Advanced Powder Technology 26 (2015) 113-118

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt



Structural and optical properties of (K,Na)NbO₃ nanoparticles synthesized by a modified sol–gel method using starch media



Advanced Powder Technology

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ARTICLE INFO

Article history: Received 19 May 2014 Received in revised form 20 August 2014 Accepted 22 August 2014 Available online 4 September 2014

Keywords: Potassium sodium niobate Sol-gel Structural properties Optical properties

ABSTRACT

Potassium sodium niobate nanopowders (KNN-NPs) were successfully synthesized by a modified sol-gel method, using starch as the stabilization and polymerization agent. Thermogravometric analysis (TGA) and differential thermal analysis (DTA) techniques were used to determine the needed temperature for the calcination of the prepared gels which is obtained to be 600 °C. Structural and optical properties of the prepared samples were investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), and UV–Vis spectroscopy. The XRD patterns of the synthesized samples confirmed that the structure of the prepared powders, calcined at 600 °C, are orthorhombic. TEM images showed that the particles of KN, NN, and KNN compounds have cubic shape with the average size of 26, 58, and 34 nm, respectively. Type of the optical band gap of the samples was found to be indirect, using UV–Vis diffused reflectance spectroscopy along with Kubelka–Munk method.

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1. Introduction

Lead-based electro-optic (EO) ceramics such as $(Pb,La)(ZrTi)O_3$ (PLZT), which has a strong EO response and good mechanical properties, became interesting materials for optoelectronic devices like EO switches or spatial light modulators. Because of the well-known environmental hazard of lead, much of the current research is oriented towards lead-free materials [1–5].

Among lead free EO materials, alkaline niobates with perovskite structure are known as good candidates for this propose, because these materials have good piezoelectric, ferroelectric, EO, and photocatalytic properties [6–10]. Potassium sodium niobate [(K_xNa_{1-x})NbO₃,(KNN)], which is a combination of anti-ferroelectrics NaNbO₃ and ferroelectric KNbO₃ show good EO properties specially at the morphotropic phase boundary (MPB) (x = 0.5) [11,12]. The common method used for synthesis of KNN powders is solid state reaction (mixed oxides) which involves one or two stages for milling as well as prolonged calcination at high temperatures. However, it is difficult to obtain dense KNN compounds using this conventional method, because of the volatility of sodium and potassium oxides at high temperatures [13,14]. A number of

solution-based powder synthesis routes have been developed and applied to prepare ceramics systems as the alternatives for the mixed oxides. Comparing to mixed oxides method, these wet chemical methods offer the potential for the synthesis of powders with smaller particle size, better chemical uniformity at lower calcination temperatures. Wet Chemical powder synthesis approaches include methods based on hydrothermal [15-17], solvothermal [18,19] and sol-gel [20-22]. Among these, sol-gel is mostly used to prepare KNN powders. In this method, it is very important to use a suitable polymerization agent to achieve homogenous powders, because it plays a vital role in controlling the formation and avoiding agglomeration of nanoparticles. Young et al used ethylene diamine tetraacetic acid (EDTA) to synthesize KNN powders with the particle size in the range of 200-300 nm at 850 °C calcination temperature [21]. Also, some natural polymers such as chitosan, gelatin and starch have been used to synthesize pure and doped metallic oxide nanopowders such as ZnO and MgO [14,23,24]. Starch adopts right-handed helical conformation in aqueous solution, in which the metal ions can make complex with hydroxyl groups due to the presence of extensive number of these groups in the molecular matrix. Starch is known as an effective polymerization agent and environmentally friendly material [25] which makes it suitable to be used as stabilizer in the green synthesis of nanopowders [23,26,27].

In this research, it has been tried to synthesize $(K_x Na_{1-x})NbO_3$ (x = 0, 0.5, 1) nanoparticles, by a simple environmental friendly

http://dx.doi.org/10.1016/j.apt.2014.08.013

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Starch + Water $_$ temperature 4(α -Glucose)_{aa} + Metal Cations $_$ temperature (Glucose-Cations) + NO₂ + $\frac{1}{2}O_2$

Fig. 1. A scheme of the occurred reactions. The metal cations are attached to starch after dissolution of starch to glucose molecules.



Fig. 2. TGA curves and the corresponding derivatives of the prepared gels.

method at low calcination temperature (comparing to solid-state reaction method). The nanoparticles were synthesized by a sol-gel method using starch as the polymerization agent. Also, we determined the type of the energy band gap of the produced nanoparticles (direct or indirect). For this propose, UV–Vis diffused reflectance spectroscopy was employed to study the optical properties and to determine the type of the optical energy band gap of the synthesized samples, which up to our knowledge has not been done before.

2. Experimental

2.1. Materials and methods

Potassium nitrate (KNO₃, ≥99% purity, Sigma–Aldrich), Sodium nitrate (NaNO₃, \geq 99% purity, Sigma–Aldrich), and Ammonium niobate (V) oxalate hydrate (C₄H₄NNbO₉·*x*H₂O, 99.99% purity, Sigma-Aldrich) were used as the starting materials. Starch (C₁₂H₂₂O₁₁, Sigma–Aldrich S9765, Soluble, ACS reagent) was used as a stabilizer and distilled water as the solvent. Certain amounts of the starting materials were taken to produce 5 g of each NaNbO₃ (NN), KNbO₃ (KN), and K_{0.5}Na_{0.5}NbO₃ (KNN) compounds. To obtain 5 g of KNN, 1.5 g potassium nitrate, 1.2 g sodium nitrate, and 10.4 g ammonium niobate (V) oxalate hydrate were separately dissolved in 5, 5 and 100 ml distilled water, respectively and then mixed together. At the same time, 25 g of starch was gradually dissolved in 100 ml distilled water kept at 70 °C, using an oil bath, while stirring until a cloudy solution was obtained. Then, the cations solution was slightly added to the starch solution, keeping the temperature at 80 °C, until a milky gel was obtained. To dry the produced gel, it was placed inside an oven for 24 h at 100 °C. The dried gel was ground in the atmosphere condition using an agate mortar and pestle and then calcined at 600 °C for 4 h. The similar process was repeated to produce NN and KN powders.



Fig. 3. DTA curve of the prepared gels.



Fig. 4. XRD patterns of the prepared samples calcined at 600 °C.



Fig. 5. XRD main peaks of the samples.

2.2. Reaction mechanisms

The semi-crystalline structure of starch is lost when the temperature of the cloudy solution reaches 70 °C. After adding the cations solution to the starch solution, the metal cations are attracted by oxygen of OH branches. By continuing the heating process to decrease the amount of water, the smaller amylose molecules start forming a network that holds water and increases the mixture's viscosity. This process is called starch gelatinization [23]. The nitrates are decomposed to nitrogen dioxide and oxygen during

 Table 1

 The crystalline phase and lattice parameters of the synthesized samples.

the heating process, and are removed from the compounds. The schematic hydrolysis process and alkaline cations attachment are shown in Fig. 1.

2.3. Characterizations

In order to find out the lowest needed calcination temperature, the dried gel was analyzed by thermogravometric (DTG-60/60, Shimadzu) and Differential thermal analysis (DTG-60/60, Shimadzu) techniques. X-ray diffraction analysis (XRD, Philips, X'pert, Cu K α) was used to study the lattice structure of the prepared samples. The morphology of the synthesized powders was examined using transmission electron microscopy technique (TEM, CM120, Philips). UV–Vis spectroscopy (Jasco, V-670) was employed to determine the type and the value of the optical energy band gap of the prepared samples.

3. Results and discussions

3.1. Thermal analysis (TGA and DTA)

The thermal behavior of the NN, KN, and KNN dried gels were analyzed using thermogravometric technique, from room temperature to 800 °C, Fig 2. The obtained TG curves of all the three prepared compounds can be divided into three main regions: 203-205 °C, 290-295 °C, and 496-522 °C. Although TGA was carried out on the dried-gel, still some water is remained which is evaporated temperature less than 200 °C. The first two regions are attributed to decomposition of the starch chains. The carboxvlic compounds are decomposed and the pyrocholor phase is formed at temperature less than 400 °C. The third region, which is related to the formation of the final products, starts at about 400 °C. It is observed from the TG curves that the lowest calcination temperature needed to obtain the fine powders of pure NN, KN, and KNN is about 600 °C. The minimum weight loss is related to decomposition of the KN dried gel, due to the higher atomic mass of potassium comparing to sodium.

Also, DTA was carried out to obtain the exothermic temperatures. Fig. 3 shows the DTA curves obtained for the dried gels of NN, KN, and KNN samples. Two peaks are detected in each curve. The first peak appears at 304 °C for all the three samples due to the decomposition of starch and formation of pyrocholor phases. The second peak is related to the minimum calcination temperature needed to obtain NN, KN, and KNN powders. The calcination temperature for KN is higher comparing to NN and KNN, which can be due to the higher chemical reactivity of Na⁺ in comparison with K⁺. The DTA results are in good agreement with the TGA. Therefore, we chose 600 °C as the calcination temperature for preparing NN, KN, and KNN compounds.

3.2. Structure analysis

X-ray diffraction analysis was carried out to investigate the structure of the prepared powders. The XRD patterns of the synthesized NN, KN and KNN powders are shown in Fig. 4. All the three samples have orthorhombic structures, corresponding to JCPDS

Materials	Crystal system	Space group	Lattice parameters			
			a (Å)	b (Å)	<i>c</i> (Å)	Volume (Å ³)
NaNbO ₃	Orthorhombic	(Pbcm)	5.515(3)	5.507(8)	15.605(4)	474.05(2)
KNbO ₃	Orthorhombic	(Bmm2)	5.687(3)	3.963(7)	5.685(2)	128.16(0)
(K _{0.5} Na _{0.5})NbO ₃	Orthorhombic	(Bmm2)	5.636(3)	3.980(1)	5.631(6)	126.33(2)



Fig. 6. Graph related to SSP method of the prepared samples calcined at 600 °C.

 Table 2

 The crystallite size and strain lattice of the synthesized samples.

Materials	Scherrer formula	Size strain plot		
	Crystallite size (D) (nm)	Crystallite size (D) (nm)	$\begin{array}{l} \text{Strain} \\ (\epsilon) \times 10^{-3} \end{array}$	
NaNbO ₃ KNbO ₃ (K _{0.5} Na _{0.5})NbO ₃	24.9(9) 24.5(3) 23.7(8)	24.5(5) 26.0(9) 23.8(5)	2.9(9) 3.9(9) 4.3(9)	

database cards (JCPDS-73-0803 for NN and JCPDS-32-0822 for KN, and KNN). Fig. 5 shows an enclosed image of the main diffraction peaks of the synthesized NN, KN, and KNN nanopowders, in the range of 30.5–33.5°. It is observed that the main diffraction peak related to NN sample occurs at higher degrees comparing to the one for KN. The ionic radius of K⁺ (1.33 Å) is bigger than Na⁺ (0.95 Å), therefore the d plane spacing of KN lattice for the main diffraction peak is bigger than that of NN. As expected, the main diffraction peak related to KNN occurs between KN and NN. The lattice parameters of the prepared NN, KN, and KNN powders were calculated using least squares refinement method, presented in Table 1.

In this study, two methods were used to evaluate the crystallite size of the synthesized samples. In the first method, the crystallite sizes were simply estimated by Scherrer's equation using the main diffraction peaks of the samples. Since in this method only one peak contributes for the calculation of the crystallite size, therefore the obtained value is not very accurate. Size strain plot (SSP) method is the one which makes it possible to consider a number of the diffraction peaks from the XRD pattern to calculate the crystallite size and also the lattice strain [28]. Accordingly, we have:

$$(d_{hkl}\beta_{hkl}\cos\theta)^2 = \frac{K}{D} \left(d_{hkl}^2\beta_{hkl}\cos\theta \right) + \left(\frac{\varepsilon}{2}\right)^2 \tag{1}$$

where *K* is a constant that depends on the shape of the particles and is about 4/3. To estimate the crystallite size and the lattice strain, the term of $(d\beta\cos\theta)^2$ is plotted against $d^2\beta\cos\theta$, as shown in Fig. 6, where β is the FWHM of the diffraction peaks, *d* is the plane's spacing, and θ is the diffraction peak angle. The obtained points are linearly fitted and the crystallite size is calculated from the slope of linearly fitted data and the lattice strain from *y*-intercept. The obtained crystallite size and lattice strain of the prepared NN, KN, and KNN samples are presented in Table 2.



Fig. 7. TEM micrographs and the corresponding size distribution histograms of (a) KNbO₃ (b) NaNbO₃ and (c) (K_{0.5}Na_{0.5})NbO₃.



Fig. 8. UV-Visible reflectance and absorbance spectra of the prepared samples calcined at 600 °C.



Fig. 9. The maximum of $d[Ln(\alpha hv)]/d[hv]$ versus hv which gives the optical band gap (E_g) .

3.3. Morphology studies

The TEM micrographs and the corresponding size distribution histograms are given in Fig. 7. The TEM images show that the KN, NN, and KNN nanoparticles have cubic shapes. It is also found out that the average particle size of the prepared KN powders is smaller than that of NN (26 nm and 58 nm for KN and NN particles, respectively). Because the same synthesis conditions were chosen to make the nanoparticles, this can be related to the chemical reactivity of Na⁺ which is higher than K⁺, causing the higher speed of growing NN nanoparticles comparing to KN. For alkali elements, the oxidation speed is increased from bottom to top therefore; NN particles are nucleated and self assembled faster compared to KN, which results to higher growing speed of the NN nanoparticles. As expected, the average particle size of the prepared KNN nanoparticles are about 34 nm which is between KN and NN average particle sizes.

3.4. Optical analysis

Study of the optical properties of the samples was based on the results obtained from UV–Vis diffused reflectance spectroscopy. The reflectance and the corresponding absorbance of the synthesized NN, KN, and KNN samples were measured in the range of 200–800 nm wavelengths, Fig. 8. It is observed that the absorption edge of the prepared NN occurs at lower wavelength compared to KN and KNN samples. The optical band gap of the specimens was calculated by Kubelka–Munk method, using Tauc relation [29].

$$(\alpha h\nu)^{\frac{1}{m}} = c(h\nu - E_g) \tag{2}$$

In this relation *m* is chosen 2 and 1/2 for the specimens having indirect and direct band gaps, respectively. By plotting $(\alpha h v)^{\frac{1}{m}}$ versus *hv*, *E*_g can be estimated from the intersection of the tangent and



Fig. 10. The optical band gap is obtained from interplotting of $(\alpha hv)^{1/m}$ versus hv (a) m = 2 and (b) $m = \frac{1}{2}$ for indirect and direct band gaps, respectively.

Table 3

The obtained energy band gap values of the synthesized samples.

Materials	Band gap (eV) (without considering <i>m</i>)	Indirect band gap (eV) (<i>m</i> = 2)	Direct band gap (eV) (<i>m</i> = 1/2)	Other works (eV)
NaNbO3	3.40	3.38	3.80	3.4 [26] 3.45 [27]
KNbO₃	3.21	3.18	3.57	3.1 [26] 3.13 [5]
(K _{0.5} Na _{0.5})NbO ₃	3.17	3.15	3.54	3.09 [28]

the *x*-axis. The density of states (DOS) studies has shown that both $KNbO_3$ and $NaNbO_3$ have indirect band gaps [30,31]. However, both direct and indirect energy band gaps have been reported for the optical band gap of KNN families [9,31,32]. Therefore, it is not clear that which value of m should be chosen to obtain the energy band gap of our synthesized samples. Eq. (2) can be rewritten as:

$$Ln(\alpha hv)^{\frac{1}{m}} = Ln(hv - E_g) \Rightarrow Ln(\alpha hv) = mLn(hv - E_g)$$

$$\Rightarrow \frac{d[Ln(\alpha hv)]}{d(hv)} = \frac{m}{hv - E_g}$$
(3)

The term $d[Ln(\alpha hv)]/d(hv)$ can be plotted versus hv and the maximum of the curve gives value of E_g with good approximation, Fig. 9. Based on this method, the values of E_g for the prepared NN, KN, and KNN samples were found to be 3.40, 3.21, and 3.17 eV, respectively. Now, to find out the exact type (direct or indirect) of our samples band gaps, both m = 2, 1/2 were selected in Tauc relation, Fig. 10. The obtained values of the band gaps are given in Table 3. As can be seen, the E_g values regarding m = 2 are closer to the values obtained by using Eq. (3). Therefore, it can be concluded that our prepared NN, KN, and KNN have indirect energy band gaps.

4. Conclusions

NN, KN, KNN nanopowders were synthesized by a simple modified sol-gel route using starch as the stabilizer agent. The needed calcination temperature was found to be 600 °C based on DTA and TGA results. The XRD patterns showed that the prepared powders have orthorhombic phase structures and no extra peaks are detected. The average size of the crystallites and the lattice strain were calculated using Scherrer formula and SSP method. TEM images showed that the prepared nanopowders have the cubic shape with the average size of 26, 58, and 34 nm for KN, NN, and KNN, respectively. UV–Vis diffused reflectance measurements were carried out in the wavelength range of 200-800 nm and using Kubelka–Munk method confirmed that the optical energy band gap of the prepared samples is indirect, with the value 3.40, 3.21, and 3.17 eV for the synthesized NN, KN, and KNN nanopowders, respectively.

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