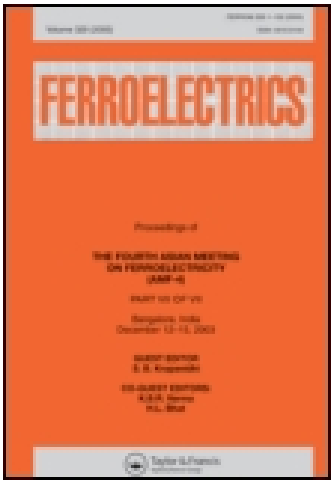

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Mechanochemical Synthesis of $K_xNa_{1-x}NbO_3$ Powders

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Mechanochemical synthesis of $K_xNa_{1-x}NbO_3$ powders, where x was from 0.1 to 0.9, has been investigated. A novel starting material of $Nb(OH)_5$ with higher reactivity than Nb_2O_5 was prepared via wet chemical method. When $x = 0.1$, the pure perovskite phase was detected. With x increasing, the second phase of $K_2Nb_8O_{21}$ was detected. When $x = 0.5$, perovskite phase were formed after milling 5h. For purposes of comparison, the starting material of Nb_2O_5 was also used to synthesize $K_{0.5}Na_{0.5}NbO_3$ powders. The morphology of particles was studied by transmission electron microscopy (TEM).

Keywords Sodium potassium niobate; Mechanochemical synthesis; Phase transitions

1. Introduction

$Pb(Zr,Ti)O_3$(PZT) piezoelectric ceramics have been widely used in actuators, accelerators, ultrasonic generators and other devices [1–3]. Owing to the environmental pollution caused by PbO in PZT ceramics, lead-free piezoelectric ceramics have attracted much attention in recent years. $(K,Na)NbO_3$(KNN) lead-free piezoelectric materials, regarding as a good candidates to replace lead-based piezoelectric materials, have been widely investigated due to their good dielectric, piezoelectric properties and a relatively high Curie temperature [4, 5].

KNN powders were usually prepared via conventional solid-state reaction routes. However, this processes involved the high calcinations and sintering temperatures, resulting the volatilization of sodium and potassium species due to their high volatilization, further lead to stochiometric deviation in the composition of the final product [5]. For the purpose of avoiding the calcination process at high temperature, the mechanochemical synthesis routes have been employed to prepare KNN powders.

Mechanochemical synthesis was initially developed for the synthesis of intermetallic and alloys compounds [6–8]. Recently, this method has been applied to synthesized nanosized oxides or ferroelectric powders [9–14]. The peculiar properties of this method was that the reaction was promoted by the mechanical energy from the milling bodies to the mixed powders [15]. In this method, the particle size of the powders was reduced, the homogeneity of the mixture was increased and the solid became more reactive [16]. Several efforts have been made to directly synthesis of ferroelectric compounds from their oxide precursors such as $PbTiO_3$(PT) [9], $Pb(Zr,Ti)O_3$ (PZT) [10], $Pb(Mg_{1/3},Nb_{2/3})O_3$(PMN) [11],

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$Pb(Zn_{1/3},Nb_{2/3})O_3$(PZN) [12], $Pb_{0.99}Nb_{0.02}[(Zr_{0.60}\ Sn_{0.40})_{0.96}Ti_{0.04}]_{0.98}O_3$(PNZST) [13] and $NaNbO_3$ (NN) [14] by mechanochemical synthesis method. Recently, T. Rojacet et al. [17] investigated the mechanochemical synthesis of KNN powders from raw material of Na_2CO_3, K_2CO_3 and Nb_2O_5. But the $(K_{0.5}Na_{0.5})NbO_3$ perovskite phase was not detected even after long time of milling, only amorphous phase of the reactants were remained.

In this work, a novel starting material $Nb(OH)_5$ with higher reactivity than Nb_2O_5 was prepared via wet chemical method. Mechanochemical synthesis of $K_xNa_{1-x}NbO_3$ powders, where x was changed from 0.1 to 0.9, has been investigated. The phase formation process and morphology of KNN powders were also characterized by XRD and TEM respectively.

2. Experimental

All chemicals and solvents were of analytic reagent grade. About 10 g of Nb_2O_5(99.9%) was placed in a polypropylene vessel and 100 ml of 40% HF was added into the vessel. Then the mixture was heated in water bath at 80°C for 8 h to ensure complete dissolution. When the dissolution was complete, the vessel was removed from the water bath and cooled down to room temperature. As superfluous ammonia water was added into the transparent solution, the white color amorphous $Nb(OH)_5$ precipitation yielded. The white residue was then separated by filtration, washed with deionized water and dried at 90°C in a desiccator. Na_2CO_3 (99.8%), K_2CO_3 (99.0%) and $Nb(OH)_5$ powders were weighed according to the formula of $K_xNa_{1-x}NbO_3$, where x was changed from 0.1 to 0.9. The mixtures were then placed in the milling vial for mechanochemical synthesis. For the sake of comparison, Na_2CO_3, K_2CO_3 and Nb_2O_5 powders were also used as raw materials to synthesize $K_{0.5}Na_{0.5}NbO_3$ powders by mechanochemical synthesis method under identical conditions.

The mechanochemical synthesis was carried out in a Fritsch pulverisette 4™ (P4) planetary ball milling system. A 225-ml tungsten carbide vial and 50 tungsten carbide balls were used. The milling speed of supporting disc (main disc) was set at 400 rpm and the rotational speed of vial was set at −800 rpm. Besides, the mass ratio of milling ball to raw

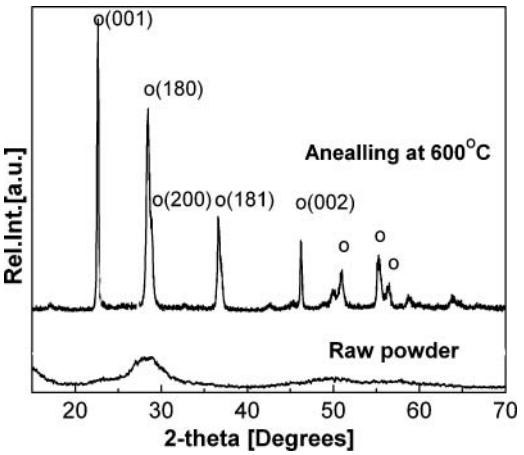

Figure 1. XRD patterns of $Nb(OH)_5$ raw powder and the same powder annealed at 600°C. (o: Nb_2O_5-JCPDS:300873;).

powder was from 30:1 to 20:1. To avoid excessive heat of the milling system, the milling was carried out 30 min steps with 30 min pauses.

X-ray diffraction(XRD) patterns of the obtained powders were identified by the Rigaku D/MAX-2400 with Cu Kα radiation at room temperature. The samples were scanned from 10° to 80° (2θ). The morphology of the powders was observed by high resolution transmission electron microscopy (HRTEM, JEOL JEM-3010).

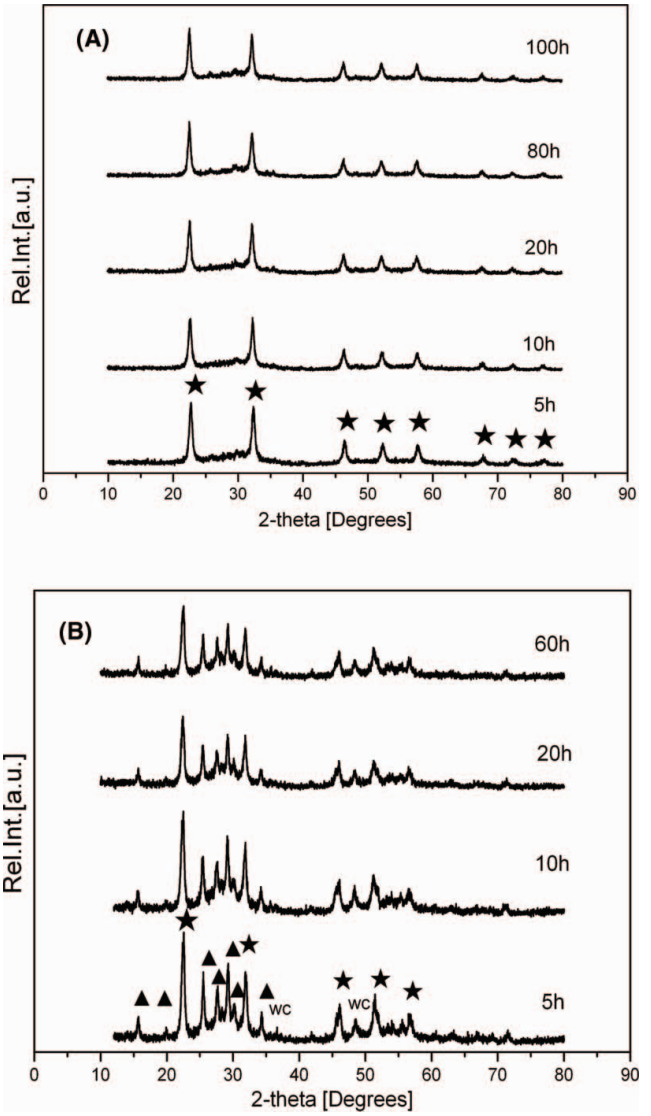

Figure 2. XRD patterns of initial mixture of Na_2CO_3, K_2CO_3 and amorphous $Nb(OH)_5$ milled for increasing time. (A): $K_{0.1}Na_{0.9}NbO_3$, (B): $K_{0.5}Na_{0.5}NbO_3$, (C): $K_{0.9}Na_{0.1}NbO_3$. (▲: $K_2Nb_8O_{21}$, ★:perovskite, WC:WC).

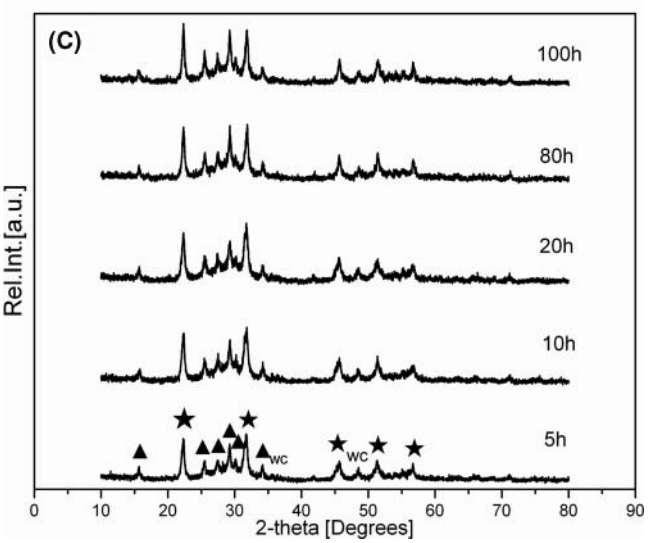

Figure 2. (Continued)

3. Results and Discussion

Figure 1 showed the XRD patterns of synthesized $Nb(OH)_5$ raw powder and annealed $Nb(OH)_5$ powder at 600°C. The broaden peaks indicated as obtained $Nb(OH)_5$ were amorphous. After annealling at 600°C new peaks were observed clearly accompanied by the disappearance of amorphous phase, which indicated the amorphous phase of $Nb(OH)_5$ transformed into the orthorhombic Nb_2O_5 (JCPDS: 300873) phase.

The initial mixture of Na_2CO_3(JCPDS:19-1130M), K_2CO_3(JCPDS:16-0820M) and amorphous $Nb(OH)_5$ were milled for 5∼100h by mechanochemical synthesis. The XRD patterns were shown in Fig. 2:(A), (B), (C). Referring to Fig. 2(A), it was clearly shown that $K_{0.1}Na_{0.9}NbO_3$ with pure perovskite phase was detected after milling 5 hours. The diffraction intensities of the perovskite phase increased with increasing of milling time firstly and became stable after 20 hours which indicated the milling process reached the states of dynamic equilibrium between crystalline reducing by mechanical milling and crystalline growth by mechanochemical reaction. When $x = 0.5$, Fig. 2(B) also clearly showed that the $K_{0.5}Na_{0.5}NbO_3$ perovskite phase were formed after milling 5 hours. However, the second phase of $K_2Nb_8O_{21}$ (JCPDS:31-1060) was detected and a quantity of amorphous phase of $Nb(OH)_5$ was remained which indicated the reaction between those compound wasn't complete even after 60 hours milling. The diffraction peaks at 2θ of 35.6° and 48.3° attributed to WC (JCPDS:25-1047H) were also observed which was due to a minor contamination from the milling processing. The WC contamination from the milling processing became more serious when the mass ratio of milling ball to raw powder increased. Similar to $x = 0.5$, Fig. 2(C) showed the perovskite phase was formed when $x = 0.9$, while the second phase of $K_2Nb_8O_{21}$ was also detected. Moreover, the phase composition was almost not changed after milling for 100 h.

Figure 3 shown XRD patterns of the mixture with different composition after 5 h milling. When x was changed from 0.1 to 0.9, the perovskite phase was formed after milling 5 h in every composition. With x increasing, the second phase of $K_2Nb_8O_{21}$ was also increased obviously. Comparing Na^+ with K^+, the ionic radius of Na^+ was smaller than

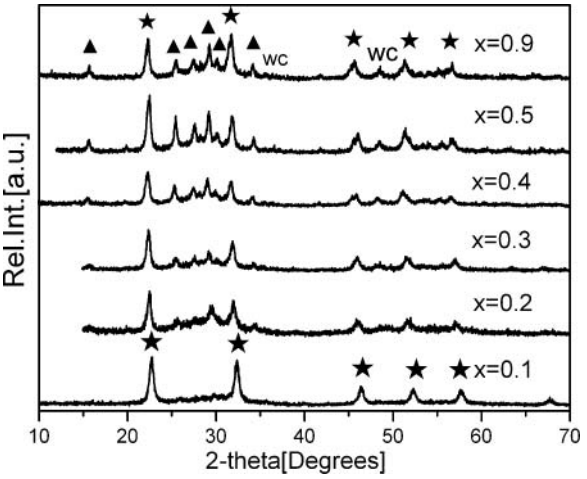

Figure 3. XRD patterns of initial mixture of Na_2CO_3, K_2CO_3 and $Nb(OH)_5$ milled for 5h, corresponding to a molar ratio of $K_xNa_{1-x}NbO_3$, where x was from 0.1 to 0.9. (▲: $K_2Nb_8O_{21}$, ★:perovskite, WC:WC).

that of K^+, resulting Na^+ easily entered into A site in ABO_3 perovskite structure during mechanochemical synthesis process. As a result, the appearance of the $K_2Nb_8O_{21}$ phase was caused by the relative hardness of K^+ entering into A site in ABO_3 during synthesis process, thus leading to the relative excess of Nb^{5+}.

For the sake of comparison, Na_2CO_3, K_2CO_3 and Nb_2O_5 (JCPDS: 37-1468M) powders were also synthesized by mechanochemical synthesis method. Figure 4 showed XRD patterns of the different initial mixture Nb_2O_5 and $Nb(OH)_5$ with Na_2CO_3, K_2CO_3 milled for 10 h to prepare $K_{0.5}Na_{0.5}NbO_3$. As can be observed in Fig. 4(A), the diffraction

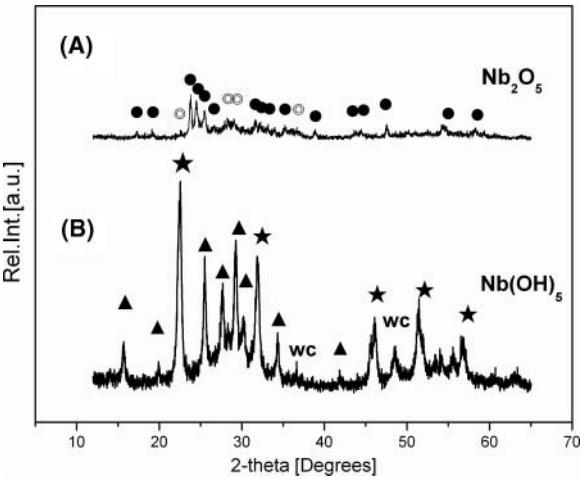

Figure 4. XRD patterns of the different initial mixture milled for 10h to prepare $K_{0.5}Na_{0.5}NbO_3$. (A): Nb_2O_5, Na_2CO_3 and K_2CO_3 (B): $Nb(OH)_5$, Na_2CO_3 and K_2CO_3. (●:Monoclinic Nb_2O_5, ○: Orthorhombic Nb_2O_5, ▲: $K_2Nb_8O_{21}$, ★:perovskite, WC:WC).

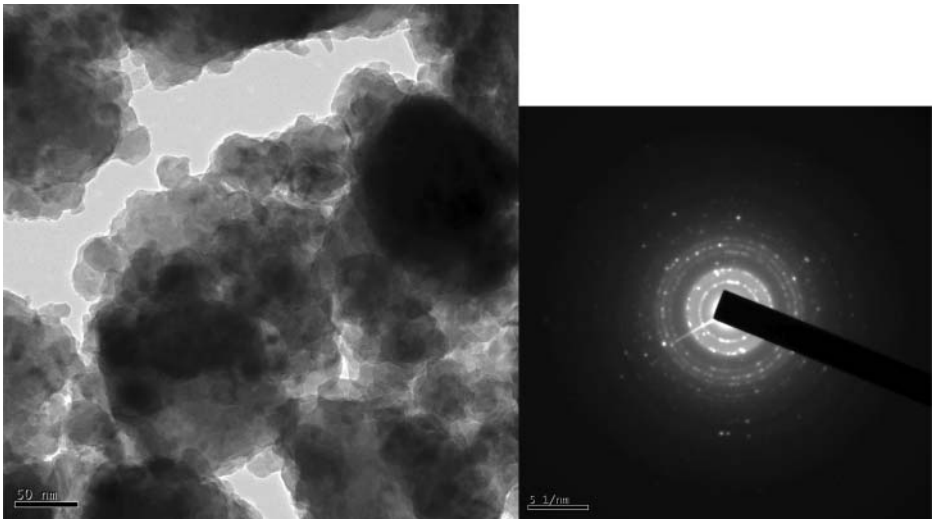

Figure 5. TEM and SAED image of the 20h milled $K_{0.5}Na_{0.5}NbO_3$ using initial materials of Na_2CO_3, K_2CO_3 and $Nb(OH)_5$.

peaks corresponding to the Na_2CO_3 and K_2CO_3 disappeared, showing that both of them become amorphous. During the synthesis process, the only detectable peak was Nb_2O_5, indicating that $K_{0.5}Na_{0.5}NbO_3$ with perovskite phase didn't formed by mechanochemical synthesis method. At the same milling condition, in Fig. 4(B), the $K_{0.5}Na_{0.5}NbO_3$ with perovskite phase were successfully formed after milling 10 hours using the initial material of $Nb(OH)_5$, Na_2CO_3 and K_2CO_3. As a result, the mechanochemical process failed to synthesize $K_{0.5}Na_{0.5}NbO_3$ powders with Nb_2O_5. In contrast, the $K_{0.5}Na_{0.5}NbO_3$ powders with perovskite phase can be prepared by mechanochemical synthesis method, when the starting materials of $Nb(OH)_5$ with higher reactivity used.

The particle size and morphology characteristics of the powders obtained by mechanochemical synthesis were observed by TEM. Figure 5 showed the TEM image of the $K_{0.5}Na_{0.5}NbO_3$ powders after 20 h milling using the initial material of Na_2CO_3, K_2CO_3 and $Nb(OH)_5$. As can be observed, the powder was constituted by nanosized crystalline particles about 20∼30 nm in dimension and these nanosized crystalline particles aggregated together to build up irregularly shaped agglomerates with 150∼300 nm. Selected area electron diffraction (SAED) pattern showed that the majority of particles were crystalline corroborated the result by XRD.

4. Conclusion

A study concerning the mechanochemical synthesis of $K_xNa_{1-x}NbO_3$ powders has been carried out from the initial mixture of Na_2CO_3, K_2CO_3 and $Nb(OH)_5$ which was prepared by wet chemical method. $K_xNa_{1-x}NbO_3$ nanopowders with perovskite structure were detected after milling 5 h, where x was changed from 0.1 to 0.9. When $x = 0.1$, the pure perovskite structure was detected. With x increasing, the second phase of $K_2Nb_8O_{21}$ was detected. When $x = 0.5$, KNN phase were formed after milling 5 h. A comparison study using different initial materials of Na_2CO_3, K_2CO_3 and Nb_2O_5 was carried out. It was failed to synthesize $K_{0.5}Na_{0.5}NbO_3$ powders due to the low reactivity of Nb_2O_5.

Acknowledgments

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