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Mechanochemical Synthesis of $NaNbO_3$, $KNbO_3$ and $K_{0.5}Na_{0.5}NbO_3$

T. Rojac*), M. Kosec, B. Malič, J. Holc
Jožef Stefan Institute, Electronic Ceramics Department, Jamova 39, 1000 Ljubljana, Slovenia

Abstract:
Mechanochemical synthesis of the $K_{0.5}Na_{0.5}NbO_3$ solid solution (KNN) is studied. In order to explore the mechanochemical interactions between the constituents in the Na_2CO_3 – K_2CO_3 – Nb_2O_5 system, $NaNbO_3$ and $KNbO_3$ as the boundary compositions of the KNN solid solution are also studied. It has been shown that $NaNbO_3$ can be prepared by a single-step mechanochemical synthesis, while in the case of K_2CO_3 and Nb_2O_5, and Na_2CO_3, K_2CO_3 and Nb_2O_5 mixtures, only amorphisation occurs even after prolonged milling.
Keywords: *Mechanochemical synthesis, niobates, solid solution, milling.*

1. Introduction

$K_{0.5}Na_{0.5}NbO_3$ solid solution (KNN) is a well known piezoelectric material with suitable characteristics for applications as high-frequency delay line transducers due to the combination of a high electromechanical coupling coefficient and low dielectric constant [1,2]. The main drawback of conventional solid-state processing of KNN is volatilization of alkaline oxides at high temperatures, which leads to an off-stoichiometry and, as a result, undesirable secondary phases are formed. Furthermore, particle coarsening often takes place during synthesis, which in turn diminishes the sinterability of the resulting powder and deteriorates the piezoelectric response. One of the ways to minimize or avoid such problems is mechanochemical synthesis.

Recently, the influence of different starting compounds (i.e. oxides, hydroxides and carbonates) on the course of the mechanochemical reaction during milling has been studied. It has been shown to be possible to synthesize a variety of ferroelectric materials, such as $PbTiO_3$ (PT) [3], $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) [4], $Pb(Sc_{0.5}Ta_{0.5})O_3$ (PST) [5] and $SrBi_4Ti_4O_{15}$ (SBIT) [6] in a single step starting from oxide precursors. On the other hand, Senna and co-workers developed a novel soft mechanochemical procedure using a mixture of oxides and hydroxides as the starting compounds [7]. In this case the synthesis temperature, required to obtain the final product, can be reduced after a relatively low input of mechanical energy.

In the last few years, great efforts have been made in order to synthesize various ceramic compounds by mechanochemical synthesis starting from a powder mixture of carbonates and oxides, such as $BaTiO_3$ [8-12], $SrTiO_3$ and Sr_2TiO_4 [13], $Sr_3Ti_2O_7$ [14], $SrFeO_{2.5}$ [15], $LiFeO_2$ [16], $(Ba_xSr_{1-x})TiO_3$ ($0<x<1$) [17] and $BaAl_2Si_2O_8$ [18]. However, the

*) Corresponding author: tadej.rojac@ijs.si

final products were not formed during milling. In these cases, the powders are mechanically activated and, as a result, the synthesis temperature can be reduced. In contrast, Miloševic and co-workers [19,20] showed that it is possible to prepare Na_2SeO_3 by a single-step mechanochemical treatement starting from a mixture of Na_2CO_3 and SeO_2. Similar observations were made for the mechanochemical synthesis of $LiMn_2O_4$, where Li_2CO_3 reacts with MnO_2 almost completely [21].

Recently, mechanochemical synthesis has been employed to prepare $NaNbO_3$ starting from a powder mixture of Na_2CO_3 and Nb_2O_5 [22]. However, $NaNbO_3$ was not formed during milling. It was found that 30 days of milling leads to lowering of the temperature required for the completion of the reaction between Na_2CO_3 and Nb_2O_5 from 750 °C (for untreated powder mixture) to 600 °C (for 30-days treated powder mixture).

In our work, a study of mechanochemical synthesis of the $K_{0.5}Na_{0.5}NbO_3$ solid solution is presented. In order to explore mechanochemical interactions in the Na_2CO_3 – K_2CO_3 – Nb_2O_5 system, mechanochemical syntheses of NaNbO3 and KNbO3 as the boundary compositions of the solid solution were also studied.

2. Experimental

Na_2CO_3 (Alfa, 99.95-100.05 %), K_2CO_3 (Aldrich, 99+ %) and Nb_2O_5 (Alfa, 99.5 %) were used as starting compounds for the mechanochemical synthesis of $NaNbO_3$, $KNbO_3$ and $K_{0.5}Na_{0.5}NbO_3$. The alkaline carbonate powders were dried at 200 °C for 1 hour prior to use due to their high hygroscopic nature. The high-energy ball-milling was carried out in a planetary mill Retsch PM 400, specially equipped for mechanical alloying, operating the rotational speed of 300 rpm. A 125 ml YSZ vial and 40 YSZ balls with diameters of 10 mm were used as the milling equipment. The mixtures of the starting compounds were weighed and placed in the vial with a ball-to-powder weight ratio of 25:1. The powders were mechanochemically treated for various times ranging from 0 (untreated) to 40 hours.

X-ray powder diffraction analysis (XRD) with Cu Kα radiation (Bruker AXS-D4 Endeavor) was used to follow the changes in the phase composition during mechanochemical treatment. In order to protect the hygroscopic samples from the environment, XRD patterns of the mixtures of K_2CO_3 and Nb_2O_5 after various milling times were recorded by covering the powders with a polymeric foil.

3. Results and discussion

3.1. Mechanochemical synthesis of $NaNbO_3$

Fig. 1 shows the XRD patterns of the initial mixture of Na_2CO_3 and Nb_2O_5, and after mechanochemical treatment for 5, 10, 20 and 40 hours. The starting powder mixture is composed of Na_2CO_3 [23] and Nb_2O_5 [24], both belonging to the monoclinic crystal singony. After 5 hours of milling the Na_2CO_3 peaks disappear, whereas the intensities of Nb_2O_5 peaks are reduced. The broadening of Nb_2O_5 peaks indicates a reduction of the particle size and a degree of amorphization, which takes place under mechanical energy. After 5 hours of milling the strongest $NaNbO_3$ peaks were detected [25], which indicates that the mechanochemical reaction between Na_2CO_3 and Nb_2O_5 is triggered by mechanical energy.

The intensities of $NaNbO_3$ peaks increase with increasing mechanochemical treatment time, from 5 to 10 hours, while the intensities of Nb_2O_5 peaks decrease. In the powder that was mechanochemically treated for 20 hours, $NaNbO_3$ is the predominant phase detected by XRD. However, minor peaks attributed to tetragonal ZrO_2 [26] were also detected. They are due to contamination from the milling vial and balls.

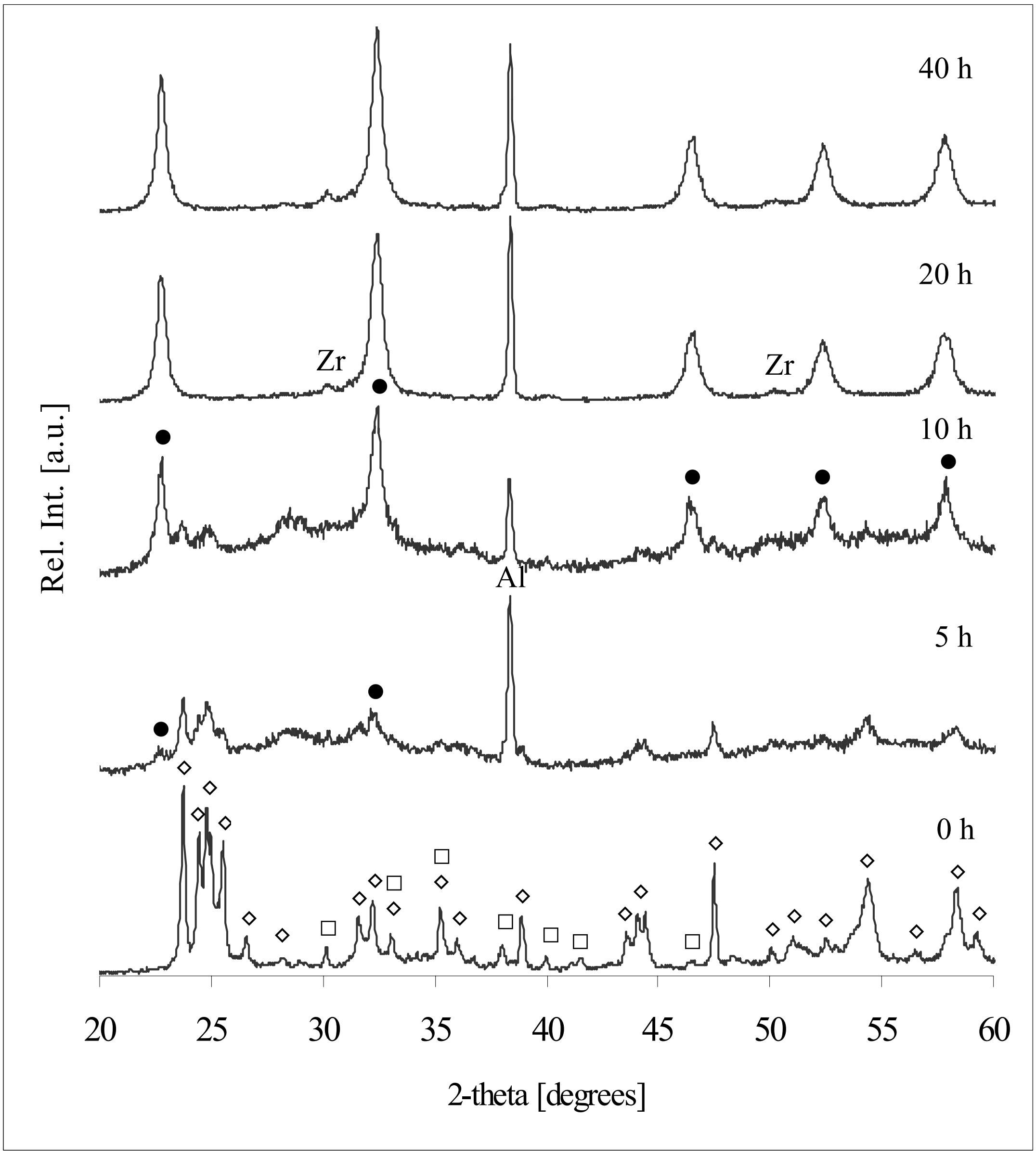

Fig. 1 XRD patterns of the initial mixture of Na_2CO_3 and Nb_2O_5 (0 h) and after mechanochemical treatment for 5, 10, 20 and 40 hours (notation: ϒ Na_2CO_3, ⊇ Nb_2O_5, ● $NaNbO_3$, Al aluminium (sample holder), Zr ZrO_2).

3.2. Mechanochemical synthesis of $KNbO_3$

The XRD patterns of the powder mixture of K_2CO_3 and Nb_2O_5 mechanochemically treated for 10, 20 and 40 hours, together with that of the starting powder mixture are shown in Figure 2. The initial mixture is composed of monoclinic K_2CO_3 [27] and monoclinic Nb_2O_5 [24]. After 10 hours of high-energy milling the peaks corresponding to K_2CO_3 disappear. Similarly to $NaNbO_3$ synthesis, Nb_2O_5 peaks are still present after 10 hours of milling. Further milling from 10 to 20 hours does not influence the phase composition, showing that the mechanochemical reaction between K_2CO_3 and Nb_2O_5, which would yield $KNbO_3$, does not occur. After 40 hours of milling the Nb_2O_5 peaks disappear, which indicates that Nb_2O_5 is probably in an amorphous state. According to XRD, no formation of $KNbO_3$ is observed even after 40 hours of milling.

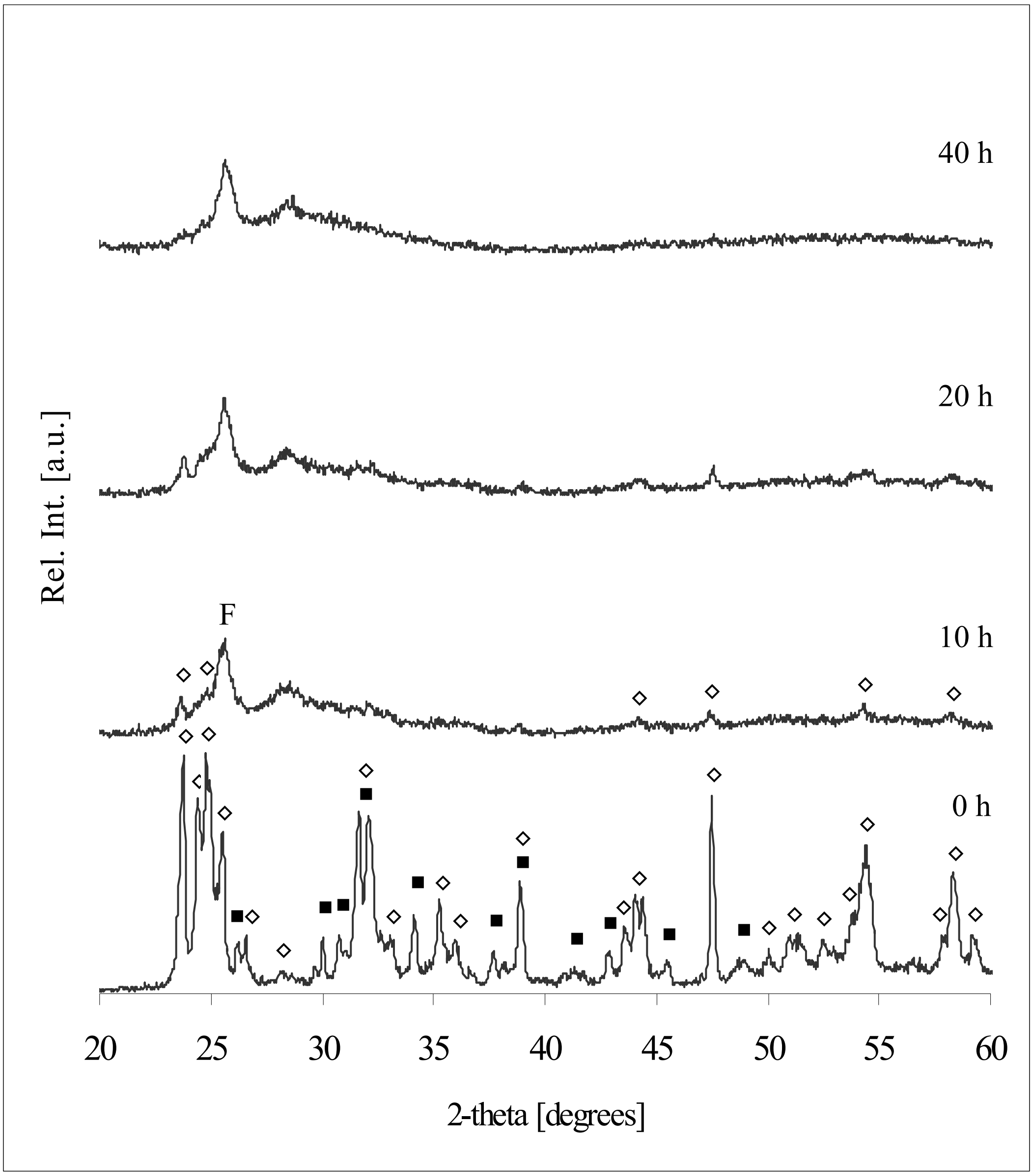

Fig. 2 XRD patterns of the initial mixture of K_2CO_3 and Nb_2O_5 (0 h) and after mechanochemical treatment for 10, 20 and 40 hours (notation: ■ K_2CO_3, ◇ Nb_2O_5, F polymer foil for the protection of the hygroscopic samples from the environment).

3.3. Mechanochemical synthesis of $K_{0.5}Na_{0.5}NbO_3$

The results of XRD analysis for mechanochemical synthesis of the $K_{0.5}Na_{0.5}NbO_3$ solid solution using Na_2CO_3, K_2CO_3, and Nb_2O_5 as the starting compounds are shown in Figure 3. After 5 hours of milling the only peaks present are those of Nb_2O_5. However, after 10 hours of milling almost all of the Nb_2O_5 peaks disappear. No peaks belonging to the

$K_{0.5}Na_{0.5}NbO_3$ solid solution are observed, which indicates that the mechanochemical reaction between reactants, i.e. Na_2CO_3, K_2CO_3, and Nb_2O_5 does not occur after 10 hours of milling. Even prolonged milling results in an amorphisation of the reactants, similarly as in the case of the $K_2CO_3 – Nb_2O_5$ mixture.

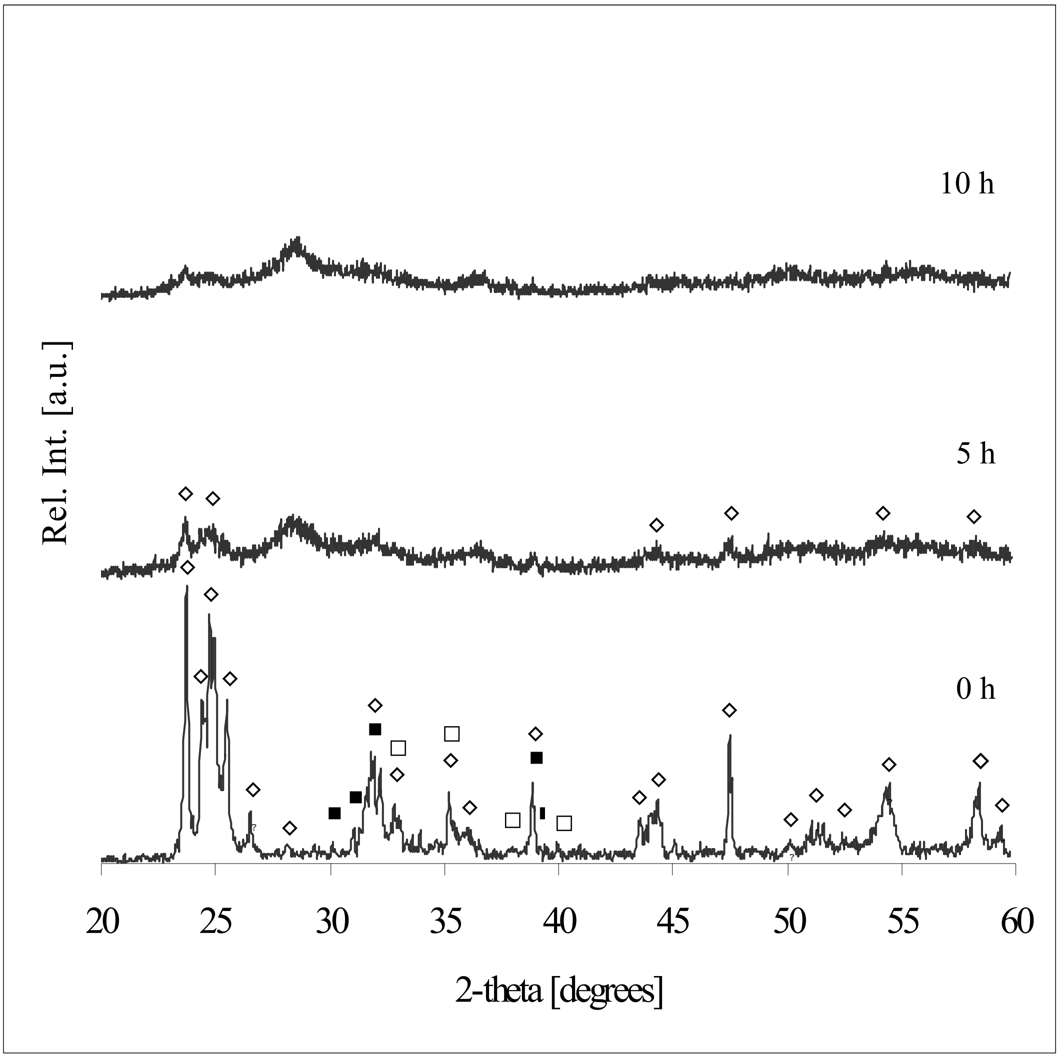

Fig. 3 XRD patterns of the initial mixture of Na_2CO_3, K_2CO_3 and Nb_2O_5 (0 h) and after mechanochemical treatment for 5 and 10 hours (notation: □ Na_2CO_3, ■ K_2CO_3, ◇ Nb_2O_5).

4. Conclusions

Mechanochemical synthesis of the $NaNbO_3$, $KNbO_3$ and $K_{0.5}Na_{0.5}NbO_3$ solid solution starting from a powder mixture of alkaline carbonates and niobium (V) oxide is studied. Na_2CO_3 and Nb_2O_5 react during milling, yielding $NaNbO_3$ after 20 hours of high-energy milling. This implicates advantages in terms of the possibility to synthesize $NaNbO_3$ by high-energy milling instead of calcination at elevated temperatures. In contrast, the mechanochemical reaction between K_2CO_3 and Nb_2O_5 does not occur even after 40 hours of milling. Similar observations were made for the $Na_2CO_3 – K_2CO_3 – Nb_2O_5$ mixture. In both cases, prolonged milling results in a formation of amorphous products.

5. Acknowledgement

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6. References

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Резюме: *Изучен механохимический синтез твердого раствора $K_{0,5}Na_{0,5}NbO_3$ (KNN). С целью исследования механохимических взаимодействий между составляющими в системе $Na_2CO_3 – K_2CO_3 – Nb_2O_5$, исследованы также $NaNbO_3$ и $KNbO_3$ в качестве граничного состава KNN твердого раствора. Показано, что $NaNbO_3$ можно приготовить в ходе одной операции, в то время как в случае смесей K_2CO_3 и Nb_2O_5 и Na_2CO_3, K_2CO_3 и Nb_2O_5 даже после продолжительного времени измельчения происходит только аморфизация.*

Ключевые слова*: Механохимический синтез, ниобаты, твердые растворы, измельчение.*

Садржај: *Проучена је механохемијска синтеза чврстог раствора $K_{0,5}Na_{0,5}NbO_3$ (KNN). У циљу проучавања механохемијских интеракција између конституената у систему $Na_2CO_3 - K_2CO_3 - Nb_2O_5$, такође су проучени $NaNbO_3$ и $KNbO_3$ као граничне композиције KNN чврстог раствора. Показано је да се $NaNbO_3$ може припремити механохемијском синтезом током једне операције, док се у случају мешавина K_2CO_3 и Nb_2O_5, и Na_2CO_3, K_2CO_3 и Nb_2O_5 чак и после продуженог млевења одиграва само аморфизација.*

Кључне речи*: Механохемијска синтеза, ниобати, чврсти раствор, млевење.*