Structural analysis of Bi$_3$TiNbO$_9$ prepared by mechanical activation

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Abstract. The synthesis by high energy mechanical activation and structural characterization of the phases of Bi$_3$TiNbO$_9$ are described. A fluorite-like metastable phase was identified upon heating the activated powders in the temperature range of 593 to 823 K, followed by formation of the stable Aurivillius phase above 873 K. The crystallization temperature of the fluorite phase increases with milling time. From Rietveld analysis of X-ray diffraction patterns, the fluorite cell parameter is shown to decrease, while rutile TiO$_2$ increases with milling time.

1. Introduction

The mechanical activation of the powder precursors in the system Bi$_2$O$_3$-TiO$_2$-Nb$_2$O$_5$ allows for the formation of a stable Aurivillius Bi$_3$TiNbO$_9$ (BTN) phase, with a high Curie temperature (~ 1213K) that provides for piezoelectric ceramics at high temperature [1, 2]. Sintering at low temperature leads to a metastable fluorite phase, which shows a great sensitivity to humidity, as has been reported by our group [3].

Dense ceramics on this system were prepared by mechanical activation as reported in the work of Moure et al. [4, 5], using low energy milling. Amorphous precursors were obtained with this technique after milling for 3000 h. The free energy stored in crystalline damage and continuous surface creation 0 are understood as the resource that greatly diminishes the subsequent new crystalline phase formation temperatures.

In this report, high energy ball milling was used to obtain amorphous precursor powders. X ray diffraction and Rietveld analysis were used for crystalline structure determination. Thermal stability and phase transformations in the BTN system were analyzed as functions of milling time.

2. Experimental

BTN precursor powders were prepared from stoichiometric mixtures of analytical grade powders of Bi$_2$O$_3$ (Baker), Nb$_2$O$_5$ (GGS Chemicals) and TiO$_2$ (Aldrich).

Mechanical activation was performed in a high energy SPEX-8000 shaker mill with hardened steel balls in a WC vial in air with a 10:1 balls to charge ratio.

Thermal characteristics were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis in a TA Instruments SDT-2960 dual DSC-TG in dry air, with heating ramp of 20 K/min. Samples with milling times from 2 to 48 h were analyzed. Partial heat treatment of the
samples was performed in the thermobalance for further structural analysis. X-ray powder diffraction data was collected both with a Siemens D–5000, and a Shimadzu XRD-6000 diffractometers, with Cu-Kα radiation, in the Bragg-Brentano geometry. Cell parameter determination, position and atomic occupation were refined with the FULLPROF suite [7] for samples milled from 12 to 24 h.

Having not found a previous report on the structural model of the fluorite phase, the refinement was based on the isomorphic structure of the δ-Bi₂O₃ phase. The latter is a high temperature variant which can be retained down to room temperature by doping with transition elements, and lanthanides. In this work, the best fit was obtained using the structural model developed by Chen et al. [8] (an Fm-3m cubic structure, with 0.54201 nm cell parameter) in the resolution of the structure of the solid solution Bi₂O₃–Yb₂O₃. The refinement of the Aurivillius phase Bi₃TiNbO₉ was started with the Nalini et al. [9] model with A₂Ti₃m orthorhombic structure and a=0.54248 nm, b=0.53864 nm, c=2.50392 nm cell parameters.

3. Results

A series of TG-DSC traces, taken from powders milled for 2 to 48 h is shown in Fig. 1. The temperature at the first exothermic peak increases with milling time, while the second peak remains stable at nearly 600ºC.

From the XRD analysis of powders after heating at temperatures between the two exothermal events, and after the second one, a metastable fluorite phase is identified after the first peak, and a stable Aurivillius phase is seen after the second peak. An incipient formation of the metastable fluorite phase is identified, also, in the as-milled powders after milling for 24 h. These powders display the two exothermic peaks at 773 and 898 K.

![Figure 1. DSC traces for different milling time (exothermic events in positive direction).](image)

The Rietveld analysis (R_Bragg = 3.13) of a sample sintered after milling for 12 h results in 97.4% (vol.) of BTN fluorite-like phase with cell parameter a = 0.55080 nm, and 2.54% (vol.) of rutile TiO₂. After 24 h milling, 95.5% (vol.) is BTN fluorite phase with cell parameter a = 0.54447 nm and 4.52% 95.5% (vol.) is rutile TiO₂ (R_Bragg = 3.85). These refinements show that the occupation of anionic sites (32f) is 23%, 4% higher than in the starting model.

Analysis of samples milled for other lengths of time result in the cell parameter of the fluorite phase decreasing with milling time, as shown in Figure 2.

![Figure 2.](image)
The Rietveld analysis of samples sintered after milling for 12 h results in 84.0% Aurivillius BTN and 16.0% of Bi$_2$TiO$_{20}$ (bcc structure isomorphic to γ-Bi$_2$O$_3$) ($R_{\text{Bragg}} = 17.4$). After milling for 24 h the Rietveld refinement shows only Aurivillius BTN phase ($R_{\text{Bragg}} = 20.4$).

**Figure 2.** Cell parameters behavior vs. milling time for fluorite phase

### 4. Conclusions

High energy mechanical activation of mixtures of Bi$_2$O$_3$, TiO$_2$ and Nb$_2$O$_5$ yields an essentially amorphous precursor, except for an incipient fluorite phase for milling times of 24 h or more. This precursor is formed in times one order of magnitude lower than previously reported for low energy milling.

The crystallization of metastable BTN fluorite phase was obtained in the 593 - 823 K range, with concomitant rutile TiO$_2$. Sintering at temperature higher than 873 K leads to the stable Aurivillius BTN phase.

A good adjustment for the Rietveld analysis is obtained for BTN fluorite phase using the δ-Bi$_2$O$_3$ model. In contrast, BTN Aurivillius refinement yields a relatively high $R_{\text{Bragg}}$ which can be ascribed to a deficient structural model of the compound. At high milling times, the BTN fluorite phase presents TiO$_2$ crystallization and decreasing cell parameter.

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### References

[1] D. Su, J.S. Zhu, Q.Y. Xu, J.S. Liu, Y.N. Wang, Micro. Eng., 66 (2003) 825
[2] A. Castro, P. Millán, L. Pardo, B. Jiménez, J. Mater. Chem, 9 (1999) 1313
[3] R. Ávila, A. Castro, V. Martin, L.M. Fernández, H.E. Ulloa, *Sensitivity to water of Bi$_3$TiNbO$_9$*, XIII Simposio Sociedad Chilena de Física, Concepción, 13-15 Nov. 2002, Concepción, Chile.
[4] A. Moure, L. Pardo, C. Alemany, P. Millán, A. Castro, J. Euro. Ceram. Soc., 21 (2001) 1399
[5] A. Moure, A. Castro, L. Pardo, Acta Mater 52 (2004) 945
[6] K. Chattopadhyay, V. Varghese, Mater. Sci. Eng., A 375-377 (2004) 72
[7] J. Rodríguez-Carvajal, Laboratoire Léon Brillouin CEA-CNRS, (2001)
[8] X. L. Chen, F.F. Zhang, Y.M. Shen, J.K. Liang, W.H. Tang, Q.Y. Tu, J. Solid State Chem., 139 (1998) 398
[9] G. Nalini, G.N. Subbanna, T.N. Guru Row, Materials Chemistry and Physics, 82 (2003) 663