Synthesis and characterization of $NaSbO_3$ compound

E. Ramírez-Meneses*
Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada,
Instituto Politécnico Nacional,
Km 14.5 Carretera Tampico - Puerto Industrial C.P. 89600 Altamira, Tamaulipas, MÉXICO.

E. Chavira
Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Ciudad

M. A. Domínguez-Crespo
Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada,
Instituto Politécnico Nacional, Km 14.5 Carretera Tampico - Puerto Industrial C.P. 89600 Altamira, Tamaulipas, MÉXICO.

R. Escamilla
Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Ciudad Universitaria AP 70-360,
04510 México D.F., MÉXICO.

J. O. Flores-Flores
Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México, Ciudad Universitaria,
A.P. 70-186, C.P. 04510 México D.F.

A. B. Soto-Guzmán
Departamento de Física, Centro de Investigación y de Estudios Avanzados,
Instituto Politécnico Nacional,
A.P. 14-740, C.P. 07000, México D.F.
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In this study we sintered $NaSbO_3$ compound at 860 ºC from Na_2CO_3 and Sb_2O_3, detailed structural and microstructural of the compound were studied. Refinement of the X-ray diffraction (XRD) patterns by method of Rietveld indicate that the crystal structure of $NaSbO_3$ belongs to the trigonal system with hexagonal symmetry, space group $R\bar{3}$(No.148), lattice parameters a = 5.2944(4) Å, c = 15.9469(8) Å and volume V = 387.124(0) Å^3 with Z = 6. Scanning electron microscopy (SEM) analysis displayed that sintered samples at temperatures lower than 750 ºC have a favorable effect on the homogeneity of the samples.

Keywords: Perovskites, alkaline metal antimonates, Chemical synthesis, X-ray diffraction

1. Introduction

The crystal structure of the antimony compounds $A_4Sb_4O_8(X_4O_{12})$ (A=K, Rb, Cs, Tl; X=Si, Ge) was studied by Pagnoux et al.[1]. The structure of these compounds is built up from layers of cross-linked infinite chains of corner-sharing SbO_6 octahedra running along the a and b axes, which are held together, via corner sharing, by four-membered rings of corner-sharing SiO_4 tetrahedral (Si_4O_{12}). This three-dimensional structural network creates intercrossing octagonal and pentagonal tunnels where the A cations are located. The open framework of $[Sb_4O_8(X_4O_{12})]_4^-$ allows ion exchange and fast ionic transport, and many frameworks structures containing sodium ions are good ionic conductors [1,2]. H. Y-P. Hong et al. have reported cubic disordered phases of the compounds $MSbO_3$ (M=Li, Na, K, Rb, Tl, and Ag). The authors mentioned that the cubic structures of $NaSbO_3$ and $AgSbO_3$ displayed a space group *Im3* with a rigid SbO_3 subarray consisting of pairs of edge-shared octahedra sharing common corners. The importance of these compounds is related to the electronic properties which are compared with the super ionic conductors $M_2O{\cdot}11Al_2O_3$ β-alumina [3]. Later, B. Wang et al. obtained the ilmenite phase of $NaSbO_3$ crystallized in the trigonal system with hexagonal symmetry, space group $R\bar{3}$(No.148), Z=6, V=385.98(4) Å^3 and a=5.2901(3) Å, c=15.926(2) Å, cell parameters. The structure of ilmenite $NaSbO_3$ consists of alternating layers of edge-sharing SbO_6 and NaO_6 octahedra (see Fig. 2). The authors determined the ionic conductivity of the ilmenite phase (3.0×10^{-5} S·cm^{-1} at 400 °C) and concluded that this phase exhibit lower ionic conductivity compared to that of the metastable cubic $NaSbO_3$ (5.6×10^{-2} S·cm^{-1} at 300 °C) which have been attributed to the structural low dimensionality, strong Na^+ - oxygen bond, and high sodium occupancy factor [2].

*e-mail: esramirez@ipn.mx

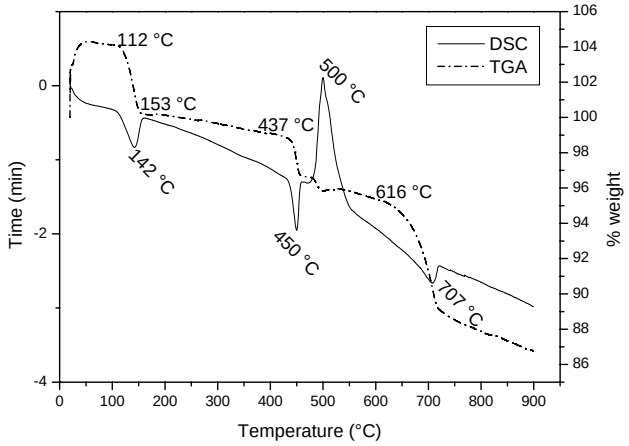

Figure 1. TGA and DSC diagram of the reagents mixture.

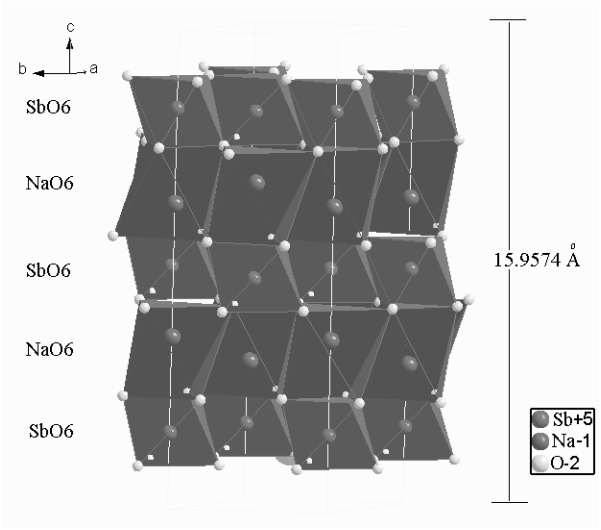

Figure 2. Unit cell of ilmenite $NaSbO_3$ showing the layers of edge-sharing of SbO_6 and NaO_6 octahedra between layers.

On the other hand, Mizoguchi H. et al. synthesized the $NaSbO_3$ compound under high pressure at 10.5 GPa and 1150 ºC in a uniaxial split sphere anvil type press (USSA-2000) [4]. The structure is an orthorhombic distorted perovskite with space group Pnma, and cell parameters of a = 5.43835 (6) Å, b = 7.66195 (8) Å and c = 5.3820 (5) Å. It showed to be a white insulator with an optical band gap of 3.4 eV. This compound was the first ternary perovskite prepared containing Sb^{5+} on the octahedral site. The authors found that the octahedral tilting distortion in this compound is much larger than expected from ionic radii considerations. In fact, the distortion is driven by a second-order Jahn-Teller distortion originating on oxygen that can be traced back to strong Sb-O covalent bonding. In this way, a conflict arises between the strong covalent bonding interactions at oxygen that favor a large octahedral tilting distortion and the repulsive Na-O interactions that oppose excessive octahedral tilting. This conflict destabilizes the perovskite topology, thereby stabilizing the ilmenite polymorph under ambient conditions. Shqau also reported the preparation of pure $NaSbO_3$ by thoroughly mixing equimolar proportions of dried Na_2CO_3 and Sb_2O_4 in an agate mortar and firing the mixture at 1110 ºC for 8 h [5].

As it can be observed, the synthesis method and reaction conditions play an important role on the structural characteristics of the final $MSbO_3$ compound and affect its potential applications in the industry.

Therefore, in this work we reported the synthesis of $NaSbO_3$ with ilmenite-type structure obtained by solid-state reaction a lower temperature reaction than those reported by B. Wang et al. [2] and Shqau K. [5] for the formation of this compound. The structure was characterized by powder X-ray diffraction, Rietveld analysis, SEM and electron diffraction pattern.

2. Experimental

Polycrystalline samples of $NaSbO_3$ were synthesized by solid state reaction in a molar ratio of 1:1 for Na_2CO_3 (STREM, 99.99% purity) and Sb_2O_3 (CERAC, 99.99% purity). Prior to weighting, Na_2CO_3 was preheating during 20-25 min. at 100 °C for dehydration in a Felisa oven (± 5 ºC). To determine, the optimal reaction conditions of the Na_2CO_3-Sb_2O_3 mixture, thermal analysis were carried out in a TGA-DSC simultaneous thermal analyzer (Nestzch, Jupiter STA449C), with an air flux of 60 ml/min with a heating rate of 10 °C/min. Thereafter, the obtained product was grounded, pelletized between 2 - 2.5 Ton·cm^{-2} with a diameter of 13 mm and a thickness of 1 mm approximately and heated at 860 °C for 273 h in air to synthesize. The reaction was carried out in an electric furnace (±4 °C) in a platinum crucible. In order to analyze, the temperature effect and annealing time on the morphological characteristics of the surface of the synthesized samples; the specimens were sintered at two different temperatures 600 and 750 °C for 168 h in air.

Phase identification of the samples was done with an X-ray diffractometer Siemens D5000 using Cu Kα radiation and a Ni filter. Intensities were measured at room temperature in steps of 0.02°, for 8.5 s, in the 2θ range 3° – 120°. The crystallographic phases were identified by comparison with the X-ray patterns of the JCPDS database. The crystallographic parameters were obtained using a Rietveld refinement program, Rietica v 1.7.7 [6], with multi-phase capability. Scanning electron microscopy (SEM) analysis was performed in a Leica–Cambridge Stereoscan 440, equipped with an Oxford/Link System electron probe microanalyser (EPMA). Sample for TEM analysis was prepared by slow evaporation of a drop of the colloidal solution (prepared dissolving the sample in toluene)

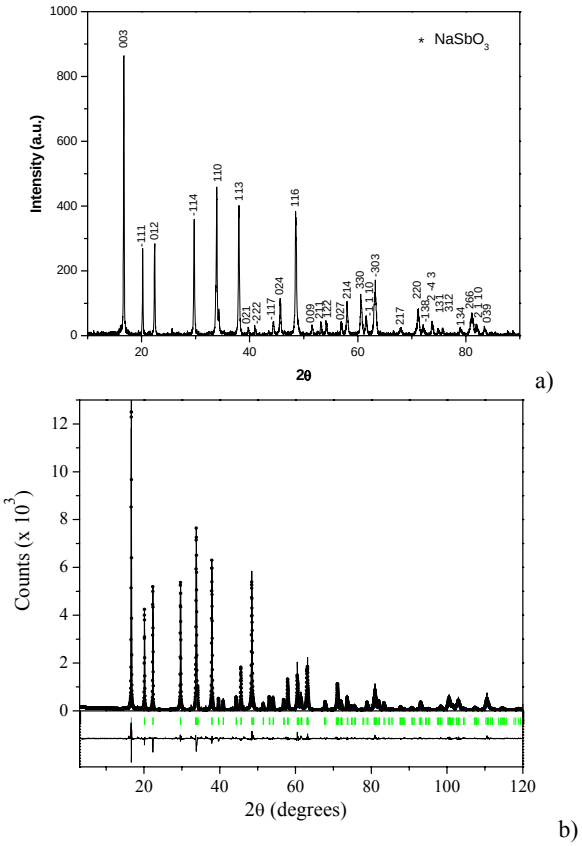

Figure 3. (a) XRD indexed pattern of the pellet synthesized at 860 ºC and (b) X-ray diffraction patterns as observed, calculated and the difference profile for the final cycle refinement of $NaSbO_3$ with $R\bar{3}$(No.148) space group.

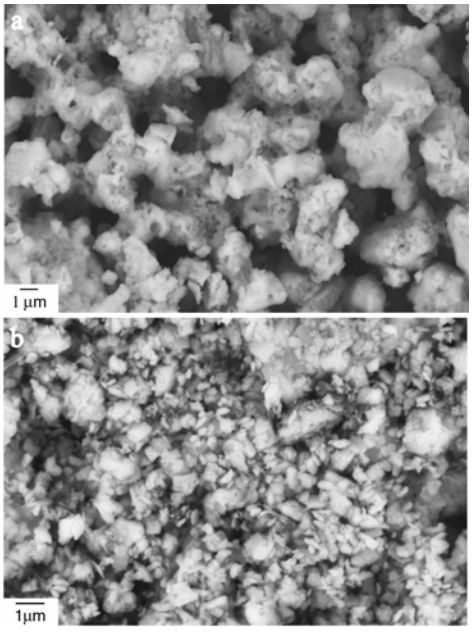

Figure 4. SEM micrographs of ilmenite powders obtained at 860 °C for 273 h (a) after completion solid state reaction (ilmenite formation) and (b) subsequent consolidation at 2.5 ton cm^{-2}.

deposited onto a carbon-covered copper grid. TEM studies were performed on a JEOL-1200 EX electron microscope.

3. Results and discussion

The heating thermogram with TGA-DSC diagrams in both heating and cooling regimes (10 °C/min in air) of the reagents mixture are shown in Fig.1. In general, the endothermic and exothermic peaks in the heating - cooling regime associate with the loss weight percent in TGA-DSC curves are clearly observed.

A loss of water molecules between 112 and 153 °C of the sodium carbonate was observed according to the following endothermic reaction. This dehydration is also shows up on TGA curve.

$$Na_2CO_3 \bullet xH_2O \rightarrow Na_2CO_3 + xH_2O \uparrow \qquad (1)$$

The endothermic (between 437- 450 °C) and exothermic changes (470 - 500 °C) have been correlated with the decomposition of the sodium carbonate.

This was corroborated by weighting the sample before the decomposition procedure. However, the formation of the sodium oxide is carried out after 500 °C as we suggested in the next reaction.

$$Na_2CO_3 \rightarrow Na_2O + CO_2 \uparrow \qquad (2)$$

Finally, the endothermic peak and the intermolecular loss weight observed between 660 and 707 °C is associated with the formation of $NaSbO_3$ ilmenite structure and its corresponding oxygen elimination.

$$Na_2O + Sb_2O_3 + O_2 \rightarrow 2\ NaSbO_3 \qquad (3)$$

It suggested that after 707 °C $NaSbO_3$ ilmenite is being formed (Fig.2). According to the TGA-DSC results and phase diagrams [7], 860 °C has been selected as temperature reaction assuming that the complete reaction is carried out in the system. To confirm this asseveration and study structural features of the $NaSbO_3$ compound at 860 ºC, XRD data have been collected and analyzed by Rietveld refinement. According to XRD data shown at Fig. 3(a), well crystallized, $NaSbO_3$ was obtained. The X-ray diffraction pattern of the sample was Rietveld-fitted taken into account the space group $R\bar{3}$ (No.148). The observed, calculated and the difference profile for the final cycle of refinements are shown in Fig**.** 3(b) and the structural parameters obtained from the Rietveld refinements are shown in Table 1.

Several works in the literature have obtained ilmenite compound at temperatures upper to 900 ºC, this temperature depends of start materials and synthesis process. Wang *et. al.* [2] have proposed the preparation of ilmenite phase in two steps from a mixture containing $NaNO_3$, Sb_2O_5 and SiO_2. The mixture was preheated in air at 500 °C for 3 h and then held at 1300 °C for 3 h. Sato *et al*.[8] have prepared $NaSbO_3$ compound with the same

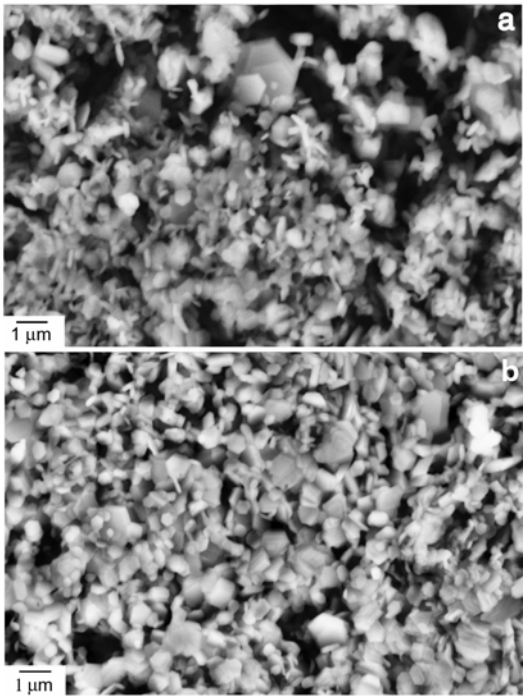

Figure 5. SEM micrographs from sintered pellets at 750 °C (a) and 600 °C (b) for 168 h.

mixture reagents in air, at 900 °C for 16 h. Whereas, Mizoguchi *et al.* [4] have also reported the ilmenite structure used $NaNO_3$ and Sb_2O_3 as starting materials and the reaction temperature was 997 ºC during 5 h. Recently, Nalbandyan *et al.* [9] synthesized the $NaSbO_3$ compound for one hour at 550 ºC, from $NaNO_3$, Sb_2O_3 and Na_2CO_3 . In all the above instances, starting antimonate and sodium nitrates are used. In this study we prepared the ilmenite phase at 860 ºC without $NaNO_3$.

The representative SEM micrographs taken from polycrystaling $NaSbO_3$ after completion solid state reaction (ilmenite formation see Fig. 3) and subsequent consolidation at 2.5 ton cm^{-2} are shown in Figures 4a-b. As can be seen, the ilmenite polycristals consist of agglomerates with irregular shape and porous appearance (Fig. 4a). The porous vary from 0.2 to 0.5 µm in diameter and the average size of the agglomerates was between 1 to 3 µm. As it is known, a homogeneous surface to reach uniform physicochemical properties is desired during materials processing, therefore, ilmenite polycristals were consolidated at 2.5 ton cm^{-2} and the morphology of the specimens was also analyzed by SEM measurements. SEM micrographs show that the pellets displayed a diminishing in the crystal size in the range of 0.2 - 1.4 µm and also in the porous appearance of the samples (Fig. 4b).

The temperature effect on morphological changes of the pellets during sintering process was also analyzed at 600 and 750 ºC for 168 h. Fig. 5a-b depicts SEM images of $NaSbO_3$ compound consolidated after sintering process at 600 and 750 °C for 168 h, respectively. In general, it can be observed that the samples display slightly changes in their morphology, which it can be appreciated in homogenous crystal size and less porosity. However, comparing both temperatures, we believed that sintered temperatures smaller than 750 ºC have a favorable effect on the homogeneity of the samples. Inclusive, a well defined shape of the crystals can be observed. The average crystal size was close to 0.3 µm and 0.7 for 750 and 600 ºC, respectively. Fig. 6 shows the electron diffraction pattern of ilmenite $NaSbO_3$ policrystals obtained at 860 °C for 273 h. The lattice parameters were calculated using the relation $\lambda L/R = d_{hkl}$ where, L is the variable distance between the specimen and the analyzing crystal =100 cm, λ is the wavelength of the incident ray beam = 0.0334 Å, R is the distance between the center and the different spots and d_{hkl} is the space between the planes in the atomic lattice.

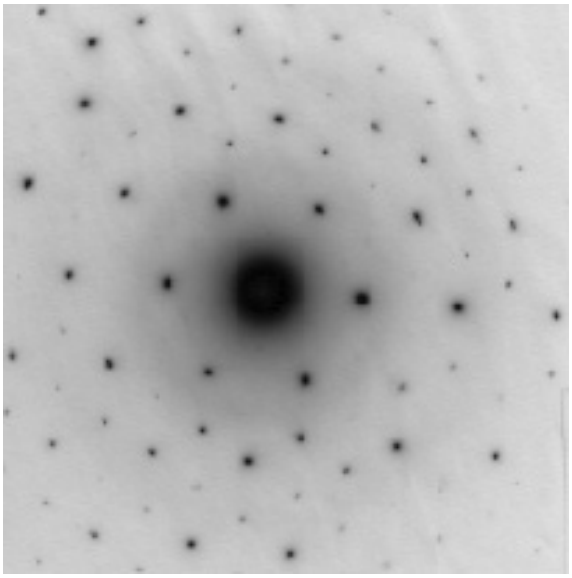

Figure 6. Electron diffraction pattern of ilmenite $NaSbO_3$ powders obtained at 860 °C for 273 h.

The lattice parameters obtained were a = 5.3194 Å and c = 16.032 Å, which are slightly different from those obtained by Rietveld refinement. This difference is supposedly due to the TEM pattern which was carried out supposed a single crystal, while the results of the parameters cell obtained by Rietveld refinement technique is a detail average of all the crystals in the sample.

According to the results, the surface roughness and hence the surface area become visible diminished after consolidation and sintering process of the pellets at 600 ºC, which reflects also the rather high density and homogeneity that can be reached of the material at these experimental conditions. We believed that longer times than 168 h could help to reach a better performance in future applications.

4. Conclusions

The synthesis of $NaSbO_3$ compound with ilmenite-type structure was obtained at lower temperature reaction (860 ºC) than those reported for the formation of this compound

(without $NaNO_3$, 900 ºC) [2] and (1100 ºC) [5]. Rietveld refinements show that the synthesized compound corresponds to ilmenite phase of $NaSbO_3$ in the trigonal system with hexagonal symmetry and space group $R\bar{3}$ (No.148). SEM analysis displayed that sintered samples at temperatures lower than 750 ºC have a favorable effect on the homogeneity of the samples, which is desired for industrial applications.

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