

Proc. of the International Conference on Mechanochemistry and Mechanical Alloying, Kraków, Poland, June 22–26, 2014

Comparative Study of Phases Forming in Niobium-Antimony Oxides System upon High Temperature Treatment and High-Energy Ball Milling

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The compound SbNbO_4 that is formed in a ternary system of Nb–Sb–O has been obtained for the first time by high-energy ball milling of the equimolar mixture of oxides $\text{Sb}_2\text{O}_3/\text{Nb}_2\text{O}_5$ in argon atmosphere. This compound was characterised by X-ray diffraction, differential thermal analysis- thermal gravimetry, infrared, and scanning electron microscopy methods and its properties were compared with those of SbNbO_4 also obtained as a result of high-temperature reaction between the same oxides and also in argon atmosphere. As shown by differential thermal analysis results, irrespective of the method of synthesis, SbNbO_4 is stable in argon atmosphere up to $\approx 1125^\circ\text{C}$ and in air up to $\approx 800^\circ\text{C}$. The compound can be applied as a photocatalyst in the reaction of producing hydrogen from water.

DOI: [10.12693/APhysPolA.126.938](https://doi.org/10.12693/APhysPolA.126.938)

PACS: 81.05.-t

1. Introduction

As follows from the information on the binary systems of niobium and antimony oxides, describable by the formula Nb–Sb–O, there are no phases formed in this system in which both antimony and niobium would be at the highest oxidation state, +5. The formation of the compounds SbNbO_4 , $\text{Sb}_3\text{Nb}_3\text{O}_{13}$ and $\text{Sb}_{0.67}\text{Nb}_2\text{O}_6$, in which antimony and/or niobium are at lower oxidation states has been reported and the formation of a solid solution SbNbO_4 described by the formula $\text{SbSb}_x\text{Nb}_{1-x}\text{O}_4$, where $0.0 < x < 1.0$ has been signalled [1–13]. With regard to its application potential, the most attention has been paid to SbNbO_4 in which antimony is at +3 and niobium at +5 oxidation state. This compound was for the first time obtained in the 1960s by Roth and Waring [2] as a result of heating of oxides Sb_2O_3 and Nb_2O_5 mixture sealed in platinum ampoules, at temperatures from the range 995–1103 °C for many hours. According to the authors of [9] this compound can be obtained also by the solid state reaction when a mixture $\text{Sb}_2\text{O}_3/\text{Nb}_2\text{O}_5$ is heated in argon atmosphere at 900 °C for 2 h. Single crystals of this compound have been also obtained by the hydrothermal method at temperatures from the range 400–450 °C under a pressure from the range 650–670 atm [3–7]. The structure of the compound SbNbO_4 has been determined [6–9] and its physicochemical properties (including electric, magnetic, optical and photocatalytic ones) have been established [4–6, 9]. According to the updated results [9] it crystallises in the orthorhombic

system ($a = 5.568 \text{ \AA}$, $b = 11.811 \text{ \AA}$, $c = 4.938 \text{ \AA}$) and has a lamellar structure. Nb ions are octahedrally coordinated with the oxygen atoms to build NbO_6 octahedra. They are connected by sharing four corners, and Sb^{3+} ions are located in between these octahedral layers. The Sb^{3+} ions are surrounded by six oxygen atoms, forming strongly distorted SbO_6 [9]. It is known that SbNbO_4 is a ferroelectric in the temperature range from ≈ 400 to $\approx 600^\circ\text{C}$ [5] and that it shows photocatalytic activities for H_2 evolution from water splitting [9]. For this reason it has been a subject of great interest.

Taking into regard the current state of knowledge on the properties of SbNbO_4 , and in particular its possible use as a ferroelectric photocatalyst [9], the main aim of our study was to establish if this compound can be obtained by any other method than the hitherto used high-energy ball milling. As follows from the review on mechanochemistry [14] the methods based on this principle not only satisfy the criteria of green chemistry but they also permit a fast and easy synthesis of different composites, including those of micro- and nanomaterials of desired electric, magnetic and catalytic properties [15, 16].

This study was also undertaken to compare the fundamental physicochemical properties of SbNbO_4 obtained from the equimolar mixture of $\alpha, \beta\text{-Sb}_2\text{O}_3/\text{T-Nb}_2\text{O}_5$ by the mechanochemical method and by the high-temperature solid state reaction.

2. Experimental

2.1. Materials synthesis, equipment and procedures

The polycrystalline samples of SbNbO_4 were prepared by using two different methods, namely:

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1. Mechanochemical synthesis (MChS) using laboratory planetary ball mill Pulverisette-6 (Fritsch GmbH, Germany) with vessel and balls of zirconia, rpm = 500, BPR = 1 : 20, time = 5 h and under argon atmosphere.
2. High-temperature synthesis (HTS) in a horizontal tube furnace (CTF 12/65/550, Carbolite, UK) in the atmosphere of deoxidised argon (99.996%) flowing at the rate 5 dm³/h.

For the mechanochemical synthesis appropriate amounts of T-Nb₂O₅ and Sb₂O₃ (both of 99.99% purity, Aldrich, USA) were mixed in a stoichiometric molar ratio to SbNbO₄ and then milled at the time of 1.5, 3.0, and 5.0 h.

For the high-temperature synthesis the same reagents were mixed and pressed into pellet discs with 10 mm in diameter. These discs were heated in the atmosphere of argon at 600, 650, 700 in 24 h stages respectively. Both methods are described, *inter alia*, in the works [15–18].

2.2. Characterization of as-synthesized materials

The as-synthesized materials were analysed via a powder X-ray diffraction with a Cu K_α source on an X'Pert and Empyrean Philips instrument, for 2θ = 10°–45° with a step size of 0.02°. The identification of the material was made according to a JCPDS Table: 30-873, 5-534, 11-689, 86-2243.

The microstructure and morphology of the obtained polycrystals were examined with the use of an electron scanning microscope — SEM (JSM-6100, JEOL, Japan).

IR spectroscopy analysis was made by the use of Spectrometer (Specord M80, Carl Zeiss) (tablets with KBr in molar ratio 1:300).

The obtained samples were also subjected to examination by the differential thermal analysis–thermal gravimetric (DTA–TG) method with the use of a SDT 2960 apparatus, made by the TA Instruments Company. The measurements were taken in argon atmosphere, within the temperature range 20–1300°C, at the heating rate of 10 deg/min. The tests were conducted in corundum crucibles. The mass of the samples was ≈ 20 mg.

3. Results and discussion

As follows from analysis of phase composition (XRD) of the samples obtained after subsequent stages of mechanochemical synthesis from the equimolar mixture of oxides α, β-Sb₂O₃/T-Nb₂O₅ in argon (the commercial Sb₂O₃ is a mixture of two polymorphic varieties α and β), the monophase product containing only SbNbO₄ was obtained after 5 h of high-energy ball milling. A comparison of the fragments of diffractograms obtained for the samples synthesised (Fig. 1), significant amount of SbNbO₄ is formed in the reaction mixture already after 1.5 h of milling.

It has been also established that as a result high-temperature heating of the same mixture of the oxides

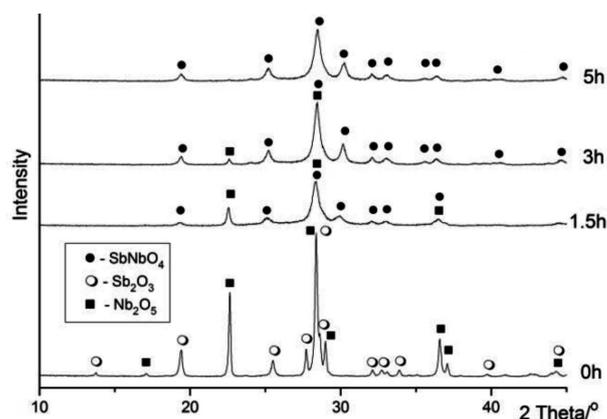


Fig. 1. Fragments of XRD diffractograms of the equimolar initial mixture of Sb₂O₃/Nb₂O₅ and the mixture after high-energy ball milling for 1.5, 3.0, and 5 h.

in a tube furnace under flowing argon, the pure compound SbNbO₄ is obtained after three 24 h stages of the reactants heating at 600, 650, and 700°C. A fragment of XRD diffractogram of the equimolar mixture of Sb₂O₃/Nb₂O₅ and the product obtained after its heating at 700°C (24 h) is shown in Fig. 2.

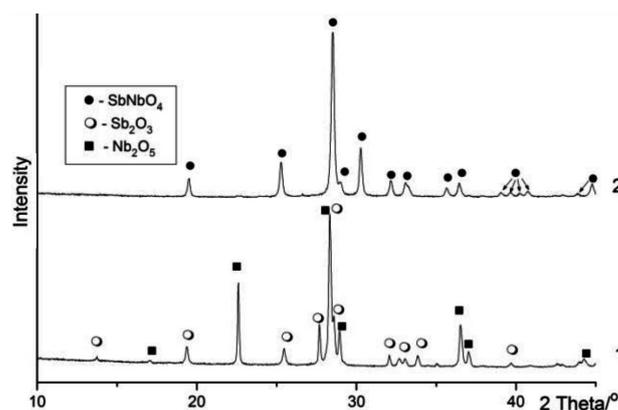


Fig. 2. Fragments of XRD diffractograms of (1) the equimolar mixture Sb₂O₃/Nb₂O₅ and (2) the compound SbNbO₄ obtained from this mixture as a result of high-temperature synthesis.

Analysis of XRD diffractograms of the samples after the first (1.5 h) and second (3 h) stage of milling and after the first (600°C–24 h) and second (650°C–24 h) stage of heating permitted assigning their diffraction lines mainly to the set characterising the compounds SbNbO₄ and T-Nb₂O₅, with SbNbO₄ the dominant phase. The samples should also contain the unreacted Sb₂O₃ which was not identified because of very low relative intensity of the XRD lines characterising this oxide in the diffractograms of the mixtures containing SbNbO₄ and T-Nb₂O₅ (see Fig. 1).

The phase composition of all samples studied containing SbNbO₄ proved that, irrespective of the method of synthesis, antimony(III) oxide reacts with niobium(V) oxide according to the equation



In order to establish the thermal stability of SbNbO_4 , the monophasic samples (HEM and HTS) were subjected to DTA–TG studies in argon and in air atmosphere.

The DTA curves of SbNbO_4 obtained as a result of mechanochemical synthesis (Fig. 3) or a high-temperature reaction (Fig. 4) in argon atmosphere on heating up to 1300°C show one endothermic effect starting at $1125 \pm 10^\circ\text{C}$.

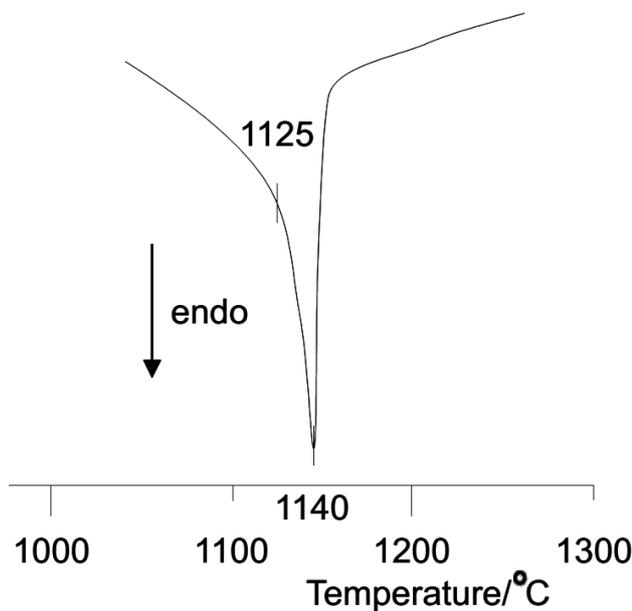


Fig. 3. The DTA curve of SbNbO_4 in argon atmosphere (MChS).

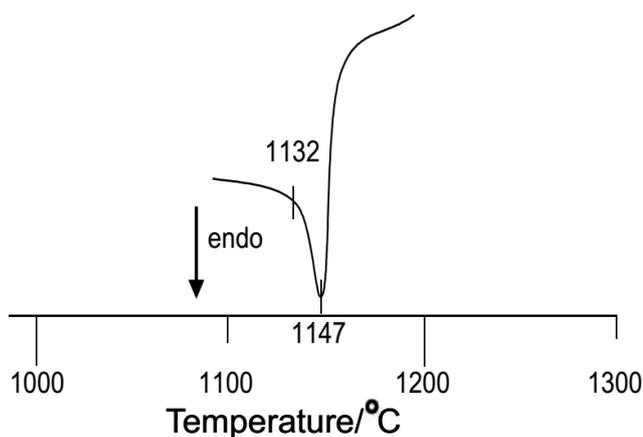
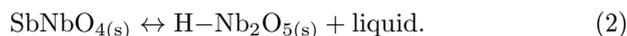


Fig. 4. The DTA curve of SbNbO_4 in argon atmosphere (HTS).

On the basis of XRD results obtained for samples HEM and HTS, additionally heated at 1135°C for 2 h and then rapidly cooled to room temperature, the endothermic effect marked on DTA curves was attributed to incongruent melting of SbNbO_4 , according to the peritectic reaction



A solid product of SbNbO_4 melting in anaerobic atmosphere is thus $\text{H-Nb}_2\text{O}_5$.

The DTA curve recorded for SbNbO_4 in air atmosphere, irrespective of the method of synthesis, revealed almost the same effects, see Fig. 5. The first broadened and poorly resolved exothermic effect starts at $\approx 780^\circ\text{C}$, while the second endothermic one starting at 1040°C has a clearly marked inflection point at 1060°C .

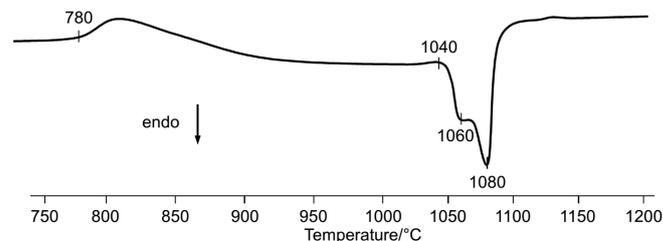


Fig. 5. The DTA curve of SbNbO_4 in air atmosphere.

The XRD phase analysis of SbNbO_4 heated in air at 800°C for 2 h revealed the presence of $\alpha\text{-Sb}_2\text{O}_4$ and $\text{T-Nb}_2\text{O}_5$. This result indicated that compound SbNbO_4 is stable in air up to about 800°C , then at higher temperatures it undergoes decomposition to the initial oxides, which is accompanied by oxidation of Sb_2O_3 to $\alpha\text{-Sb}_2\text{O}_4$. Additional heating of the products of SbNbO_4 decomposition in air at 800°C for 48 h led to the formation of solid solutions $\text{SbSb}_{1-x}\text{Nb}_x\text{O}_4$ and $\text{Nb}_{2-x}\text{Sb}_x\text{O}_5$.

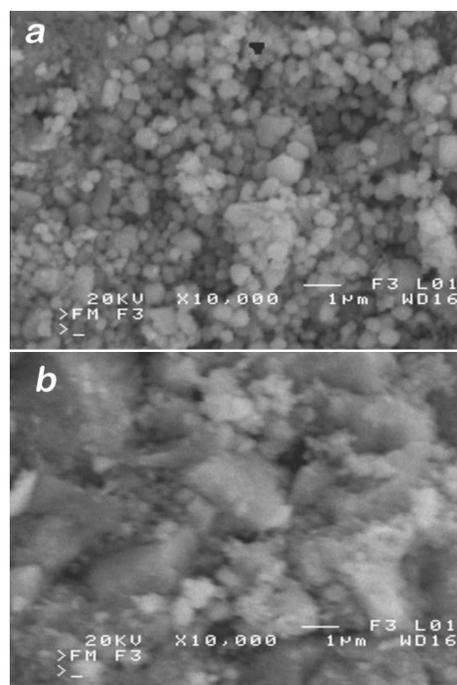


Fig. 6. SEM images of SbNbO_4 synthesised by (a) high temperature and (b) mechanochemical method.

At the next stage of the study, the compound SbNbO_4 obtained by the two above-described methods was subjected to scanning electron microscopy (SEM). Figure 6a and b reveals differences in the morphology of SbNbO_4 crystals obtained by the high-temperature reaction in solid phase (6a) and by mechanochemical synthesis (6b). The compound SbNbO_4 obtained by the mechanochemical synthesis has crystals of irregular shapes and inhomogeneous distribution of sizes. Unexpectedly, the largest crystals of SbNbO_4 of poorly developed walls were those obtained by high-energy ball milling. Their size varied from $\approx 5 \mu\text{m}$ to $0.1 \mu\text{m}$ (100 nm), while the size of crystals of this compound obtained by the high-temperature synthesis varied from 0.15 to $1 \mu\text{m}$.

Taking into account the SEM images (Fig. 6b) and analysis of XRD line widths (Fig. 1 — 5 h MChS) obtained for SbNbO_4 synthesised by mechanochemical method, it cannot be excluded that this product contains small amount of amorphous compound besides the crystal form of the compound.

It is worth noting that the resulting SbNbO_4 by mechanochemical method had bright orange color when prepared by high temperature was white.

SbNbO_4 synthesised by the two methods described above, samples HEM and HTS, have been subjected to IR study. The spectra of the two samples were almost identical. The only difference was that the absorption bands in the IR spectrum of the compound synthesised by the high-temperature treatment were slightly better developed (Fig. 7).

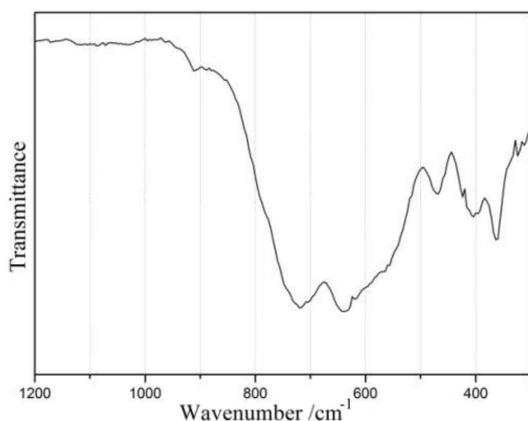


Fig. 7. IR spectrum of SbNbO_4 obtained by high-temperature reaction.

The IR spectrum of SbNbO_4 shows the absorption bands of the maxima at 720, 636, 616, 468, 424, 404 and 364 cm^{-1} . On the basis of literature, the bands with the maxima at 720, 636, 616 and 468 cm^{-1} , can be with a high probability assigned to the stretching vibrations (ν) of M–O bonds in the NbO_6 octahedrons and in strongly deformed SbO_6 octahedrons [19–23]. The bands peaking at 720 and 468 cm^{-1} are assigned to the stretching vibrations of Nb–O bond with the oxygen atom joining

two NbO_6 octahedrons via a shared vortex. The bands peaking at 324 and 310 cm^{-1} correspond to the deformation vibrations (δ) O–M–O in SbO_6 and NbO_6 polyhedrons sharing edges and vortices [21–23]. This quantitative analysis of the IR spectrum of SbNbO_4 is in good agreement with literature data [7–9] implying that the structure of this compound contains joined NbO_6 octahedrons and strongly deformed SbO_6 octahedrons.

4. Conclusions

1. The compound SbNbO_4 can be obtained from equimolar mixture of $\text{Sb}_2\text{O}_3/\text{Nb}_2\text{O}_5$ as a result of solid state reaction in argon atmosphere not only by the high-temperature treatment but also by a much shorter and easier process of high-energy ball milling.
2. Unexpectedly, the mean size of SbNbO_4 crystals obtained by the mechanochemical method is much greater than that of the crystals obtained by high-temperature treatment.
3. Irrespective of the method of synthesis, SbNbO_4 is stable in argon atmosphere up to $\approx 1125^\circ\text{C}$, above which it undergoes incongruent melting with development of solid state $\text{H-Nb}_2\text{O}_5$, while in air atmosphere at $\approx 800^\circ\text{C}$ it undergoes decomposition to Sb_2O_3 and Nb_2O_5 accompanied by oxidation of Sb_2O_3 to $\alpha\text{-Sb}_2\text{O}_4$.
4. IR spectra confirmed that the compound obtained by the two methods is built of NbO_6 octahedrons and strongly deformed SbO_6 octahedrons.

Acknowledgments

This study was supported by the projects DEC-2012/05/N/ST8/03764 (National Science Centre Poland) and DS/C-1/KWC/2014 ZUT/BMN 517-10-020-3604/17 (Polish Ministry of Science and Higher Education).

References

- [1] C. Keller, *Z. Anorg. Allg. Chem.* **318**, 89 (1962) (in German).
- [2] R.S. Roth, J.L. Waring, *Am. Mineral.* **48**, 1348 (1963).
- [3] V.I. Popolitov, *Inorg. Mater.* **32**, 228 (1996) (in Russian).
- [4] V.I. Popolitov, A.N. Lobachev, V.F. Peskin, L.N. Sirkin, N.N. Feoktistova, *Kristallografiya* **19**, 573 (1974) (in Russian).
- [5] V.I. Popolitov, L.A. Ivanova, S.Yu. Stephanovitch, V.V. Chetchkin, A.N. Lobachev, Yu.N. Venevtsev, *Ferroelectrics* **8**, 519 (1974).
- [6] A.M. Sych, V.I. Popolitov, L.A. Eremenko, *Zh. Neorg. Khimii* **19**, 2397 (1974) (in Russian).

- [7] V.I. Ponomarev, O.S. Filipenko, L.O. Atovmyan, N.V. Rannev, S.A. Ivanov, Yu.N. Venetsev, *Kristallografiya* **26**, 341 (1981) (in Russian).
- [8] A.C. Skapski, D. Rogers, *J. Chem. Soc. Chem. Commun.* **23**, 611 (1965).
- [9] S.H. Kim, S. Park, Ch.W. Lee, B.S. Han, S.W. Seo, J.S. Kim, I.S. Cho, K.S. Hong, *Int. J. Hydrog. En.* **37**, 16895 (2012).
- [10] T.N. Blanton, C.L. Barnes, D.J. Eichorst, *Powder Diffr.* **8**, 188 (1993).
- [11] D. Zhou, H. Wang, H. Zhou, X. Xie, X. Yao, Y. Cheng, *J. Mater. Sci.* **42**, 8387 (2007).
- [12] A.C. Skapski, *Acta Chem. Scand.* **20**, 580 (1966).
- [13] K.M. Ok, N.S.P. Bhuvanesh, Shiv P. Halasyamani, *J. Solid State Chem.* **161**, 57 (2001).
- [14] P. Baláž, M. Achimovičová, M. Baláž, P. Billik, Z. Cherkezova-Zheleva, J. Manuel Criado, F. Delogu, E. Dutková, E. Gaffet, F.J. Gotor, R. Kumar, I. Mitov, T. Rojac, M. Senna, A. Streletskii, K. Wieczorek-Ciurowa, *Chem. Soc. Rev.* **42**, 7571 (2013).
- [15] E. Filipek, G. Dąbrowska, *J. Alloys Comp.* **523**, 102 (2012).
- [16] E. Filipek, G. Dąbrowska, M. Piz, *J. Alloys Comp.* **490**, 93 (2010).
- [17] P. Dulian, W. Bąk, K. Wieczorek-Ciurowa, Cz. Kajtoch, *Mater. Sci.-Poland* **31**, 462 (2013).
- [18] J. Rakoczy, J. Nizioł, K. Wieczorek-Ciurowa, P. Dulian, *React. Kinet. Mech. Catal.* **108**, 81 (2013).
- [19] S. Bahfenne, R.L. Frost, *Appl. Spectrosc. Rev.* **45**, 101 (2010).
- [20] S.J. Gilliam, J.O. Jensen, A. Banerjee, D. Zeroka, S.J. Kirkby, C.N. Merrow, *Spectrochim. Acta A* **60**, 425 (2004).
- [21] M. Ziolk, I. Nowak, *Catal. Today* **78**, 543 (2003).
- [22] N. Ballarini, F. Cavani, C. Giunchi, S. Masetti, F. Trifiro, D. Ghisletti, U. Cornaro, R. Catani, *Top. Catal.* **15**, 111 (2001).
- [23] E. Filipek, M. Kurzawa, G. Dąbrowska, *J. Therm. Anal. Calorim.* **60**, 167 (2000).