Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 27 (2007) 2265–2271

www.elsevier.com/locate/jeurceramsoc

A study of the mechanochemical synthesis of $NaNbO_3$

T. Rojac [a,*], O. Masson [b], R. Guinebretière [b], M. Kosec [a], B. Malič [a], J. Holc [a]

[a] *Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia*
[b] *Science des Procédés Céramiques et de Traitements de Surface, Université de Limoges, Faculté des Sciences, 123 Avenue Albert-Thomas, 87060 Limoges, France*

Received 11 May 2006; received in revised form 11 July 2006; accepted 21 July 2006
Available online 11 September 2006

Abstract

We have studied the mechanochemical synthesis of $NaNbO_3$, prepared from a powder mixture of Na_2CO_3 and Nb_2O_5. The formation of $NaNbO_3$ during milling was followed using thermal analysis and X-ray diffraction. According to the thermogravimetric analysis, after 20 and 40 h of milling there was still some residual carbonate, while the X-ray diffraction shows $NaNbO_3$ as the major crystalline phase present in the mixture. Based on the quantitative XRD phase analysis, the residual reactants were amorphous and as such undetectable with the X-ray diffraction. Furthermore, an X-ray line-broadening analysis was used to determine the $NaNbO_3$ crystallite size and the microstrain. A decrease in the $NaNbO_3$ crystallite size coupled with an increase in the amount of microstrains was found from 10 to 40 h of mechanochemical treatment. Finally, the TEM analysis confirmed the $NaNbO_3$ crystallite size determined by the X-ray line-broadening analysis.

Keywords: Milling; X-ray methods; Niobates; Mechanochemical synthesis

1. Introduction

Sodium niobate ($NaNbO_3$) has been widely studied because of its implication in the field of environmentally friendly lead-free piezoelectric materials. $NaNbO_3$ is known as an antiferroelectric perovskite-type compound, which can transform into a ferroelectric one by chemical doping. As an example, a substitution of the Na in $NaNbO_3$ with K or Li induces ferroelectricity in the otherwise antiferroelectric $NaNbO_3$.[1,2] At the end of the 1950s, it was found that the $NaNbO_3$-based solid solution, namely $(K_xNa_{1-x})NbO_3$ (KNN) with the composition $x = 0.5$, possesses good piezoelectric properties.[3,4] Since then, KNN and related solid solutions, such as (K, Na)NbO_3–$LiTaO_3$ have been part of intensive research, and today they are considered as possible alternatives for the widely used lead-based piezoelectric materials, such as the Pb(Zr, Ti)O_3 (PZT) solid solution.[5–7]

Alkaline niobates are usually prepared by conventional solid-state synthesis routes. However, high temperatures and long annealing times are often required to obtain a pure final product. The problem with preparing alkaline niobates is that these high temperatures can lead to the volatilisation of alkaline species, resulting in the formation of undesirable secondary phases. Furthermore, good homogeneity of the starting compounds, which is essential to avoid the formation of secondary phases, requires wet milling and this represents an additional step in the synthesis procedure. In order to overcome these problems, a new, alternative way for the synthesis of alkaline niobates must be undertaken. Mechanochemical synthesis is considered as an alternative preparation method, where good homogeneity and low synthesis temperatures can be combined in a one-step synthesis route.

A study of the mechanochemical synthesis of $NaNbO_3$ using a starting powder mixture of Na_2CO_3 and Nb_2O_5 is presented in reference.[8] As shown by the authors, after 30 days of activation in a vibratory mill, a powder mixture with increased reactivity was achieved. Single-phase $NaNbO_3$ was obtained by heating the activated mixture at lower temperature, i.e., 600 °C, than usually required for conventional solid-state synthesis. In order to decrease the mechanochemical activation time, more-reactive sodium reagents were used, such as NaOH and Na_2O.[9] High reactivity and therefore difficult handling of the Na_2O resulted in an off-stoichiometry. Consequently, a secondary phase was formed upon heating the activated precursor. By using NaOH or Na_2O instead of Na_2CO_3 as the starting compounds, the activa-

---

[*] Corresponding author. Tel.: +386 1 477 38 34; fax: +386 1 477 38 87.
E-mail address: tadej.rojac@ijs.si (T. Rojac).

0955-2219/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2006.07.017

tion time in the vibratory mill was reduced from 30 to 7 days. In order to further improve the synthesis of $NaNbO_3$ a mixed wet-chemistry and mechanochemical activation technique was proposed.[9] In this case, a single-phase $NaNbO_3$ was prepared by heating the 2-days activated mixture at 700 °C.

In our previous work,[10] we showed that an appropriate mechanical energy input leads to the formation of nanosized $NaNbO_3$ powder directly during milling from a mixture of Na_2CO_3 and Nb_2O_5. Furthermore, we synthesized $NaNbO_3$ at different ball-impact energies and found that a minimum cumulative kinetic energy is required in order to obtain crystalline $NaNbO_3$ directly during milling.[11] Here, we present a more detailed study of the mechanochemical synthesis of $NaNbO_3$.

In a mechanochemical process, a fraction of the kinetic energy of the colliding balls is transferred from the balls to the powders. Comminution or multiple rupture of the particles, resulting in a reduction of their size and the simultaneous increase in the specific surface area, and the formation of structural defects during milling are only examples of the numerous phenomena that occur as a result of high-energy ball impacts. One of the ways to follow the mechanochemical formation of a compound is to measure the crystallite size and amount of crystal defects formed as a result of the mechanochemical treatment. In order to follow the evolution of the $NaNbO_3$ mechanochemical formation, the crystallite size and microstrains were determined after different milling times by means of X-ray line-broadening analysis. Since the formation of $NaNbO_3$ is accompanied by the release of CO_2, the synthesis was followed by determining the residual carbonate species in the powder mixture after mechanochemical treatment by means of thermogravimetric and evolved-gas analysis. Finally, the particle morphology of the mechanochemically treated powder was analysed by transmission electron microscopy.

2. Experimental

2.1. Mechanochemical synthesis

A sample containing 1.42 g of Na_2CO_3 (Alfa, 99.95–100.05%) and 3.58 g of Nb_2O_5 (Alfa, 99.5%), corresponding to the molar ratio of Na/Nb = 1:1, was weighed out. The Na_2CO_3 powder was dried at 200 °C for 1 h before use because of its hygroscopic nature. The powder mixture of 5 g was placed in a milling vial and subjected to a mechanochemical treatment for up to 40 h.

The mechanochemical treatment was performed using a Retsch PM 400 planetary mill. For this type of mill, the ratio of the vial's rotational speed to the supporting disk's rotational speed is 2, and the distance between the rotational axes is 15 cm. A 125-ml yttria-stabilized zirconia (YSZ) milling vial (height 4.4 cm, diameter 6 cm) was used together with 40 YSZ milling balls (YZT Grinding Media, Nikkato Corp., diameter 10 mm, density 6.3 g/cm^3). A small aperture of about 5 mm in the washer of the vial cover was made in order to allow the release of CO_2 during milling. The planetary mill was set to a rotational mode that changes the rotational direction of the vial and the disk every 70 s. The disk's rotational speed was set to 300 min^{-1}. To characterize the samples about 0.3 g of the powder was removed from the milling vial after 10, 20 and 40 h of the mechanochemical treatment.

In order to make comparisons with the mechanochemically treated samples, a powder mixture of Na_2CO_3 and Nb_2O_5, subsequently referred to as the non-milled mixture, was prepared by mixing the constituents manually in an agate mortar together with acetone.

2.2. Powders characterization

The thermogravimetric analysis (TG) was performed using a NETZSCH STA 409 analyser. The samples were dried at 70 °C for at least 12 h before the analysis. About 50 mg of the samples was placed in a Pt/Rh crucible and heated from 70 to 900 °C with a heating rate of 10 °C/min and a flowing air atmosphere. A simultaneous evolved-gas analysis (EGA) was performed using a Balzers Thermostar GSD 300 T mass spectrometer.

XRD patterns were recorded using a home-made diffractometer built in collaboration with the INEL company. The primary beam is supplied by a sealed tube associated with an one-reflection Ge(1 1 1) flat monochromator, which allows the selection of the Cu $K\alpha_1$ radiation. The diffracted beams are collected using a 90° curved position-sensitive detector (PSD) and the samples are placed at the centre of this curvature.[12] In order to record the diffraction peaks at high 2θ angles, the XRD data were collected in two 2θ ranges from 0° to 90° and from 50° to 140° by moving the position of the PSD.

The amount of amorphous phase, which contributes to the XRD background and subsequently referred to as the "XRD amorphous phase", was determined by mixing the samples with a known amount, i.e., 30 wt%, of Al_2O_3 (Alcoa A-16, >99%). The quantitative phase analysis was done using the Rietveld refinement procedure.[13] The details of the method are given elsewhere.[14]

The particle morphology of the powder after 40 h of mechanochemical treatment was characterized using a JEOL 2010 FX transmission electron microscope.

2.3. X-Ray line-broadening analysis

The X-ray line-broadening analysis of the mechanochemically synthesized $NaNbO_3$ was first performed using the pattern-decomposition method.[15] The $NaNbO_3$ diffraction peaks were fitted with the Voigt function using the Peakoc software.[16] It is well known that both the instrument and the specimen contribute to the line broadening, so that the instrumental resolution function was measured beforehand using the line-profile standard reference material LaB_6 (NIST, SRM660). In order to construct the Williamson–Hall plot[17] and evaluate the isotropic behaviour of both crystallites and microstrains the Langford's "Voigt function method" was applied.[15]

Due to the significant $NaNbO_3$ diffraction-line overlapping, the subsequent analysis was done using the Rietveld refinement method.[13] The crystallographic data for the orthorhombic $NaNbO_3$ were taken from the ICSD database.[18] The refinements were performed using the Fullprof suite software package.[19]

The modified Thompson-Cox-Hastings pseudo Voigt function (Mod-TCH pV) was used as the profile-shape function. Using the Mod-TCH pV function, the apparent domain size and the apparent microstrain can be determined directly from the refinement parameters of the function taking into account the instrumental broadening.[20] Assuming a spherical crystallite shape, the mean diameter of the crystallites, D, was calculated from the apparent domain size, ε, using Eq. (1).[15]

$$D = \frac{4}{3} \times \varepsilon \tag{1}$$

3. Results and discussion

The thermogravimetric and the differential thermogravimetric (DTG) curves for the non-milled Na_2CO_3–Nb_2O_5 powder mixture (0 h) and after 10, 20 and 40 h of mechanochemical treatment are shown in Fig. 1A. The results of the evolved-gas analysis of H_2O and CO_2 for the same samples are shown in Fig. 1B. The thermal behaviour of the non-milled Na_2CO_3–Nb_2O_5 mixture (0 h) is characterized by a multi-step weight loss in the temperature range from 350 to 800 °C as can be seen from the TG and DTG curves. The entire weight loss corresponds to the

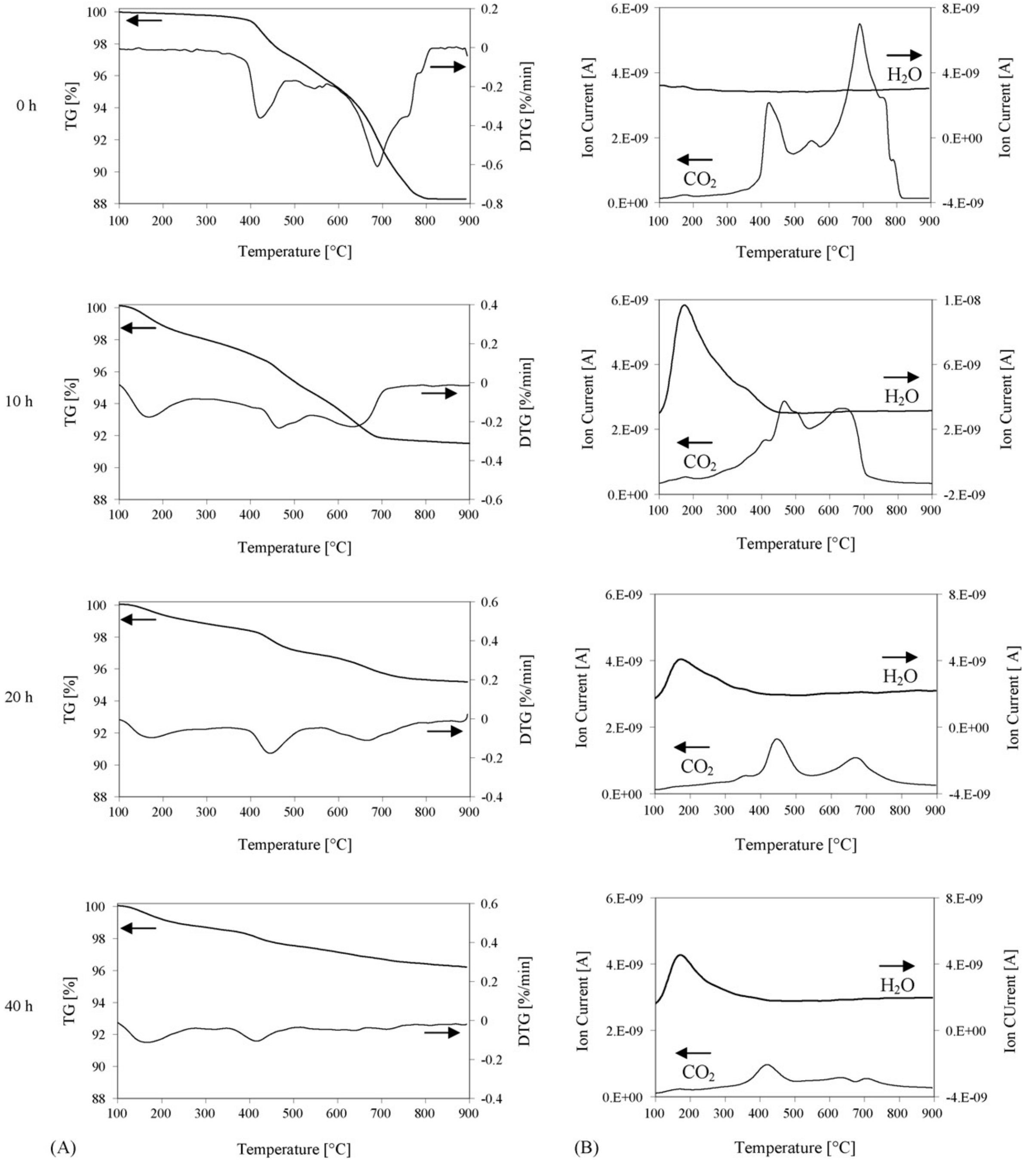

Fig. 1. (A) Thermogravimetric and differential thermogravimetric curves and (B) evolved-gas analysis of H_2O and CO_2 for the non-milled Na_2CO_3–Nb_2O_5 powder mixture (0 h) and after 10, 20 and 40 h of mechanochemical treatment.

CO_2 release, and amounts to a total of 11.7%. This value is in good agreement with the theoretical weight loss of 11.8%, calculated for the complete decomposition of Na_2CO_3 in a Na_2CO_3–Nb_2O_5 1:1 molar mixture. This means that Na_2CO_3 reacts with Nb_2O_5, leaving CO_2, in a broad temperature range from 350 to 800 °C.

The sample milled for 10 h loses weight in several steps in the temperature range 350–700 °C. In this temperature range CO_2 is released, as can be seen from the EGA curve. An additional weight loss, not observed for the non-milled sample, appears at around 170 °C. Based on the EGA, the weight loss corresponds to the removal of H_2O. This means that an amount of water was accumulated in the sample during the 10 h of milling from the moisture present in the atmosphere. Furthermore, the total weight loss from 100 to 900 °C is 8.6%, which is less than for the non-milled sample, indicating that some carbonate was consumed during the first 10 h of milling.

In the sample milled for 20 h, the weight loss around 170 °C due to water removal is still present. From the EGA, it can be seen that the CO_2 removal takes place in two major steps, at 440 and 670 °C. This coincides with the two peaks on the DTG curve that appear at the same temperature. The total weight loss in the temperature range 100–900 °C amounts to 4.8%. This value is smaller in comparison with the 10-h milled sample, which means that more carbonate is additionally consumed from 10 to 20 h of milling.

Finally, after 40 h of milling, the main differences in comparison with the 20-h milled sample can be found in the CO_2 removal. First of all, the weight loss around 440 °C and the corresponding peak of the CO_2 removal shift to a lower temperature, i.e., 420 °C. Secondly, the weight loss around 670 °C almost disappears, which means that even more carbonate is consumed from 20 to 40 h of milling. The total weight loss corresponding exclusively to the CO_2 release, i.e., from 350 to 900 °C, amounts to 2.3%. If calculated in terms of Na_2CO_3 being present in the mixture, this would mean that there is 19 wt% of residual Na_2CO_3. At this stage, we are able to conclude that the mechanochemical reaction, in terms of residual carbonate, is not completed even after 40 h of mechanochemical treatment.

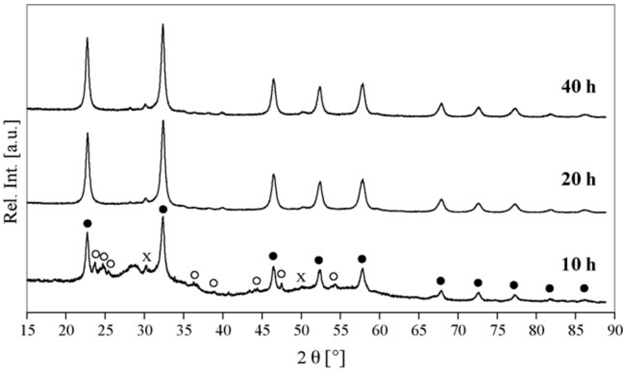

Fig. 2. XRD patterns of Na_2CO_3–Nb_2O_5 powder mixture after 10, 20 and 40 h of mechanochemical treatment (notation: (○) Nb_2O_5, (●) $NaNbO_3$, (x) ZrO_2).

Fig. 2 shows the XRD patterns of the Na_2CO_3–Nb_2O_5 mixture after 10, 20 and 40 h of mechanochemical treatment. After 10 h of milling, the peaks corresponding to the orthorhombic $NaNbO_3$[21] and the monoclinic Nb_2O_5[22] are detected. Weak peaks at 30.2° and 50.3° 2θ are also observed, and they belong to the strongest ZrO_2 reflections.[23] This is due to a minor contamination from the milling equipment. The high background in the XRD pattern suggests the presence of an amorphous phase, which is formed as a result of the mechanochemical treatment. Further milling from 10 to 20 h leads to the complete disappearance of the Nb_2O_5 peaks. This indicates that crystalline Nb_2O_5 is consumed during milling. After 20 h of milling, all the peaks can be ascribed to the orthorhombic $NaNbO_3$,[21] except the small ones at 30.2° and 50.3° 2θ, which belong to ZrO_2. No appreciable differences in the XRD pattern are observed after 40 h of mechanochemical treatment in comparison with the 20-h milled sample. Additionally, after 10, 20 and 40 h of milling no peaks relating to Na_2CO_3 are detected in the XRD patterns, suggesting that the Na_2CO_3 long-range structural periodicity has been ruined due to the mechanochemical treatment. Finally, it should be noted that after 10 h of milling a broad peak around 28.7° 2θ can be observed and it coincides with one of the strongest reflections of the orthorhombic Nb_2O_5.[24] This could mean that during milling the monoclinic Nb_2O_5 transforms partially to the orthorhombic form. Similar observations have been made after milling monoclinic Nb_2O_5 in a vibratory mill.[25] However, on the basis of the appearance of a single peak, we were not able to confirm this.

From the XRD patterns in Fig. 2, we note that the major crystalline phase present after 20 and 40 h of milling is $NaNbO_3$. In contrast, the TG and EGA from Figs. 1A and B show that after 20 and 40 h of milling, there is still some residual carbonate in the mixture, since a noticeable weight loss due to the CO_2 release is observed upon heating the sample to 900 °C. Therefore, we can infer that the mixture still contains residual carbonate and niobium oxide in a form that is undetectable with X-ray diffraction. In order to elucidate this point, the 40-h milled sample was heated at 900 °C with the same heating rate used for the thermal analysis, i.e., 10 °C/min. The sample was then quenched, put immediately into a dessicator to cool down and analysed so that a comparison with the results of the thermal analysis was possible. The corresponding XRD patterns before and after the quenching experiment are shown in Fig. 3. After quenching at 900 °C the $NaNbO_3$ peaks narrow, indicating an increase in the $NaNbO_3$ crystallite size. The reduction of the width of the $NaNbO_3$ peaks is also confirmed by the splitting of some peaks that are typical for the orthorhombic $NaNbO_3$.[21] Additionally, a decrease in the background level is evident, which is related to a decrease in the amount of amorphous phase. Finally, the ZrO_2 peaks are still present after the quenching experiment, suggesting that ZrO_2 does not react with the niobate to any significant extent during heating.

The amount of XRD amorphous phase before and after the quenching experiment was determined using the Rietveld refinement method. Since the ZrO_2 peaks are relatively weak in intensity and do not overlap with the main $NaNbO_3$ peaks they were excluded from the refinement procedure. The results give 42 wt% of XRD amorphous phase before quenching and 5 wt% after quenching at 900 °C. At the same time, based on the TG/EGA analysis in Fig. 1, the sample loses 2.3 wt% of CO_2

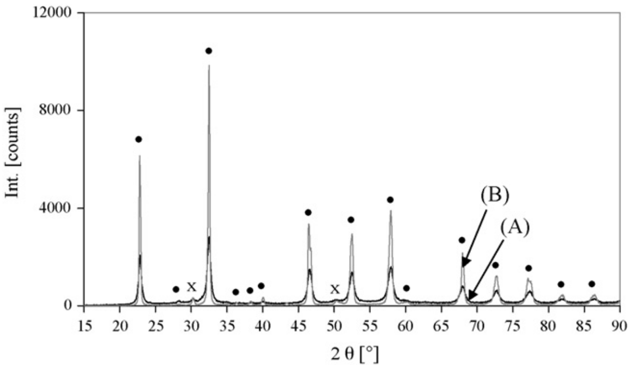

Fig. 3. XRD patterns of: (A) 40-h mechanochemically treated Na_2CO_3–Nb_2O_5 powder mixture and (B) after subsequent heating and quenching in air at 900 °C (notation: (●) $NaNbO_3$, (x) ZrO_2).

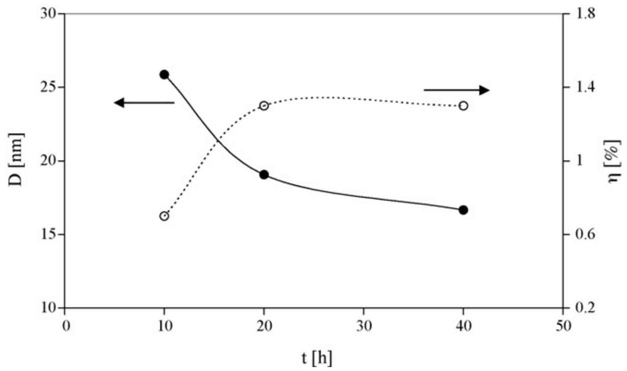

Fig. 5. Crystallite diameter D and apparent microstrain η of $NaNbO_3$ as a function of the mechanochemical treatment time.

upon heating to 900 °C. The CO_2 removal, which occurs as a result of the reaction between residual sodium carbonate and niobium oxide, and the corresponding decrease of the amount of the XRD amorphous phase, when the 40-h milled sample is heated at 900 °C, confirm that the residual reactants are amorphous and as such undetectable with the X-ray diffraction. Assuming that the stoichiometry is preserved after milling and all of the carbonate reacts upon heating to 900 °C, the amount of residual reactants after 40 h of milling is calculated from the weight loss, and amounts to 20 wt%. In contrast, the quantity of the XRD amorphous phase for the same sample is 42 wt%. Since we have not observed any secondary phases throughout the experiments, we conclude that the mechanochemically activated sample contains probably some amorphous $NaNbO_3$ besides the residual reactants, which react upon heating to 900 °C. Finally, it should be pointed out that after quenching at 900 °C, 5 wt% of XRD amorphous phase is still present in the mixture. This could be explained by taking into consideration kinetic factors, since the sample was immediately quenched after reaching 900 °C, eventually preventing complete crystallization.

Fig. 4 shows the Williamson–Hall plot, i.e., the reciprocal integral width of the specimen broadening β_f^* as a function of the reciprocal interplanar spacing d^*, of the $NaNbO_3$ after 10, 20 and 40 h of mechanochemical treatment. The plot was constructed using the individual-profile-fitting method.[15] The reciprocal integral width β_f^* for all three samples increases linearly with increasing d^*. A minor scatter around a straight line can be observed, which indicates that both the crystallites and microstrains are isotropic. Additionally, a non-zero intercept and slope suggest measurable size and strain broadening effects, respectively.

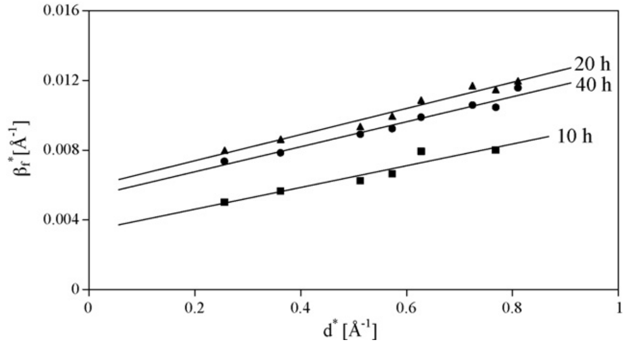

Fig. 4. Williamson–Hall plot of $NaNbO_3$ after 10, 20 and 40 h of mechanochemical treatment.

Due to the significant $NaNbO_3$ diffraction-peak overlapping, related to the orthorhombic crystal system of $NaNbO_3$, the Rietveld refinement method was applied in order to separate the size and microstrains effects. The results are shown in Fig. 5. After 10 h of milling, the $NaNbO_3$ average crystallite diameter and apparent microstrain are 26 nm and 0.7%, respectively. With further milling up to 20 h the $NaNbO_3$ average crystallite size decreases to 19 nm, while at the same time the apparent microstrain increases to 1.3%. Finally, after 40 h of milling, the $NaNbO_3$ average crystallite size further decreases to 17 nm, whereas the apparent microstrain is unchanged, i.e., 1.3%. The results clearly show that in the period between 10 h of milling, when $NaNbO_3$ is formed from the Na_2CO_3–Nb_2O_5 powder mixture (Fig. 2), and 40 h of milling, comminution of $NaNbO_3$ crystallites takes place as evidenced by the decrease in the crystallite size. At the same time the increase of the apparent microstrain from 0.7 to 1.3% suggests that an amount of defects has been formed in the $NaNbO_3$ crystal structure as a result of high-energy ball impacts during the mechanochemical treatment.

The sample milled for 40 h was studied using TEM (Fig. 6). In Fig. 6A, we can see that the powder is composed of agglomerates with an irregular shape. The SAED of the particles under consideration is shown in the inset of Fig. 6A, where a simulated SAED[26] of $NaNbO_3$ (ICSD 89317) is added for comparison. The experimental SAED rings match with the simulated ones, confirming the presence of $NaNbO_3$. The experimental SAED shows distinct and sharp rings typical for well-crystallized $NaNbO_3$. The sample is composed of particles ranging from a few nanometres up to approximately 25 nm, as can be seen from the dark-field image (Fig. 6B). This is in accordance with the average crystallite size of 17 nm determined by X-ray line-broadening analysis. The particles are more or less spherical, confirming the isotropic size-broadening effect encountered in the X-ray line-broadening analysis.

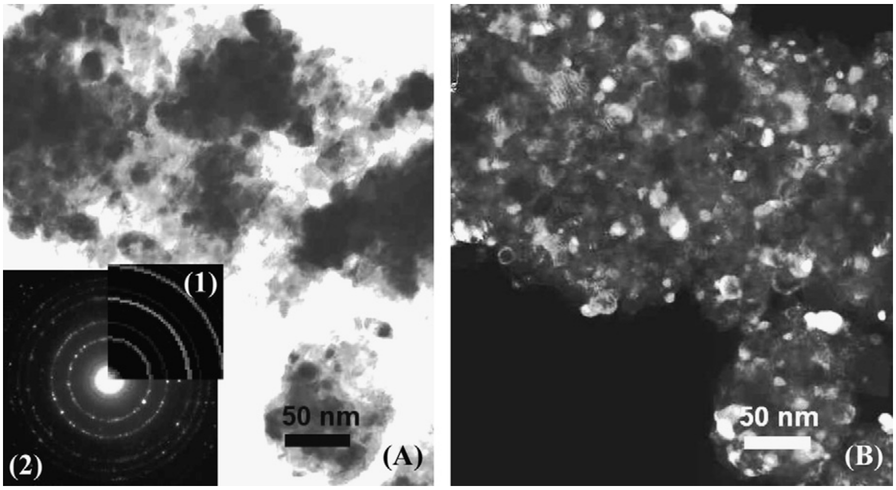

Fig. 6. (A) Bright-field and (B) dark-field TEM micrographs of the powder subjected to 40 h of mechanochemical treatment. The inset shows: (1) simulated ($NaNbO_3$, ICSD 89317) and (2) experimental SAED patterns of the powder.

4. Conclusion

The mechanochemical synthesis of $NaNbO_3$, prepared from a powder mixture of Na_2CO_3 and Nb_2O_5, was investigated by thermal analysis, X-ray diffraction analysis and transmission electron microscopy. According to the thermogravimetric analysis, a weight loss due to the release of CO_2 is observed for the samples after 20 and 40 h of milling, suggesting the presence of residual reactants in the mixture. In contrast, the X-ray diffraction analysis shows that after the same milling times the major crystalline phase present in the mixture is $NaNbO_3$. After heating the 40-h milled sample to 900 °C a decrease in the amount of XRD amorphous phase from 42 to 5 wt% is observed, as determined by the Rietveld refinement method. We can conclude that the residual reactants are amorphous and as such undetectable with X-ray diffraction. Furthermore, comminution of $NaNbO_3$ crystallites takes place from 10 to 40 h of milling, resulting in a decrease of their average diameter. At the same time an increase in the amount of microstrains or defects in the $NaNbO_3$ crystal structure is observed. Finally, the calculated $NaNbO_3$ average crystallite diameter after 40 h of mechanochemical treatment is within the size range observed by transmission electron microscopy.

Acknowledgements

The work was supported by the Slovenian Research Agency. Financial support from the Slovenian-French bilateral project (Proteus, BI-FR/03-001) is gratefully acknowledged. Ms. Jana Cilenšek is acknowledged for the thermal analysis.

References

1. Jaffe, B., Cook Jr., W. R. and Jaffe, H., *Piezoelectric Ceramics*. Academic Press, London, New York, 1971, pp.193–194.
2. Henson, R. M., Zeyfang, R. R. and Kiehl, K. V., Dielectric and electromechanical properties of (Li, Na)NbO_3 ceramics. *J. Am. Ceram. Soc.*, 1977, **60**(1–2), 15–17.
3. Egerton, L. and Dillon, D. M., Piezoelectric and dielectric properties of ceramics in the system potassium–sodium niobate. *J. Am. Ceram. Soc.*, 1959, **42**(9), 438–442.
4. Jaeger, R. E. and Egerton, L., Hot pressing of potassium–sodium niobates. *J. Am. Ceram. Soc.*, 1962, **45**(5), 209–213.
5. Malič, B., Bernard, J., Holc, J., Jenko, D. and Kosec, M., Alkaline-earth doping in (K, Na)NbO_3 based piezoceramics. *J. Eur. Ceram. Soc.*, 2005, **25**, 2707–2711.
6. 6 Malič, B., Jenko, D., Bernard, J., Cilenšek, J. and Kosec, M., Synthesis and sintering of (K, Na)NbO3 ceramics. In *Solid State Chemistry of Inorganic Materials IV. Materials Research Society Symposium Proceedings 755*, ed. M. A. Alario Franco, M. Greenblatt, G. Rohrer and M. S. Whittingham, 2003, pp. 83–88.
7. Saito, Y., Takao, H., Tani, T., Nonoyama, T., Takatori, K., Homma, T., Nagaya, T. and Nakamura, M., Lead-free piezoceramics. *Nature*, 2004, **432**, 84–87.
8. Castro, A., Jimenez, B., Hungria, T., Moure, A. and Pardo, L., Sodium niobate ceramics prepared by mechanical activation methods. *J. Eur. Ceram. Soc.*, 2004, **24**(6), 941–945.
9. Hungria, T., Pardo, L., Moure, A. and Castro, A., Effect of mechanochemical activation on the synthesis of $NaNbO_3$ and processing of environmentally friendly piezoceramics. *J. Alloys Compd.*, 2005, **395**(1–2), 166–173.
10. Rojac, T., Kosec, M., Malič, B. and Holc, J., Mechanochemical synthesis of $NaNbO_3$. *Mater. Res. Bull.*, 2005, **40**, 341–345.
11. Rojac, T., Kosec, M., Malič, B. and Holc, J., The application of a milling map in the mechanochemical synthesis of ceramic oxides. *J. Eur. Ceram. Soc.*, in press, available at www.sciencedirect.com.
12. Guinebretière, R., Boulle, A., Masson, O. and Dauger, A., Instrumental aspects in X-ray diffraction on polycrystalline materials. *Powder Diffr.*, 2005, **20**(4), 294–305.
13. Rietveld, H. M., Line profiles of neutron powder-diffraction peaks for structure refinement. *Acta Cryst.*, 1967, **22**, 151–152.
14. Kuscer, D., Meden, A., Holc, J. and Kosec, M., *J. Am. Ceram. Soc.*, in press.
15. Langford, J. I., The use of the Voigt function in determining microstructural properties from diffraction data by means of pattern decomposition. In *Proceedings of the International Conference Accuracy in Powder Diffraction II*, 1992, pp. 110–126.
16. Masson, O., *Peakoc*, *Profile fitting computer program*. SPTCS Limoges, France [olivier.masson@unilim.fr].
17. Williamson, G. K. and Hall, W. H., X-ray line broadening from filled aluminium and wolfram. *Acta Metall.*, 1953, **1**, 22–31.
18. ICSD 89317.
19. Rodriguez-Carvajal, J., *FullProf Program*. LLB, CEA/Saclay, France [www-llb.cea.fr/fullweb/fp2k/fp2k.html].

20. Young, R. A., *The Rietveld Method*. Oxford University Press, Oxford, New York, Toronto, 1993, p. 8.
21. JCPDS 33-1270.
22. JCPDS 37-1468.
23. JCPDS 80-0965.
24. JCPDS 30-0873.
25. Ikeya, T. and Senna, M., Amorphisation and phase transformation of niobium pentoxide by fine grinding. *J. Mater. Sci.*, 1987, **22**, 2497–2502.
26. Dražič, G., *Powder SAED Simulation*. IJS Ljubljana, Slovenia [goran.drazic@ijs.si].