfer in the lattice of  $\text{NaNbO}_3$ .

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