Green synthesis and characterization of ANbO$_3$ ($A = \text{Na, K}$) nanopowders fabricated using a biopolymer

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Received 26 November 2016
Revised 14 April 2017
Accepted 17 April 2017
Published 1 June 2017

Lead-free sodium niobate (NaNbO$_3$, NN) and potassium niobate (KNbO$_3$, KN) nanopowders were successfully synthesized by a simple and green synthesis process in gelatin media. Gelatin, which is a biopolymer, was used as stabilizer. In order to determine the lowest calcination temperature needed to obtain pure NN and KN nanopowders, the produced gels were analyzed by thermogravimetric analyzer (TGA). The produced gels were calcined at 500°C and 600°C. The structural and optical properties of the prepared powders were examined using X-ray diffraction (XRD) technique, transmission electron microscopy (TEM), and UV–Vis spectroscopy. The XRD results revealed that pure phase NN and KN nanopowders were formed at low temperature calcination of 500°C and 600°C, respectively. The Scherrer formula and size-strain plot (SSP) method were employed to estimate crystallite size and lattice strain of the samples. The TEM images show that the NN and KN samples calcined at 600°C have cubic shape with an average particle size of 60.95 and 39.29 nm, respectively. The optical bandgap energy of the samples was calculated using UV–Vis diffused reflectance spectra of the samples and Kubelka–Munck relation.

Keywords: Green synthesis; NaNbO$_3$; KNbO$_3$; sol–gel; gelatin.

PACS numbers: 73.63.Bd, 74.25.Gz, 77.84.Dy

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1. Introduction

NaNbO$_3$ (NN) and KNbO$_3$ (KN) compounds have orthorhombic structure at room temperature and high Curie temperature.$^{1-3}$ NaNbO$_3$ is an anti-ferroelectric perovskite oxide with unique physical and chemical properties, such as low density, high sound velocity, and photocatalysis.$^{1,3,4}$ KNbO$_3$ is a ferroelectric material with extremely high nonlinear optical and high electromechanical coupling coefficients.$^{3,5,6}$ However, it is difficult to achieve pure phase KN and NN powders with high density using solid-state reaction method because of the volatility of sodium and potassium oxides at high temperatures.$^{6-8}$

One way to solve this problem is synthesizing at low processing temperature and reducing the particle size of the finally prepared sample.$^9$ Some important chemical methods, such as hydrothermal, solvothermal, coprecipitation and sol–gel, have been employed in the synthesis of micro and nanopowders.$^{10-13}$ Recently, researchers have concentrated on the synthesis of NN and KN nanopowders by sol–gel route. In this method, using a suitable stabilizer agent, such as citric acid (CA), triethanolamine (TEA), or ethylene diamine tetraacetic acid (EDTA), is extremely important to obtain homogenous powders since it plays a very important role in controlling the formation and preventing agglomeration of nanoparticles.$^{6,14}$ Yang et al. used a mixture of EDTA and CA as stabilizer to synthesize KN powders at calcination temperature of 850$^\circ$C.$^6$ Recently, researchers have focused on the green synthesis of nanopowders due to environmental considerations. In green synthesis of nanoparticles, choice of a green solvent and a nontoxic stabilizer is very important. Some biopolymers such as chitosan, cellulose and starch have been employed to synthesize nanopowders. In our previous paper synthesis of NN and KN nanoparticles using starch biopolymer as stabilizer has been reported.$^7$ Starch is known as an environmentally friendly material which is used in green synthesis of nanoparticles.$^7$

Gelatin is an inexpensive biopolymer composed of collagen, which has been used as stabilizer to synthesize nanopowders.$^8$ Gelatin, which has a long chain structure, controls the growth of particles, while simultaneously preventing them from agglomeration.$^{15}$

In this research, KN and NN nanopowders were synthesized for the first time by a facile green synthesis method at low calcination temperature. Gelatin and distilled water were used as stabilizer agent and solvent, respectively. In addition, structural and optical properties of prepared samples were studied.

2. Experimental Procedure

In order to prepare NN and KN nanopowders, potassium nitrate (KNO$_3$, $\geq$ 99% purity, Sigma-Aldrich), sodium nitrate (NaNO$_3$, $\geq$ 99% purity, Sigma-Aldrich), and ammonium niobate (V) oxalate hydrate (C$_4$H$_4$NNbO$_9$·xH$_2$O, 99.99% purity, Sigma-Aldrich) are used as starting materials. Gelatin type B from bovine skin (Sigma-Aldrich) was used as a stabilizer and distilled water as solvent. To obtain 3 g
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of NN nanopowders, 1.56 g of sodium nitrate, and 6.54 g of ammonium niobate (V) oxalate hydrate were separately dissolved in distilled water and then mixed together. At the same time, 15 g of gelatin was gradually dissolved in 50 mL distilled water at 60°C. Then, the alkali metal solution was added slowly to the gelatin solution, keeping the temperature at 80°C, until a viscous gel was obtained. The produced gel was calcined at 500°C and 600°C for 4 h with heating rate of 4°C/min. A similar route was repeated to produce KN nanopowders.

TGA (DTG-60/60, Shimadzu) was employed for thermal analysis of the prepared gel. XRD analysis (Philips, X’pert, CuK$_\alpha$) and TEM (CM120, Philips) were used to investigate the structural properties and morphology of the prepared powders. The value of the energy bandgap of the prepared samples was calculated using UV–Vis spectroscopy (Jasco, V-670).

3. Results and Discussion

3.1. Thermal analysis

Figures 1(a) and 1(b) show the TGA curves of the produced NN and KN gels and their corresponding derivative (DrTGA is abbreviation of derivate of TGA), respectively. The TG analysis was carried out starting from room temperature up to 800°C with a heating rate of 5°C/min. For the temperatures up to 550°C, mass losses of 66% and 51% have occurred for NN and KN gels, respectively. As shown in Figs. 1(a) and 1(b), the TGA curves can be divided into three main parts: Room temperature (RT) to 150°C, 150–400°C and 400–550°C with main peaks of 70°C, 235°C, 462°C and 85°C, 236°C, 508°C for NN and KN gels, respectively. The first and second parts are related to the initial loss of water and the decomposition of the organic materials, respectively. The pyrochlore phase is formed at about 300°C. The third part is related to the formation of the perovskite structure. The maximum peak of third part is at 462°C and 508°C for NN and KN, respectively. It is found
from the TGA results that the lowest calcination temperature needed to obtain the fine powders of pure NN is lower than that of pure KN. It can be due to the higher chemical reactivity of Na$^+$ in comparison with K$^+$. The weight loss of KN is lower than that of NN gel due to higher atomic mass potassium compared to sodium.

3.2. Structural properties

In order to examine the structural properties of prepared samples, XRD technique was used. The XRD patterns of the synthesized NN and KN samples are shown in Figs. 2(a) and 2(b). The resulting XRD patterns show that NN and KN have been crystallized in a perovskite structure with orthorhombic phase, corresponding to database cards (JCPDS 73-0803 for NN and JCPDS 32-0822 for KN). It can be found from XRD results, which the NN samples calcined at 500°C and 600°C have pure orthorhombic phase. In the XRD pattern of KN calcined at 500°C, some small unwanted peaks are observed, which can be attributed to K$_4$Nb$_8$O$_{17}$ (JCPDS 076-0977). By increasing the calcination temperature, these unwanted peaks disappear in the XRD pattern of the KN calcined at 600°C. Any extra peaks related to pyrochlore and impurity phase in XRD patterns of NN calcined at 500°C and 600°C are detected. Figure 3 shows an enlarged image of the main diffraction peaks of the synthesized samples, in the range of $30–34^\circ$. The main diffraction peak gets sharper as the calcination temperature increases, which is an indication of crystallinity enhancement as well as the crystallite size increase. In addition, it is observed that (111) diffraction peak of the KN has shifted to lower angles by increasing calcination temperature, while no considerable shift for NN is detected. Furthermore, the main peak of NN samples occurs at higher degrees than the main peak of 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.
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Fig. 3. XRD main peaks of the prepared samples.

The average crystallite size ($D$) of the prepared samples was estimated using Scherrer formula ($D = \frac{k\lambda}{\beta_{hkl}\cos \theta}$), where $\beta_{hkl}$ is the full width at half maximum (FWHM) of the $(hkl)$ diffraction peak. The obtained results of Scherrer formula are not very accurate since in this method only one peak is used for the calculation of the crystallite size. Size strain plot (SSP) method is the one which makes it possible to consider several diffraction peaks from the XRD pattern to calculate the crystallite size ($D$) and also the lattice strain ($\varepsilon$). Accordingly, we have

$$ (d_{hkl}\beta_{hkl}\cos \theta)^2 = \frac{K}{D}(d_{hkl}^2\beta_{hkl}\cos \theta) + (\varepsilon/2)^2, \quad (1) $$

where $K$ is a constant that depends on the shape of the particles and is about $4/3$. As shown in Fig. 4, the $(d_{hkl}\beta_{hkl}\cos \theta)^2$ term is plotted versus $d_{hkl}^2\beta_{hkl}\cos \theta$ and is linearly fitted data to calculate the $D$ and $\varepsilon$. The slope and the intercept of the linearly fitted data and $x$-axis give $D$ and $\varepsilon$, respectively. The obtained crystallite size and lattice strain of the prepared NN and KN are presented in Table 1. The obtained $\varepsilon$ of prepared samples in this work are bigger than those of reported in our previous paper.  

3.3. Morphology analysis

The TEM images and the corresponding size distribution of the NN and KN calcined at 600°C are given in Figs. 5 and 6. The TEM images show that the particles of the NN and KN samples have cubic shapes with smooth surface. The average particle sizes obtained are 60.95 and 39.29 nm, for NN and KN, respectively, which are more similar to the calculated crystallite size. It is due to the presence of gelatin as stabilizer which prevent particles from agglomerating. It is observed that the average particle size of prepared NN is bigger than that of KN. The higher speed of
Fig. 4. SSP plot of the NN and KN samples calcined at 500°C and 600°C.

Table 1. The crystalline phase and lattice parameters of the synthesized samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcination temperature (°C)</th>
<th>Crystal system</th>
<th>Space group</th>
<th>Scherrer formula</th>
<th>SSP method</th>
<th>$D$ (nm)</th>
<th>$\varepsilon$ from TEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>KN</td>
<td>500</td>
<td>Orthorhombic</td>
<td>(Bmm2)</td>
<td>$y = 0.0065x + 6E-05$</td>
<td>$R^2 = 0.9931$</td>
<td>21.29</td>
<td>0.015</td>
</tr>
<tr>
<td>KN</td>
<td>600</td>
<td>Orthorhombic</td>
<td>(Bmm2)</td>
<td>$y = 0.0059x + 9E-05$</td>
<td>$R^2 = 0.9408$</td>
<td>21.74</td>
<td>0.019 39.29</td>
</tr>
<tr>
<td>NN</td>
<td>500</td>
<td>Orthorhombic</td>
<td>(Pbcm)</td>
<td>$y = 0.0065x + 7E-05$</td>
<td>$R^2 = 0.9335$</td>
<td>25.36</td>
<td>0.017</td>
</tr>
<tr>
<td>NN</td>
<td>600</td>
<td>Orthorhombic</td>
<td>(Pbcm)</td>
<td>$y = 0.006x + 0.0001$</td>
<td>$R^2 = 0.8241$</td>
<td>24.47</td>
<td>0.020 60.95</td>
</tr>
</tbody>
</table>

Growing NN comparing to KN, it can be related to the chemical reactivity of Na\(^+\) which is higher than K\(^+\).\(^7\)

3.4. Optic properties

The optical properties of the samples were studied based on the results obtained from UV–Vis diffused reflectance spectroscopy, in the range of 200–800 nm wavelengths. Figure 7 shows the reflectance and absorbance spectra of the NN.
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Fig. 5. TEM image of (a) NN and (b) KN samples calcined at 600$^\circ$C.

Fig. 6. Size distribution histogram of (a) NN and (b) KN samples calcined at 600$^\circ$C.

and KN samples calcined at 600$^\circ$C. It is seen that the absorption edge of the prepared KN nanopowders ($\lambda = 390$ nm) is higher than that of the KN nanopowders ($\lambda = 365$ nm). The optical band gap ($E_g$) of the samples was calculated using the UV–Vis diffused reflectance spectra and Tauc relation

$$ (\alpha h\nu)^n = c(h\nu - E_g), $$

(2)
Fig. 7. UV–Vis absorbance and reflectance spectra of the prepared samples calcined at 600°C.

Fig. 8. Plot of $(\alpha h\nu)^{1/2}$ versus photon energy $(h\nu)$.

where $c$ is a constant, $h\nu$ is the incident photon energy, and $\alpha$ is absorption coefficient calculated using the Kubelka–Munk function which is given by $\alpha = (1 - R)^2 / 2R$, where $R$ is the reflectance value.\cite{7,9,18} In relation (2), $n$ is 2 and $1/2$ for the samples with direct and indirect bandgaps, respectively.\cite{7,9} By plotting $(\alpha h\nu)^n$ versus $h\nu$, $E_g$ can be determined from the intersection of the tangent and the $x$-axis, Fig. 8. The density of states (DOS) studies have shown that both KNbO$_3$ and NaNbO$_3$ have indirect bandgaps.\cite{19} There is another way to calculate $E_g$ without knowing the exact type of bandgap (direct or indirect). Equation (2) can be rewritten as

$$\ln(\alpha h\nu)^n = \ln(h\nu - E_g) \Rightarrow$$

$$\ln(\alpha h\nu) = \left(\frac{1}{n}\right) \ln(h\nu - E_g) \Rightarrow$$

differentiate $\Rightarrow \frac{d[\ln(\alpha h\nu)]}{d(h\nu)} = \frac{1}{n} \frac{1}{h\nu - E_g}$. \hspace{1cm} (3)
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![Figure 9](image)

**Fig. 9.** The maximum of $d[\ln(a\nu)]/d[h\nu]$ versus $h\nu$, which gives the optical bandgap ($E_g$).

**Table 2.** The obtained energy bandgap values of the synthesized samples calcined at 600°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorption edge (nm)</th>
<th>$E_g$ (corresponding of absorption edge) (eV)</th>
<th>$E_g$ (without considering $n$) (eV)</th>
<th>$E_g$ (Indirect, $n = 1/2$) (eV)</th>
<th>Other works (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KN</td>
<td>390</td>
<td>3.18</td>
<td>3.24</td>
<td>3.19</td>
<td>3.10 [18]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.13 [4]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.21 [7]</td>
</tr>
<tr>
<td>NN</td>
<td>365</td>
<td>3.40</td>
<td>3.53</td>
<td>3.40</td>
<td>3.40 [18]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.34 [17]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.40 [7]</td>
</tr>
</tbody>
</table>

The term $d[\ln(a\nu)]/d(h\nu)$ can be plotted versus $h\nu$ and the maximum of the curve gives $E_g$ with good approximation, Fig. 9. Based on this method, the values of $E_g$ for the prepared NN and KN nanopowders were found to be 3.53 and 3.24 eV, respectively. The results of optical studies of the samples are summarized in Table 2.

**4. Conclusion**

NN and KN nanopowders were synthesized by a simple green synthesis method using gelatin biopolymer as a stabilizing agent at low calcination temperature. The prepared NN and KN gels were calcined at 500°C and 600°C to obtain pure phase NN and KN nanopowders. The XRD patterns show that the prepared samples crystallize in perovskite structure with orthorhombic phase. It is observed some small unwanted peaks in the XRD pattern of KN calcined at 500°C, disappeared by increasing the calcination temperature. No extra peaks related to the impurities or pyrochlore phases are detected for samples calcined at 600°C. In addition, it is observed that the main diffraction peak of the KN has shifted to lower angles by
increasing calcination temperature, while no considerable shift for NN is detected. The line broadening of the prepared samples was analyzed by Scherrer formula and SSP method. The TEM image of samples revealed that NN and KN nanopowders calcined at 600°C have cubic shapes with average particles size of 60.95 and 39.29 nm, respectively. The optical band gap of the prepared samples was calculated from UV–Vis diffused reflectance spectra. The \( E_g \) of NN and KN nanopowders calcined at 600°C were calculated without considering \( n \) (type of bandgap).

References