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Molten Salt Synthesis and Crystal Structure of $Bi_5Ti_3FeO_{15}$

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ABSTRACT

Molten salt synthesis (MSS) of ceramics is an alternative to sol-gel and ceramic methods. Phase purity, as well as particle shape and size, may be effectively controlled by MSS. In the present study, magnetoelectric Aurivillius phase $Bi_5Ti_3FeO_{15}$ is obtained by MSS. Experimental setting for reaction control is described. Typical crystallites exhibit plate-like shape with noteworthy size uniformity and aspect ratio. The crystal structure of the investigated phase is analyzed by synchrotron x-ray powder diffraction. Rietveld refinement results for crystal symmetry, cell parameters and atomic positions are given. Space group is Fmm2. Cell parameters (in Å) are: $a = 41.157(1)$, $b = 5.4420(2)$, $c = 5.4759(2)$.

Keywords: Molten salts synthesis; crystal structure; Aurivillius; Rietveld

INTRODUCTION

Materials formed by low-symmetry crystals exhibit useful anisotropy. Depending on the preparation method, crystal morphology reflects the mentioned anisotropy. This fact facilitates obtaining highly texturized samples, whose properties approximate those of the single-crystal [1].

So-called Aurivillius phases [2], with generic formula $(BiO_2)\cdot(A_{n-1}B_n O_{3n+1})$, are formed by n perovskite layers sandwiched between two bismuth oxide layers. They exhibit ferro-piezoelectric [3, 4] and eventually magnetoelectric

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[5] properties. Characteristic crystal morphology is plate-like, with plate surface parallel to the bismuth oxide layers [6]. Remarkable anisotropy of electrical properties has been reported for Aurivillius phases [7].

Large single-crystals of Aurivillius phases are needed for measuring the tensors of their fundamental physical properties, for high-resolution studies of their electronic structures, for developing precise piezo- and magnetoelectric transducers. Nano-crystals of ferroic and multiferroic phases are required to solve important basic and applied problems. What are the critical sizes for existence of ferroic and multi-ferroic phenomena? How electric and magnetic orders relate to each other in the nanometric scale?

Profitable use of Aurivillius phases, from macro to nano scales, requires the setting up of effective preparation techniques. Molten salt synthesis (MSS) is revealing itself as an important competitor to other well-established methods. In this article we report the preparation by MSS and the crystallographic characterization of the Aurivillius phase $Bi_5Ti_3FeO_{15}$. Ferroelectric and magnetoelectric properties have been reported for this phase [5].

CHEMICAL BACKGROUND

We briefly compare MSS with Sol-Gel (SG) [8] and with the Ceramic Method (CM) [9].

Phase purity, as obtained by MSS, is comparable to that attained by SG. But the required reagents and procedures are not so expensive and complicated. Furthermore, particle shape may be more effectively controlled by MSS than by sol-gel.

MSS and CM use similar starting reagents (oxides, carbonates). But there exist fundamental differences between these two techniques. In CM the formation of the new phase is mediated by solid-state diffusion of atoms from a reactive phase into the other one. In MSS the use of fused salts as reaction medium allows a greater mobility of the atomic species, requiring smaller reaction times and temperatures. Control of morphological parameters is better by MSS.

Synthesis by MSS has functional advantages [10]. The method allows obtaining any amount of product, from easily available reagents. It has been successfully used to prepare super-conductors [11], ferro-piezoelectrics [8] and ferromagnetics [12].

Whereas SG and MC have been extensively applied and their theoretical foundations have been basically explained, MSS is significantly younger and it has been much less applied and explained.

The fundamental process of MSS is based on the dissolution and dissociation of the participating reagents and possibly the formation of complex ionic intermediaries [13]. Mentioned processes allow a large mobility of the atomic species and stable particle formation for the product phase. Morphology and size may be governed by controlling the reaction conditions. In this sense,

reaction temperature and time are particularly important factors to be taken into account [8].

EXPERIMENTAL

Bi$_5$Ti$_3$FeO$_{15}$ was prepared using MSS. Reagent grade Bi$_2$O$_3$, TiO$_2$ and Fe$_2$O$_3$ were stoichiometrically homogenized with a eutectic mixture of NaCl and KCl, in a ratio 1/4. Portions of this mixture were placed in covered alumina crucibles and heated during 4 hours at 800, 850, 900 and 950°C. In every reaction, heating and cooling temperature slopes were of 1°C/min. The reaction products consisted of yellow Bi$_5$Ti$_3$FeO$_{15}$ particles, with tonalities that depended on temperature. They were washed in redistilled water until total absence of chlorides. The chloride test was performed by means of a 0.5 M AgNO$_3$ solution. Final steps were drying for 6 hours at 110°C and preparation for electron microscopy and x-ray diffraction.

Morphological characterization was performed by means of scanning (SEM) and transmission (TEM) electron microscopy. Crystal structure analysis was done via Rietveld analysis of synchrotron x-ray powder diffraction. SEM was realized in a Jeol JSM 5800LV, while TEM was in a Phillips CM200. X-ray diffraction was performed in beam line 2-1 of Stanford Synchrotron Radiation Laboratory. The employed wavelength was $\lambda = 1.23985$ Å. Angular domain was $4° \leq 2\theta \leq 136°$, step $\Delta(2\theta) = 0.01°$.

RESULTS AND DISCUSSION

Electron micrographs of the samples obtained at 800, 850, 900 and 950°C, respectively denominated 800F1, 850F1, 900F1 and 950F2, are shown in Fig. 1. Sample 800F1 was observed by TEM, while samples 850F1 to 950F1 were investigated by SEM. Plate-like crystal shape and high aspect ratio, as reported in [11], are apparent. Particle size strongly depends on reaction temperature: the lower the reaction temperature, the smallest the crystallites. As temperature ranges from 800 to 950°C, particle size varies from the order of 100 nm to several μm.

A possible explanation for the observed tendency may be found in the *nucleation versus growth* competition. As temperature decreases, mobility drops off and crystal growth becomes slower. Nucleation rate is relatively enhanced and crystallite size distribution moves to smaller values.

Synchrotron x-ray diffraction pattern of sample 900F1 is shown in Fig. 2. Sample obtained at 900°C was chosen because crystal size and perfection were the best from the diffraction point of view. Smaller crystallites would produce peak broadening and larger ones would give rise to intense texture problems.

Our selection of orthorhombic vector basis is as follows. Cell vector **c** coincides with the polar axis of the structure. Vector **a** is along the large
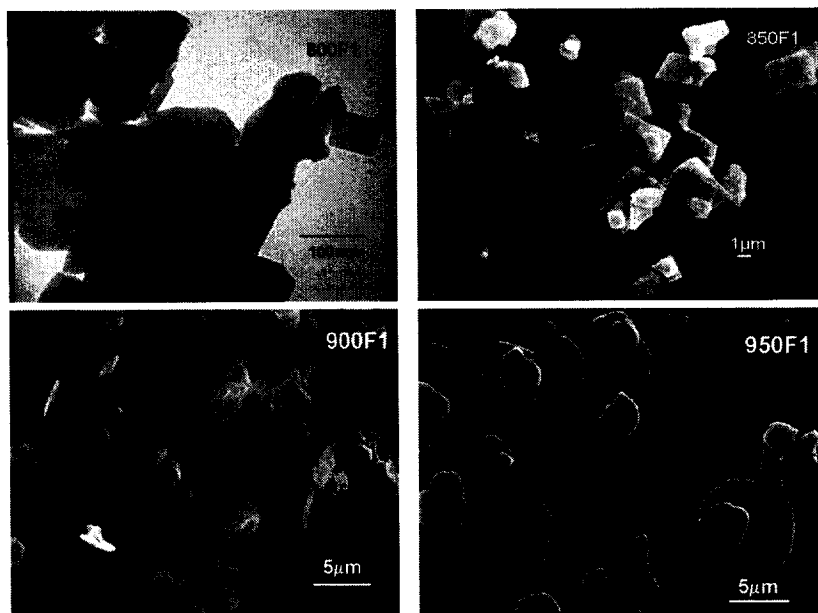
Figure 1. Micrographs of $Bi_5Ti_3FeO_{15}$ obtained at various temperatures.

dimension of the unit cell and vector **b** is a little bit smaller than **c**. The important question regarding tetragonal symmetry break-down ($b \neq c$) is investigated via the observation of the 002/020 doublet. The result of our experiment regarding this problem is highlighted by means of a zoom in Fig. 2. The
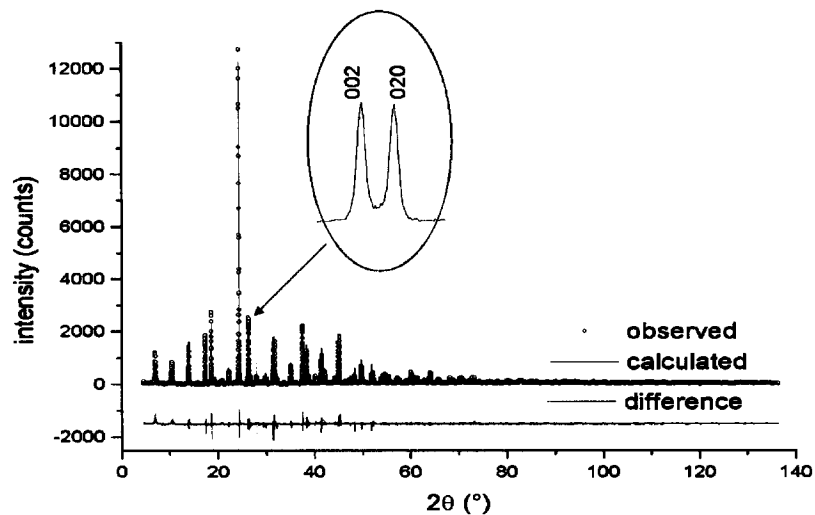

Figure 2. Observed and calculated x-ray diffraction patterns.

Table 1

Crystal structure of $Bi_5Ti_3FeO_{15}$. Space group Fmm2 Cell parameters (Å): $a = 41.157(1)$, $b = 5.4420(2)$, $c = 5.4759(2)$

Atom	x	y	z	Bisot	Multip
Bi	0.00000	0.000	0.046(4)	1.17(3)	4
Bi	0.89556(4)	0.000	0.050(4)	1.17(3)	8
Bi	0.21912(4)	0.000	0.059(4)	1.17(3)	8
Ti/Fe	0.4512(2)	0.000	0.000	0.000	6/2
Ti/Fe	0.3464(2)	0.000	0.000	0.000	6/2
O1	0.50000	0.000	−0.0130(3)	2.1(3)	4
O2	0.45369(4)	0.250	0.25000	2.1(3)	16
O3	0.25000	0.250	0.75000	2.1(3)	8
O4	0.40200	0.000	0.0130(3)	2.1(3)	8
O5	0.35031(4)	0.250	0.25000	2.1(3)	16
O6	0.30200	0.000	−0.0130(3)	2.1(3)	8

characteristic 002/020 doublet is clearly resolved in the synchrotron radiation experiment.

X-ray experimental data were processed by means of the software FullProf [14]. Following a tendency observed in four-layered Aurivillius phases [15, 16] space group Fmm2 was proposed and a satisfactory convergence was reached. The number of refined parameters (structural and instrumental) was 34. Table 1 contains the results of the performed structural analysis. Numbers in parentheses represent standard deviations. The absence of parentheses means that the considered quantity remained fixed during the refinement. Highly symmetric oxygen sites were taken as reference coordinates. Titanium/iron cations' temperature factors did not show stability during refinement. Their standard deviations were not significantly lower than their values or variations. Consequently these parameters were fixed. Final disagreement factors were $R = 12.9$, $\chi^2 = 7.86$. Figure 3 represents the investigated structure.

The final balance of the experimental work here reported is the setting up of the MSS method for obtaining plate-shaped crystals of $Bi_5Ti_3FeO_{15}$ with
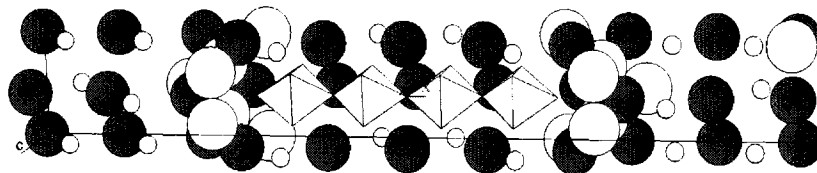

Figure 3. The crystal structure of $Bi_5Ti_3FeO_{15}$. Spheres: large white → O; small white → Ti; large gray → Bi. O atoms at the corners of Ti-coordination octahedra omitted.

controlled size distribution. The crystal structure of the investigated phase has been refined. This work contributes a promising starting material for preparing highly-textured magnetoelectric polycrystal ceramics. Present paper complements a theoretical study about the influence of texture on the properties of electroceramics, appearing in this same volume [17]. Magnetoelectric textured ceramics, considered in the mentioned article, may be obtained in practice by the method here described.

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