Funcional lead-free composite

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ABSTRACT

In the present work we report the properties of $NaNbO_3$ ceramic particles obtained by microwave-assisted hydrothermal method and its use in composites with PVDF polymer.

Results indicated that $Na_2Nb_2O_6.H_2O$ particles can be used as precursor to fabricate $NaNbO_3$ fibers-like particles. Photoluminescence spectra, shown that $NaNbO_3$ particles has emission around 445 nm, and the composites obtained using these particles emits in 565 nm. This displacement is due to different defects presented by the composite and the particles. The P-E hysteresis loop of composite shown remanent polarization of 1.5 $\mu C/cm^2$.

Keywords: Lead-free, $NaNbO_3$, microwave-assisted hydrothermal method, composites, PVDF.

1 INTRODUCTION

With technological development and the need for new ceramics materials, several studies are being carried out in order to find combine electrical properties with photoluminescence properties. Order-disorder effects can be the keys to many unsolved structural problems and unexplained structure-related properties in these materials. 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 characteristics.

Ceramic materials have great electrical and optical properties but no plastic deformation and flexibility. The composite formation between ceramic particles and polymers as PVDF can replace traditional ceramics because possibility to combine the ceramics electrical properties and the great polymers mechanical properties. This combine can produce flexible piezophotonics or piezo-phototronics devices [1].

$NaNbO_3$ is a lead-free perovskite semiconductor with well-known piezoelectric property [2]. When $NaNbO_3$ particles presents 1-D morphology the properties can be improved. A method that produce this morphology is the Microwave-assisted Hydrothermal Method (MAHM), which is a method that allows to control the architeture, size, morphology and products obtained from self-assembly process [3]. Chemical reaction and crystal nucleation have a great influence on the final structure of material.

Photoluminencence properties is necessary to aplications in piezophotonics or piezo-phototronics devices. There are several studies about photoluminescence properties of materials obtained by MAHM [4,5], but currently, the obtainment of $NaNbO_3$ particles by this method is a litle explored, as well as the $NaNbO_3$ photoluminescent property and the composite formation whit PVDF polymer.

Thus, the aim of this work is to explore the photoluminescence properties of composite and $NaNbO_3$ particles obtained by MAHM and to verify its possible use in flexible piezophotonics or piezo-phototronics devices.

2 EXPERIMENTAL DETAILS

$NaNbO_3$ ceramic particles were obtained by MAHM beginning with NaOH (7.5 $mol.L^{-1}$), Nb_2O_5 (0.696 g) and PVA solution (0.36 $g.L^{-1}$) was used as template. The reaction was carried out in a Teflon vessel model XP-1500 (CEM Corp.), in a MARS-5 (CEM Corp.) microwave digestor. The volume of precursor suspensio was 30 mL and the synthesis was carried out at 160 °C for 60 minutes of synthesis time. The product was thoroughly washed with water by centrifugation and finally dried at room temperature. After that, the particles obtained were heat treated at 550 ºC for 4 hours. For composite formation, the ceramic powder was combined whit PVDF polymer in volume fraction of 30% ceramic particles and 70% polymer and it was pressed at 190ºC.

The obtained particles were characterized by X-ray powder diffraction (XRD) using a (Rigaku-DMax/2500PC, Japan) with Cu-Kα radiation (λ = 1.5406 Å) in the 2θ range from 20 to 75° with 0.20/min. The morphology of as-prepared samples was observed using a high resolution fieldemission gun scanning electron microscopy FE-SEM (GERMA JEOL JSM 7500F Field Emission Scanning Electron Microscopeny). Photoluminescence (PL) spectra were collected with a Thermal Jarrel-Ash Monospec 27 monochromator and a Hamamatsu R446 photomultiplier. The 350 nm exciting wavelength of a krypton ion laser (Coherent Innova) was used, with the nominal output. The composite were characterized by FE-SEM, PL and Ferroelectric hysteresis measurement at room temperature was performed in a 400 VOLT Amplifier Radiant Technologies, Inc.

3 DISCUSSIONS

The X-ray diffratogram, Figure 1, shows the diffraction pattern of the powders obtained by microwave hydrothermal synthesis. Based on the results, it is observed that before thermal treatment the product was found to consist of $Na_2Nb_2O_6.H_2O$, while after undergoing thermal treatment it was converted into $NaNbO_3$ which is in line with the JCPDS file (JCPDS 33.1270). This result is similar to that obtained by Yu et al. [6].

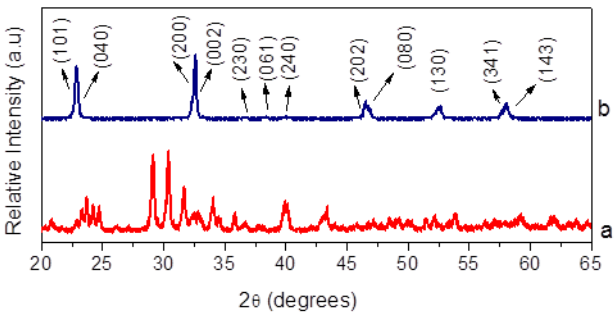

Figure 1: XRD patterns of particles obtained by MAHM: (a) before thermal treatment; (b) following thermal treatment.

FEG-SEM micrographs of as-prepared particles are shown in Figure 2. Looking at the images, it is possible to note that the sample obtained before thermal treatment ($Na_2Nb_2O_6.H_2O$) consists of fiber-like particles (Figure 2a), and the fiber-like shape was found to endure following thermal treatment (Figure 2b). This observation corroborates the XRD results (Figure 1) and suggests that the thermal treatment induced phase transformation though it did not change the particle morphology.

$NaNbO_3$ particles may exhibit polimorphism, and this depends on the chosen synthesis method [7]. By hydrothermal synthesis the polymorfism is controlled by the synthesis paramters, such as pH, precursor concentration, temperature and synthesis time. When the ain is to obtain one-direcionall morpholgy it is common the use of template [8].

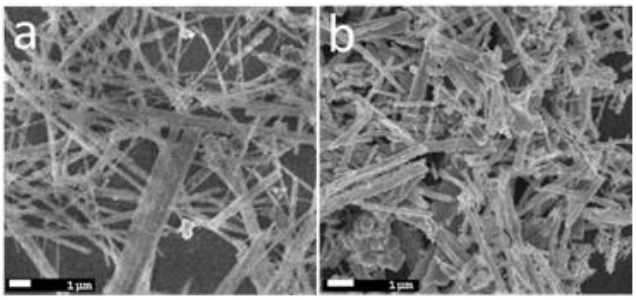

Figure 2: Images obtained by FE-SEM: (a) $Na_2Nb_2O_6.nH_2O$ before thermal treatment and (b) $NaNbO_3$ particles ($Na_2Nb_2O_6.nH_2O$ after thermal treatment).

Photoluminescence spectra of the particles (Figure 3), shown that before thermal treatment, the $Na_2Nb_2O_6.H_2O$ presents higher PL intensity, and emission around 515 nm on the other hand after thermic treatment to form $NaNbO_3$ structures there is a shift of the emission band to higher energy region of electromagnetic spectrum (445 nm) and a decreasing of PL intensity. The PL emission in this region indicated that the structural defects increasing with the change structural, and that PL emission region is associated to structure criatalline of the particles, whereas the particles present the same morphology.

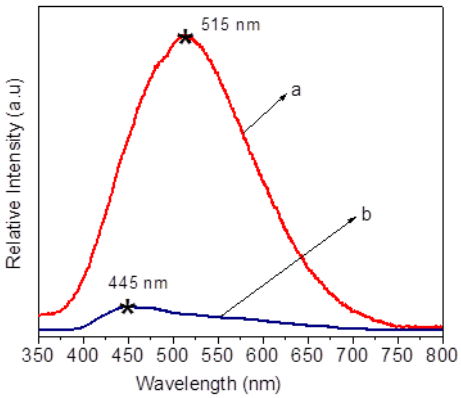

Figure 3: PL spectra of particles: (a) $Na_2Nb_2O_6.nH_2O$; (b) $NaNbO_3$ particles

By PL results was possible to check that the products are disordered at medium range, since PL is powerful probe of certain aspects of medium range such as clusters where the degree local order/disorder is linked to different types electronic transitions related to structural arrangement.

The $NaNbO_3$ is perovskite-structured and it consists in NbO_6 sharing their vertex O atoms and isolated Na atoms [9]. The PL bands can be attributed to energy levels due to the different types of electronic transitions and are related to a specific structural arranges. The photoluminescence emission is based on the local structure of NbO_6 octahedra. By similar structure analyses NbO_6 assume regular octahedron, which originate from the strong covalent bonding due to the orbital hybridization between Nb d and O 2p.

The perovskite structure is characterized by a high degree of symmetry, but the order–disordered of $NaNbO_3$ structure present a symmetry break along the O–Nb–O bonds, resulting in complex clusters with different coordination numbers ($[NbO_6]$–$[NbO_5]$) or distortions on the $[NbO_6]$–$[NbO_6]$ octahedral clusters.

Figure 4 shows the PL spectra of PVDF and composite. The PVDF presents photoluminescence emission in a near region of $NaNbO_3$ particles, but the PL band of composite shifts to 565 nm. This occour due to the differents deffects presented by composite, like surface deffects caused by hot pressing which influences in eletronic transitions.

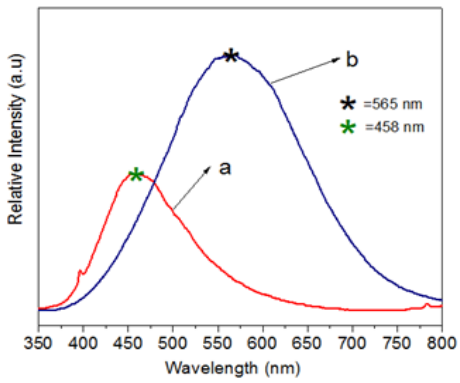

Figure 4: PL spectra of particles: (a) PVDF, (b) composite.

The *P-E* hysteresis loop of the film measured at room temperature is shown in Figure 5. The *P-E* hysteresis loop has characteristics of a ferroelectric behavior but the quality of the ferroelectricity needs to be improved, because the remaining polarization is lower (1.5 μC/cm^2).

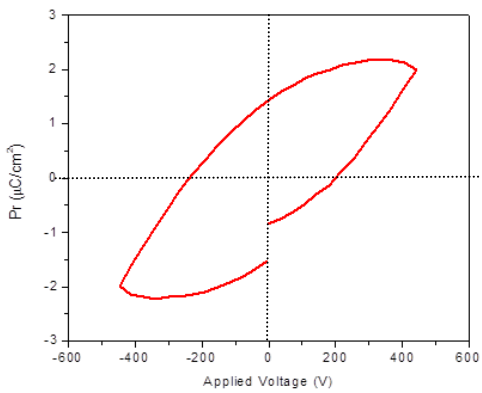

Figure 5: P-E hysteresis of $NaNbO_3$/PVDF composite.

4 CONCLUSION

In summary, $Na_2Nb_2O_6.H_2O$ fiber-like structures may be used as precursor of $NaNbO_3$ particles. After thermal treatment $Na_2Nb_2O_6.H_2O$ crystalline structure is converted to orthorhombic $NaNbO_3$ without changing of fiber-like morphology. Photoluminescence results showed that the PL emission of the particles is related to crystalline and structural defects. Composites showed shift of PL band to lowest energetic region, characteristic of surface defects. The P-E hysteresis loop of composite shown remaineing polarization of 1.5 μC/cm^2.The combination of photoluminescence properties showed by the $NaNbO_3$ particles and composite with the electrical and flexible properties presented by composite can make it possible material applied in flexible devices whit piezophotonics or piezo-phototronics properties.

5 REFERENCES

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