

Influence of Synthesis Method on the Morphology and Properties of ABO_3 Materials

P Vlazan¹, M Stoia², P Svera¹, M Poienar¹, P Sfirloaga^{1,*}

¹National Institute for Research and Development in Electrochemistry and Condensed Matter, Timisoara, Condensed Matter Department, P. Andronescu no.1, 300224, Romania,

²Faculty of Industrial Chemistry and Environmental Engineering, "Politehnica" University of Timisoara, 6 Vasile Parvan Avenue, 300223 Timisoara, Romania

*Corresponding author: paulasfirloaga@gmail.com

Abstract. Materials of potassium niobate ($KNbO_3$) with orthorhombic structure were successfully synthesized using two methods: solvothermal at 220 °C for 12 hours and sol-gel technique at 140 °C for 4h; both obtained samples were heat treated at 600 °C for 4 hours, and the influence of the synthesis methods on their properties was studied. $KNbO_3$ materials were prepared using stoichiometric amounts of $NbCl_5$, KOH as reactants and 1,2 propanediol as reaction medium. The structure and morphology of the $KNbO_3$ powders were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDAX), Fourier transform infrared (FTIR) and Raman spectroscopy.

1. Introduction

Ferroelectric and piezoelectric materials without lead with perovskite ABO_3 -type structure have attracted considerable interest among scientists due to their interesting properties.

Perovskite oxides were reported to be promising gas sensing materials due to their attractive properties such as excellent gas sensitivity, mixed ionic-electronic conductivity, great doping flexibility, ability to accommodate to large amount of dopants and defects, high melting and decomposition temperature [1,2]. Ceramics materials have been widely used in electric devices, such as ultrasonic motors, piezoelectric transformers, and acceleration sensors [3].

Potassium niobate ($KNbO_3$) is one of the most important perovskite-type materials with electro-optic, nonlinear-optic, piezoelectric, luminous, and photocatalytic properties [4]. The properties of perovskite materials are influenced by the preparation method, reaction time, or applied thermal treatment. Many synthetic methods have been reported up to now, such as solid state reaction [5], sol-gel method [6], chemical co-precipitation method [7], citrate complex precursor method [8, 9], and combustion method [10]. Also, there are many reports of powders preparation of unique shape by means of hydrothermal method which has the advantage that could not only produce fine powder but also control the morphology to form one-dimensional nanostructure or thin film [11], solvothermal method - it is very similar to the hydrothermal route the only difference being that the reaction medium consist of organic solvents. Thus the solvothermal method gains one the benefits of both the sol-gel and hydrothermal processes [12] and microwave -assisted process [13]. Use of microwave energy as the heating source of the aqueous solution, brings positive in the hydrothermal synthesis because the volumetric heating is responsible for a more homogeneous crystallization, and the fast kinetic process lowers the synthesis costs [14]. In the case



of hydrothermal synthesis, the characteristics of materials can be altered by changing certain experimental reaction parameters: temperature, time, solvent type, and other.

In this paper, we investigated the KNbO_3 perovskite materials synthesized by solvothermal and sol-gel method in order to study the effect of the synthesis method on the structural and morphological properties. The obtained powders were characterized by XRD techniques, SEM microscopy, FT-IR and Raman spectroscopy.

2. Experimental procedure

The nanostructures of KNbO_3 were synthesized by sol-gel and solvothermal method using niobium chloride (NbCl_5 , Aldrich Products), potassium hydroxide (KOH, Merck, Germany), citric acid and the organic solvent 1,2 propanediol as reaction medium. All of these starting materials were used without any further purification.

For solvothermal synthesis a mixture of 5×10^{-3} NbCl_5 was dissolved in 1,2 propanediol and KOH 7M solution was added drop by drop under continuous stirring on a magnetic stirrer. The solvothermal reaction was carried out in 50 ml autoclave Teflon-lined stainless - steel. The autoclave was heated at 220°C in air oven, reaction duration being 12 h. The precipitate obtained was separated by filtration and washed with distilled water and ethyl alcohol and then dried in the air oven at 80°C for 2 hours.

In the case of KNbO_3 powders preparation by sol-gel method, additional precursors: citric acid sol.1% as chelating agent and ethyl alcohol as gelling agent were used. Sol-gel method allows obtaining single phase compound at low temperatures.

The preparation of KNbO_3 nanostructures was achieved as follows: stoichiometric amounts of niobium (V) chloride was dissolved in 1,2 propanediol to which sol.1% citric acid was added as chelating agent and ethyl alcohol as gelling agent. Precipitation of the KNbO_3 phase was carried out with 7M sol. KOH at room temperature. After this, the temperature was raised to 140°C and was maintained at this value until a black resin was formed.

The resin obtained was then thermally treated at 600°C for 4 hours. After the thermal treatment, the compound was grinded in an agate mortar in order to obtain a powder sample which was then studied morpho-structurally.

The perovskite phase confirmation and crystal structure of the compounds were determined by the X-ray diffractometer PANalyticalX'Pert Pro MPD with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54060\text{\AA}$, at room temperature in the range $20\text{--}80^\circ$ with scan rate of 2° per minute and step size of 0.013° . The lattice parameters and the average crystallite size were calculated using HighScore Plus-software.

The morphological analysis and energy dispersive x ray analysis were achieved using scanning electron microscope (Model Inspect S).

The presence of water and other chemical bonds in the powders was determined by FT-IR spectrometry with a Shimadzu Prestige FT-IR spectrometer, in KBr pellets, in the range $400 - 4000\text{ cm}^{-1}$. Raman measurements were performed using Shamrock 500i Spectrograph (ANDOR, United Kingdom) coupled with a CCD (cooled charge-coupled device) detector. The 514.5 nm laser was used as excitation source with 2 mW power. Olympus BX51 microscope equipped with a x50 long focus objective with NA 0.40 was used to focus the laser light on the sample and collect the scattered light into the spectrometer.

3. Results and discussions

X-ray diffraction analysis was carried out to investigate the structure of the prepared powders. The XRD diffraction spectra of the samples synthesized by solvothermal (Sample (a)) and sol-gel (Sample (b)) methods are almost similar to each other, except for a minor variation (0.1°) of the peaks which are shifted to lower 2θ angle values in the case of the sample (a). The structural parameters for the KNbO_3 samples were obtained by Rietveld refinement of the powders diffraction data using X'Pert HighScore Plus software. Figure 1. shows that the samples are well-crystallized and single phase, indexed with the card JCPDS card no. 01-071-0946 and all diffraction peaks for both samples can be attributed to orthorhombic structure.

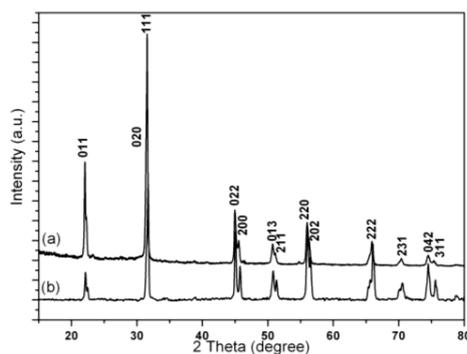


Figure 1. X-ray diffraction for KNbO₃ material obtained by solvothermal (a) and sol-gel (b) methods

The diffraction patterns for both samples have been refined with Amm2 space group. The unit cell parameters for Sample (a) are: $a = 3.97(1)$ $b = 5.67(1)$ and $c = 5.79(1)$ Å, and for Sample (b) are: $a = 3.982(4)$, $b = 5.71(1)$, and $c = 5.69(1)$ Å. It can be observed a slight increase for a and b parameter, while for c parameter a smaller value is obtained the case of Sample (b).

The crystallite size for KNbO₃ samples, synthesized by solvothermal and sol-gel methods were calculated with Scherrer's formula, as following [15]: the nanoparticle dimensions calculated were around 53.3 nm for sample (a) and 273.4 nm for sample (b).

Figure 2 shows the SEM images and EDX elemental analysis spectrum of KNbO₃ nanoparticles (a) and cubes (b) synthesized by means of solvothermal and sol-gel method, respectively.

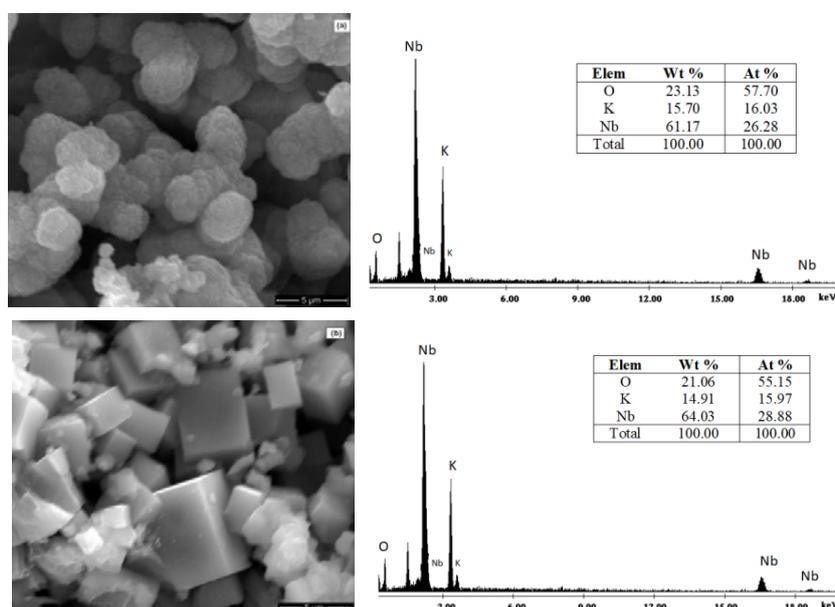


Figure 2. SEM images and EDX analysis spectrum of KNbO₃ synthesized through solvothermal (a) and sol-gel (b) method

The morphology of the particles is different among the two structure types depending on the reaction medium and obtaining method. Thus, by solvothermal method the particles have spherical shapes, agglomerated in asymmetrical formations (Figure 2a) while by sol-gel method cube-shaped particles have been obtained (Figure 2b).

Energy Dispersive X-ray analysis (EDX) was carried out to identify the purity of the KNbO_3 nanoparticles synthesized by the two methods. From the EDX analysis it was determined that the samples did not contain any impurities. High intensity peaks corresponding to Nb and K elements were clearly observed in the EDX patterns of both the samples.

Results of the FT-IR analysis show that the organic compounds are almost completely combusted during the heat treatment (see Fig. 3).

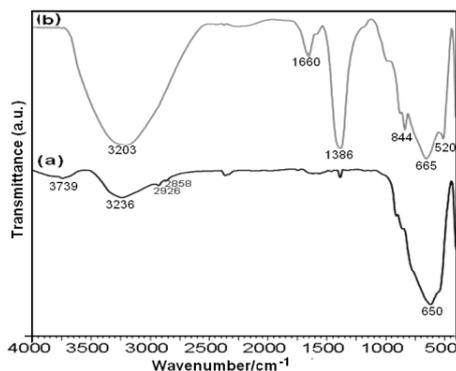


Figure 3. FT-IR spectrum of KNbO_3 synthesized through solvothermal (a) and sol-gel (b) method

Both FT-IR spectra exhibit a large band in the range $450\text{--}1000\text{ cm}^{-1}$, with a maximum around 660 cm^{-1} , characteristic for the vibrations of the Nb-O bonds [16].

The FT-IR spectra of KNbO_3 powder obtained by sol-gel method presents a wide band in the $3000\text{--}3600\text{ cm}^{-1}$ range, with a maximum at 3203 cm^{-1} , probably for the superposition of the bands characteristic to hydrogen bonded O – H groups [17] with the bands characteristic to the vibrations of C-H bonds from residual citric acid, used in synthesis [18]. The bands located at 1660 cm^{-1} and 1386 cm^{-1} can be assigned to the antisymmetric stretching and symmetric vibrations of carbon-oxygen bonds from COO- groups of the residual citric acid [19].

The Raman spectra of KNbO_3 materials obtained through different method are shown in the Figure 4. The present peaks are attributed to the KNbO_3 in crystalline form [20], more exactly in orthorhombic crystalline form [21], which correspond to transverse and longitudinal phonon modes, $B_1(\text{TO}_4)$, $B_1(\text{TO}_3)$, $A_1(\text{TO}_3)$ and $A_1(\text{LO}_3)$, observed at 281.2 , 530.0 , 596.2 and 834.6 cm^{-1} for KNbO_3 obtained by solvothermal method, and $B_1(\text{TO}_4)$, $A_1(\text{TO}_1)$, $B_1(\text{TO}_3)$, $A_1(\text{TO}_3)$ and $A_1(\text{LO}_3)$, observed at 281.2 , 294.3 , 530.0 , 596.2 and 834.6 cm^{-1} for KNbO_3 obtained by sol-gel method, respectively [22].

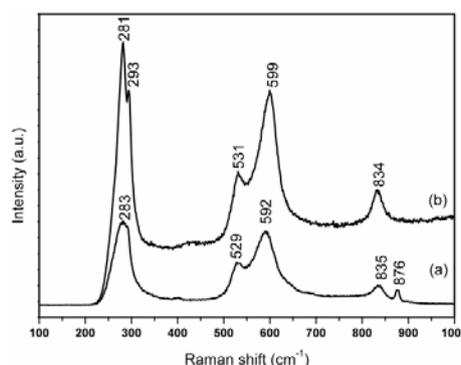


Figure 4. Raman spectra of orthorhombic KNbO_3 ($Bmm2$ space group) obtained by solvothermal (a) and sol-gel (b) methods

At 530.0 and 596.2 cm^{-1} appear Raman bands that represent a double-degenerate symmetric O–Nb–O stretching vibration, which are sensitive to the change of phase structure or presence of other compounds [23].

Increase in intensity of the peak in the Raman spectra indicates increase of grain size of materials which was obtained by sol-gel method.

4. Conclusions

KNbO_3 nanoparticles have been synthesized successfully by solvothermal and sol-gel method, using citric acid and the organic solvent 1,2 propanediol as reaction medium. The obtained materials consist of micro and nanoparticles, with orthorhombic crystallographic structure. Similar results are obtained for both samples from infrared and Raman scattering spectroscopy. Small modifications occurred due to some difference in the corresponding structures.

5. References

- [1] Moos R., Izu N., Rettig F., Reiß S., Shin W., Matsubara I. 2011 *Sensors* 11 3439
- [2] Fergus J. W. 2007 *Sensor Actuat.* 123 1169
- [3] Haertling G.H. 1999 *J Am Ceram Soc* 82 797
- [4] Wang Y., Chen Z., Ye Z., Huang J.Y. 2012 *J. Cryst. Growth* 341 42
- [5] Kinoshita T., Senna M., Doshida Y. and Kishi H. 2012 *Ceram. Int.* 38 1897
- [6] Cao Y., Xiao L., Wang W., Choi D., Nie Z., Yu J., Saraf L. V., Yang Z., Liu J. 2012 *Solid State Sci.* 14 655
- [7] Simon-Seveyrat L, Hajjaji A, Emziane Y, Guiffard B., Guyomar D. 2007 *Ceram. Int.* 33 35
- [8] Kakimoto K-I, Ito T., Ohsato H. 2009 *Ferroelectrics* 380 196
- [9] Kokubo T., Kakimoto K., Ohsato H. 2008 *Key Eng. Mater.* 368-372 1883
- [10] Kingsley J.J., Pederson L.R. 1993 *Materials Letters* 18 89
- [11] Kumada N., Kyoda T., Yonesaki Y., Takei T. and Kinomura N. 2007 *Mater. Res. Bull.* 42 1856
- [12] Nakashima K., Ueno S. and Wada S. 2014 *J. Ceram. Soc. Jpn.* 122 547
- [13] Prado-Gonjal J., Arevalo-Lopez A. M. and Moran E. 2011 *Mater. Res. Bull.* 46 222
- [14] Paula A.J., Parra R., Zaghete M.A., Varela J.A. 2008 *Mater. Lett.* 62 2581
- [15] Cullity BD 1978 *Element of X-ray Diffraction*, 2nd edition, Addison-Wesley publishing company, Reading, MA, 87
- [16] Wang Y., Yi Z., Li Y., Yang Q. and Wang D. 2007 *Ceram. Int.* 33 1611
- [17] Nohman A.K.H., Ismail H.M., Hussein G.A.M. 1995 *J Anal Appl Pyrol* 34 265
- [18] Franklin D.S. and Guhanathan S. 2014 *Polym. Bull.* 71 93
- [19] Coste S., Lecomte A., Thomas P., Merle-Mejean T., Champarnaud-Mesjard J.C. 2007 *J. Sol-Gel Sci Techn* 41 79
- [20] De Andrade J.S, Pinheiro A. G., Vasconcelos I.F., Sasaki J. M., Paiva J.A.C., Valente M.A., Sombra A.S.B. 1999 *J. Phys. Condens. Matter* 11 4451
- [21] Wan S., Zhang B., Sun Y., Tang X., You J. 2015 *Cryst. Eng.Comm.* 17 2636
- [22] Raja S., Ramesh Babu R., Ramamurthi K., Moorthy Babu S. 2018 *Ceram. Int.* 44 3297
- [23] Sun S. Ge Y., Zhao Y., Yuan X., Zhao Y. and Zhou H. 2016 *RSC Adv.* 6 113038

Acknowledgement:

This work was supported by the Demonstrative Experimental Project **48PED/2017**. The authors thank the X-ray Diffraction Laboratory from National Institute for Research and Development in Electrochemistry and Condensed Matter, Timisoara.