Research Article

Direct Synthesis of $(K_{0.5}Na_{0.5})NbO_3$ Powders by Mechanochemical Method

Nguyen Duc Van

Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Hanoi 10000, Vietnam

Correspondence should be addressed to Nguyen Duc Van; vannd@ims.vast.ac.vn

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The synthesis and structural properties of lead-free piezoelectric $(K_{0.5}Na_{0.5})NbO_3$ powders prepared by mechanochemical method using Nb_2O_5 , K_2CO_3 , and Na_2CO_3 as starting materials were reported. X-ray diffraction, infrared spectroscopy, Raman spectroscopy, and scanning electron microscopy were used to characterize the prepared samples. Results showed that, for the first time, by selecting the milling speed of 600 rpm and the ball-to-powder weight ratio of 35:1 as milling parameters, pure $(K_{0.5}Na_{0.5})NbO_3$ crystalline phase was obtained directly in the as-milled samples after 5 h of milling time. The existence of a carbonato complex between CO_3^{2-} and Nb^{5+} ions as an intermediate species of the formation of $(K_{0.5}Na_{0.5})NbO_3$ was also found.

1. Introduction

Lead-free potassium sodium niobate piezoceramics, $(K,Na)NbO_3$, have been studied intensively due to their attractive piezoelectric and ecofriendly properties [1–4]. It is, however, difficult to obtain this material with high density and stoichiometry by traditional solid-state reaction. By using this method, undoped alkali niobate-based samples were reported to be nonstoichiometric, and their density, due to their phase stability that is limited to only about 1140°C, is significantly lower than the theoretical value [5–8]. Besides, if K_2O was produced from solid-state reaction mixture, this compound began to be volatile at 800°C and led to the change in chemical stoichiometry of obtained niobates [2–4, 9]. Therefore, different synthesis routes for alkali niobate-based piezoceramics were employed such as sol-gel, Pechini, or hydrothermal synthesis [10–12]. One of the most expected alternatives to solid-state reaction route is the mechanochemical method due to the fact that it requires only widely used commercial chemicals like oxides or carbonates as starting materials and its ability of providing the preparative product at large scale comparable with that of solid-state reaction one. However, no preparative procedures of $(K,Na)NbO_3$ by this method have been reported to date although many efforts were carried out [13]. Recently, for the synthesis of alkali niobate-based materials, mechanochemical method

was used only as an assistance step to activate the reaction mixture before calcination for solid-state reaction method [14, 15].

This paper presents the synthesis and structural property of $(K_{0.5}Na_{0.5})NbO_3$ powders prepared directly by mechanochemical method.

2. Materials and Methods

All analytical grade chemicals used as starting materials for mechanochemical method, namely, K_2CO_3 , Na_2CO_3 , and Nb_2O_5 , were purchased from Aldrich. Prior to usage, all these reagents were dried at 200°C for 2 h to remove moisture. They were mixed with desired stoichiometric composition and placed in a stainless steel vial of the planetary mill, Fritsch Pulverisette 6, with a ball-to-powder weight ratio of 35:1. The mechanochemical reaction was operated with rotational speed of 600 rpm for different milling times of 3, 4, 5, and 10 h. The as-milled samples were then calcined at 700, 800, 900, 950, and 1000°C. Phase identification was performed by using an X-ray powder diffractometer, Siemens D 5000 with CuK_{α} radiation. For lattice parameter calculation, Si was used as an internal standard. A field-emission scanning electron microscope, Hitachi S 4800, an Infrared spectrometer (GX-Perkin-Elmer), and a Raman spectrometer Labram-1B (Horiba) were used to characterize the studied samples.

FIGURE 1: X-ray diffraction diagrams of the as-milled $(K_{0.5}Na_{0.5})NbO_3$ prepared mechanochemically at 600 rpm for 3, 4, 5, and 10 h.

3. Results and Discussion

X-ray diffraction (XRD) diagrams of the as-milled samples with different milling times were shown in Figure 1. $(K_{0.5}Na_{0.5})NbO_3$ phase occurred with the strongest peaks at 2θ values of 22.37, 31.82, 45.58, and 56.69° after only 3 h of milling time together with diffraction peaks of Nb_2O_5 phase (PDF card no. 27-1003) at 28.30, 36.62, and 55.06°, while the remaining Na_2CO_3 and K_2CO_3 were amorphous. By increasing the milling time further than 5 h, $(K_{0.5}Na_{0.5})NbO_3$ phase became a unique observable crystalline phase (orthorhombic, $a = 5.622(4) \text{ \AA}$; $b = 5.634(3) \text{ \AA}$; $c = 3.948(4) \text{ \AA}$) with all diffraction peaks shifted distinctly from those of either $KNbO_3$ (PDF card no. 32-0822, $a = 5.695 \text{ \AA}$, $b = 5.721 \text{ \AA}$, $c = 3.973 \text{ \AA}$) or $NaNbO_3$ (PDF card no. 33-1270, $a = 5.568 \text{ \AA}$, $b = 15.523 \text{ \AA}$, $c = 5.505 \text{ \AA}$). To our knowledge, it is the first time that this $(K,Na)NbO_3$ phase was formed directly by mechanochemical route after many efforts have been made by researchers. Rojac et al., for example, reported that no crystalline phase of $(K,Na)NbO_3$ was formed by mechanochemical reaction between Na_2CO_3 , K_2CO_3 , and Nb_2O_5 even after as long as 40 hours of milling time with the milling speed of 300 rpm and the ball-to-powder weight ratio of 25:1 [13]. Thus, in our opinion, with our selected milling parameters, a suitable milling energy was produced to facilitate for all starting materials to react mechanochemically at atomic scale simultaneously. The formation of $(K_{0.5}Na_{0.5})NbO_3$ phase was also confirmed by the presence of NbO_6 octahedra in the as-milled sample with three bands in Raman spectrum (Figure 2). The first band at 245 cm^{-1} was corresponding to a symmetric O–Nb–O bending vibration (ν_5 mode), while the second one at 613 cm^{-1} originated from a symmetric O–Nb–O stretching vibration (ν_1 mode). The third band at 862 cm^{-1} denotes the $(\nu_1 + \nu_5)$ mode. This result is in good agreement with those reported in previous works [16, 17]. The infrared (IR) spectra of the as-milled mixtures after different milling times of 3, 4, 5, and 10 h were shown in Figure 3. Similar to the case of $NaNbO_3$ synthesized mechanochemically [18], the

FIGURE 2: Raman spectrum of the as-milled $(K_{0.5}Na_{0.5})NbO_3$ prepared mechanochemically at 600 rpm for 5 h.

FIGURE 3: Infrared spectra of the as-milled $(K_{0.5}Na_{0.5})NbO_3$ prepared mechanochemically at 600 rpm for 3, 4, 5, and 10 h.

adsorption band at 1467 cm^{-1} , which is assigned for the asymmetrical C–O stretching vibration of the free CO_3^{2-} , disappeared by increasing in milling time over 4 h, and three new bands were observed at 1633, 1507, and 1338 cm^{-1} instead. The symmetrical C–O stretching vibration band at 1055 cm^{-1} , which is inactive for the free CO_3^{2-} in alkali carbonates [18, 19], was also detected in all studied samples. The existence of these new bands in milled samples was due to the lowering in symmetry of the CO_3^{2-} anion with the formation of a carbonato complex between CO_3^{2-} and Nb^{5+} ions as an intermediate species during the mechanochemical synthesis of $(K_{0.5}Na_{0.5})NbO_3$.

XRD diagrams of calcined samples were shown in Figure 4. The orthorhombic phase of $(K_{0.5}Na_{0.5})NbO_3$ began to be observed for the sample calcined at 900°C with two peak splittings $(1\ 1\ 0)/(0\ 0\ 1)$ and $(2\ 2\ 0)/(0\ 0\ 2)$ at 2θ values of 23 and 45° , respectively. Thus, the calcination temperature for these peak splittings to start is higher than that for the case of solid-state reaction method ($800\text{--}850^\circ\text{C}$) [20, 21]. It should be noted that, from the field-emission scanning

FIGURE 4: X-ray diffraction diagrams of $(K_{0.5}Na_{0.5})NbO_3$ calcined at 700, 800, 900, 950, and 1000°C.

FIGURE 5: FESEM image of the as-milled $(K_{0.5}Na_{0.5})NbO_3$ prepared mechanochemically at 600 rpm for 5 h.

electron microscopy (FESEM) image of the optimized as-milled sample as shown in Figure 5, the average grain size of about 10 nm was obtained and was significantly smaller than that (about $0.4\ \mu\text{m}$) of the samples prepared by solid-state reaction [21]. In addition, it is well known that the samples synthesized by mechanochemical method have more defects than those received by the solid-state reaction method. As a result, during the calcination of an as-milled sample, a certain heating energy was required to remove the defects and to grow up the grain and that led to these abovementioned peak splittings that occurred at higher calcination temperature.

4. Conclusion

For the first time, by selecting the milling speed of 600 rpm and ball-to-powder weight ratio of 35:1 as milling parameters, pure $(K_{0.5}Na_{0.5})NbO_3$ phase was formed directly by mechanochemical method in the as-milled product after 5 h of milling time. The results showed that the orthorhombic phase of $(K_{0.5}Na_{0.5})NbO_3$ began to be observed for the sample calcined at 900°C. In addition, the existence of a carbonate complex between CO_3^{2-} and Nb^{5+} ions as an intermediate species of the formation of $(K_{0.5}Na_{0.5})NbO_3$ prepared by mechanochemical method was confirmed by means of infrared spectroscopy.

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