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A facile sol–gel approach to synthesize KNN nanoparticles at low temperature

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ABSTRACT

Potassium sodium niobite nanoparticles (KNN-NPs) were synthesized using sol–gel method. A solution of K, Na, and Nb cations was prepared using gelatin as a stabilizer which resulted a clear gel after thermal treatment. The obtained gel was first analyzed by thermogravometric analyzer (TGA) and differential scanning calorimetry (DSC) and then calcined at different temperatures of 500, 600, 700, and 800 °C. The X-ray diffraction (XRD) patterns of the synthesized samples confirmed formation of the orthorhombic crystal phase of KNN-NPs at 500 °C. Transmission electron microscopy (TEM) observations showed a cubic morphology of KNN-NPs. Our results revealed that gelatin is an excellent candidate to be used as stabilizer for preparing nanoparticles of complex compounds including KNN-NPs.

1. Introduction

Potassium sodium niobate $(K_{1-x}Na_x)NbO_3$ compounds, in both ceramic and nanostructure forms, show high electromechanical and piezoelectric properties [1–5]. Due to these interesting properties, KNN compounds have been used widely in various applications such as sensors, actuators and transducers [6,7]. The best radial coupling factor, k_p, for these materials is obtained at $x=0.5$ ($K_{0.5}Na_{0.5}NbO_3$) [8] due to the increase of the domain orientation possibilities [9]. However, it is difficult to obtain a sample with high density using conventional and mixed oxides methods [10,11]. Since the stoichiometry plays an important role to obtain a high density samples, chemical methods result in obtaining high purity and good stoichiometry materials. Using these methods the high quality powders can be produced from homogene solutions. Several chemical methods have been used to prepare KNN powders both in micro and nano structure forms such as hydrothermal [12–15], solvothermal [12,16], precipitation [17] and sol–gel [18,19] among these methods, sol–gel is the most simple and common synthesis route which has been used to synthesize KNN micro and nanopowders. In this method it is very important to use a suitable polymerization agent. Yang et al. used EDTA and synthesized KNN powders at calcination temperature of 850 °C, with particle size in the range of 200–300 nm [20]. Gelatin is a kind of natural polymers that have been used to synthesize pure and doped metal oxide nanopowders [21–25]. Very fine and narrow size distribution nanoparticles have been obtained at lower temperature using gelatin compared to EDTA. Furthermore, gelatin is a natural material (obtained from animal's skin such as bovine (cow) and pig) with lower cost and easy to find.

In this work, KNN nanoparticles were synthesized by a simple sol–gel method at low calcination temperature. In comparison with the other published works, using gelatin as the stabilizer in order to control the growth of the nanoparticles, gives better results due to the special behavior of gelatin. Gelatin is expanded about 30 times during calcination process; therefore, can terminate the growth of the particles [25].

2. Experimental

2.1. Materials and methods

To prepare KNN-NPs, gelatin type B from bovine skin (Sigma-Aldrich) was used as a stabilizer. The starting materials were potassium nitrate (KNO_3, ≥99% purity, Sigma-Aldrich), Sodium nitrate ($NaNO_3$, ≥99% purity, Sigma-Aldrich), and ammonium niobate (*V*) oxalate hydrate ($C_4H_4NNbO_9 \cdot xH_2O$, 99.99% purity, Sigma-Aldrich) and distilled water as a solvent. To obtain 5 g of the final product, 2.94 g potassium nitrate, 2.48 g sodium nitrate and 20.97 g ammonium niobate (*V*) oxalate hydrate, were separately dissolved in 5, 5 and 100 ml distilled water respectively and then were mixed together. On the other hand, 15 g of gelatin was gradually dissolved in 100 ml distilled water at 60 °C using an oil bath while stirred at about 200 rpm to obtain a clear gelatin solution. Then the stirring speed was decreased to about 50 rpm and the cations solution was slightly added to the gelatin solution. The temperature of the oil bath was kept at 80 °C until a honey-like (color and viscosity) gel was obtained. The produced gel was rubbed on the inner walls of four crucibles and then calcined at

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different temperatures of 500, 600, 700 and 800 °C to obtain the KNN white powders.

2.2. Characterizations

In order to find out the lowest needed calcination temperature, the prepared gel was analyzed by thermogravometric analyzer (DTG-60/60, Shimadzu) and differential scanning calorimetric techniques (DSC-60/60A, Shimadzu). X-ray diffraction analysis (XRD, Philips, X'pert, Cu-$K\alpha$) was used to study the lattice structure of the prepared powders. The morphology of the KNN-NPs was examined using transmission electron microscopy (TEM, CM120, Philips). Also a particle size analyzer was used to measure the size distribution of the KNN-NPs.

3. Results and discussions

3.1. Thermal analysis

Fig. 1a shows the results of TGA of the produced gel and its corresponding derivative. The experiment was carried out from room temperature to 1000 °C. The TGA curve decreases until about 500 °C, corresponding to the mass loss of −81.72%. Three main mass loss regions are observed in the TGA curve. The first region, from room temperature to about 150 °C, shows an initial loss of water (−28.28%) with maximum weight loss rate at 96 °C. The second region, 150–400 °C, is related to the decomposition weight loss of organic material (−40.83%) with a maximum rate at 238 °C, where the pyrochlore phase is formed at about 300 °C. The third region, which is the main part of the curve, is in the range of 400 to about 500 °C which is due to the formation of the perovskite structure of KNN-NPs with 36.96% weight loss [19]. A small increase in the curve is observed above 600 °C. As is seen in the XRD pattern of the sample calcined at 500 °C, small amount of the secondary phase still is remained in the compound due to the oxygen vacancies and defects. Therefore, this increase can be attributed to the oxygen absorption, in which 3.22% weight increase is observed in the TGA curve in the range of 500–900 °C. The differential scanning calorimetry (DSC) was carried out to obtain the needed calcination temperature. DSC result is shown in Fig. 1b. Two endothermic peaks are observed at about 76 and 120 °C which are attributed to evaporation of water and decomposition of gelatin long chains, respectively. There are some small endo/exo-thermic peaks between 150 and 450 °C that are related to the formation and decomposition of the carboxylic and pyrocholor compounds before the formation of the final product. A big exothermic peak is observed at 470 °C related to the crystallization of the KNN-NPs [26]. Therefore, it is found that the calcination temperature must be chosen above 500 °C. Also, the endothermic and exothermic energies were calculated and found to be −43.36 and 1750 J/g, respectively.

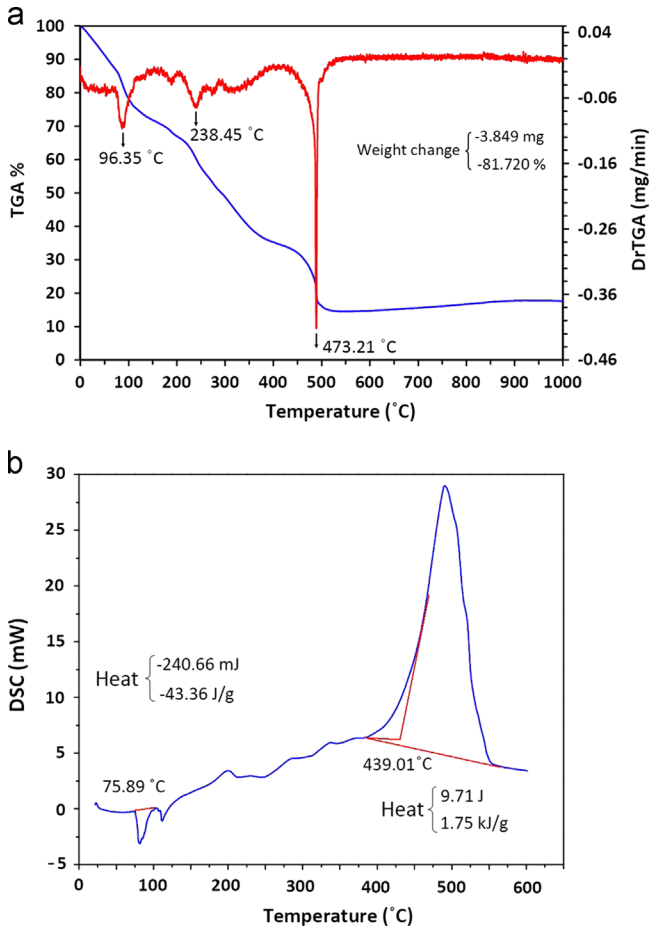

Fig. 1. Thermal analysis of KNN (a) TGA and (b) DSC.

3.2. Structural studies

Fig. 2 shows the XRD patterns of the synthesized KNN-NPs obtained at different calcination temperatures of 500, 600, 700, and 800 °C for 2 h. These results show that the KNN-NPs have been crystallized in a perovskite structure with orthorhombic phase. No other diffraction peak related to the impurities or pyrocholor phase are detected for the samples calcined at 600, 700 and 800 °C. Two small diffraction peaks, which can be attributed to KO.xKNbO$_3$ compound (PDF code: 00-052-1517) are detected in the XRD pattern of the sample calcined at 500 °C. These peaks are disappeared in the pattern of the sample calcined at 800 °C, Fig. 3a. In addition, It is observed that the peak detected at about $2\theta=46°$ is clearly splitted in to two peaks. Therefore, more detailed study was done to clarify it. Fig. 3b shows the XRD patterns of KNN-NPs prepared at calcination temperatures of 500 and 800 °C in the range of 2θ from 44.5° to 47.5°. It is observed that the peak has shifted to the left for the higher calcination temperature as is seen in Fig. 3b. Also it is shown that the diffraction peaks detected in the sample calcined at 500 °C attributed to KO.xKNbO$_3$, as mentioned earlier, are disappeared at 800 °C. Therefore the other K^+ ions and the compound structure shifted slightly from NaNbO$_3$ to KNbO$_3$ due to the larger K^+ radius (1.33 Å) than Na^+ ions (0.95 Å) [27]. The average crystallite size of the samples were calculated using Scherres's equation $D=(k\lambda/(\beta_{hkl}\cos\theta)$,

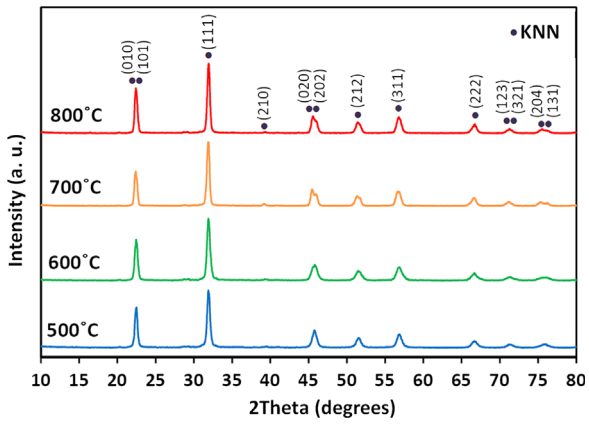

Fig. 2. XRD patterns of KNN samples calcined at different temperatures.

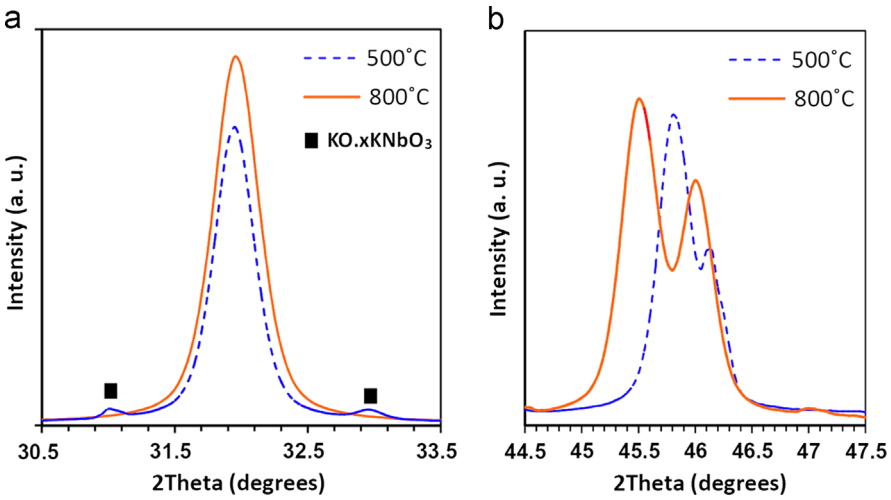

Fig. 3. XRD patterns of KNN samples calcined at 500 and 800 °C related to (a) (1 1 1) and (b) (0 2 0) and (2 0 2), diffraction peaks.

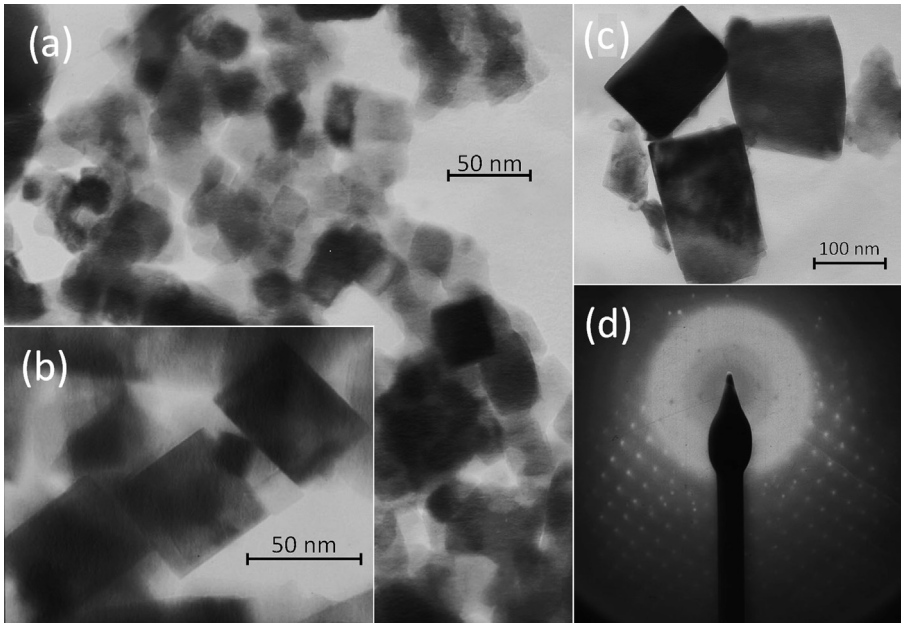

Fig. 4. TEM micrograph of KNN samples (a) and (b) calcined at 500 °C, (c) calcined at 800 °C, and (d) SAED from sample calcined at 500 °C.

where β_{hkl} is the full width half maximum (FWHM) of the (hkl) diffraction peak and is found to be 20 ± 2, 80 ± 2 nm for the samples prepared at calcination temperatures of 500 and 800 °C, respectively.

3.3. Morphology studies

The TEM images of the KNN-NPs prepared at 500 and 800 °C are presented in Fig. 4, in which Fig. 4a and b show the morphology of KNN-NPs prepared at 500 °C. It is observed that the particles have grown in a cubic form with the size of about 50 nm, whereas, the particle size of the sample prepared at 800°C are about 100 nm, Fig. 4c. As expected, the size of KNN-NPs has increased by increasing the calcination temperature. A selection area electron diffraction (SEAD) image of the sample prepared at 500 °C is shown in Fig. 4d. The clear lattice pattern confirms the high quality of the prepared KNN-NPs using this simple method.

4. Conclusion

KNN-NPs were prepared by a simple sol–gel method using gelatin as a stabilizer. The minimum calcination temperature of 500 °C was obtained from TGA and DSC results. The prepared gels were calcined at different temperatures of 500, 600, 700, and 800 °C to obtain KNN-NPs. The XRD results showed that the KNN-NPs crystallize in perovskite structure with orthorhombic phase. TEM images of KNN-NPS revealed that the particles have cubic shapes. Our results showed that gelatin is a suitable stabilizer for the synthesis of KNN-NPs due to the smaller obtained particles and lower calcination temperature compared to the other stabilizers such as EDTA.

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