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$SrBi_2Nb_2O_9$ Thin films crystallized using a low power microwave oven

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Abstract

$SrBi_2Nb_2O_9$ thin films were produced by the polymeric precursor method using an aqueous solution. The crystallization of the films was carried out using a domestic microwave oven by means of a SiC susceptor in order to absorb the microwave energy and rapidly transfer the heat to the film. Low microwave power and short time have been used. The films obtained are well-adhered, homogeneous and with good specularity, even when treated at 600 °C for 10 min. The microstructure and the structure of the films can be tuned by adjusting the crystallization conditions. Depending on the direction of the heat flux it is possible to obtain preferential oriented or polycrystalline films in the microwave oven for 10 min. The microstructure presented a polycrystalline nature with spheroid small mean grain size when the susceptor is placed above the substrate. When the susceptor is placed below the substrate, the films presented platelet grains with mean grain size around 250 nm and a 00l orientation. For comparison, films were also prepared by the conventional method at 700 °C for 2 h.

Keywords: Ferroelectric; Microwave; $SrBi_2Nb_2O_9$; Thin films

1. Introduction

Ferroelectric materials have been extensively studied due to their potential applications mainly as thin films. The most popular ferroelectric material for nonvolatile memory applications are $PbZr_xTi_{1-x}O_3$ (PZT), due to their high Curie temperature and large remnant polarization. In spite of these properties, these materials have serious fatigue degradation problems which can be solved by changing the electrode.[1,2]

As alternative material, those belonging to the Aurivillius family $Bi_2O_2^{2+}(A_{m-1}B_mO_{3m+1})$, among them $SrBi_2Nb_2O_9$ (SBN), $SrBi_2Ta_2O_9$ (SBT), $Bi_4Ti_3O_{12}$ (BIT), have received great attention. It is well known that the Aurivillius composition SBT has ferroelectric behavior at room temperature, but the main disadvantage is the required temperature for obtaining well crystallized films, around 800 °C, which is not compatible with the IC technology. That is why, recently another Aurivillius compound, SBN, has received great attention. Well crystallized SBN films can be obtained at 650–700 °C, which represents a considerable gain.[3–5]

Several methods have been used for SBT and SBN synthesis, such as pulsed laser deposition (PLD),[6–8] metal-organic chemical vapor deposition (MOCVD),[9–11] deposition solution (sol-gel,[3,12,13] metalorganic deposition (MOD), [14,15] polymeric precursors[16,17]). Among chemical solutions methods, the soft-solution processing, for fabrication in aqueous solution, has been searched.[18]

For obtaining good crystallized films, heat treatment at high temperatures for a long time is necessary, normally 2 h. These long heat treatments can cause several damages to the stack, leading to interdiffusion between the film and the substrate, and sometimes loss of stoichiometry (due to volatile cation). So, it is important to decrease the temperature and time of the thermal treatment.

Microwave energy is being developed as a new tool for high-temperature processing of materials. This technology has received great attention due to the advantages observed with microwave processing, which

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include: reduced processing costs, better production quality, new materials and product, among others. With proper understanding and control, many technically important materials can be heated rapidly, uniformly, selectively, less expansively and with greater control than is possible with conventional methods.[19–21]

In this work, microwave energy to promote a rapid thermal way for the crystallization of the film was investigated with the advantage of reducing the time and, in some cases, the temperature of the thermal treatment.

2. Experimental

The preparation of the SBN deposition solution was fully described elsewhere.[16,17] Briefly: niobium ammonium oxalate (CBMM), strontium carbonate (Aldrich) and bismuth oxide (Aldrich) were used as starting regents. The metallic cations were dissolved in a citric acid aqueous solution followed by a polyesterification reaction with ethylene glycol. So, the homogeneous distribution of the cations in the polymeric chain leads to a very stoichiometric controlled compound.

The films were deposited onto $Pt/Ti/SiO_2/Si$ substrates by spinning the deposition solution at 5000 rpm for 20 s. After deposition, the films were treated at 400 °C for 2 h, for elimination of the organic material. The desired thickness was obtained by several cycles of deposition and thermal treatment at 400 °C. The films were heat treated at 600, 650 and 700 °C for 10 min in a domestic microwave oven (CCE, M301, 2.45 GHz, 900 W) by means of a SiC susceptor in order to absorb the microwave energy and rapidly transfer the heat to the film. The crystallization was performed changing the position of the SiC susceptor. Firstly, the SiC susceptor was placed below the substrate; in a second experiment, the SiC susceptor was placed above the film. The objective was to investigate if the position of the susceptor would influence the crystalline structure of the film. For comparison, SBN films were also heat treated for 2 h at the same temperatures in a conventional furnace.

After crystallization, the films were characterized by X-ray diffraction (RIGAKU, DM Max 2500PC), 40 kV and 150 mA from 20 to 60° 2Θ, following the phase evolution. AFM (DIGITAL, Nanoscope 3A) was used to analyze the surface topography and roughness. Electrical measurements were carried out in a HP4192A impedance analyzer for dielectric properties and the hysteresis loops were measured on a ferroelectric tester (RADIANT, RT 6000HVS).

3. Results and discussion

The XRD patterns for the films treated at 600, 650 and 700 °C in the conventional furnace are displayed in Fig. 1. At 600 and 650 °C the films present the perovskite phase coexisting with the intermediate fluorite phase characterized by an intense peak at 28.3° and by some broad characteristic peaks. At 700 °C, the peaks related to the perovskite phase are well defined. It can be observed that the films are polycrystalline, with no preferential orientation.

For comparison, films were prepared using a domestic microwave oven at the same temperatures, for 10 min. The XRD results are shown in Fig. 2. At 600 °C only the intermediate fluorite phase is observed, no perovskite peaks were detected. It is possible to verify that, for the film treated at 650 °C for 10 min, the intermediate fluorite phase is clearly observed, as well as

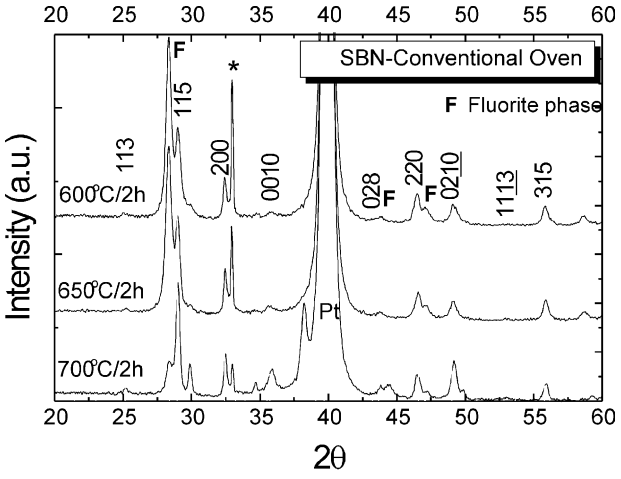

Fig. 1. XRD patterns for the films crystallized at 600, 650 and 700 °C for 2 h in a conventional furnace (*substrate).

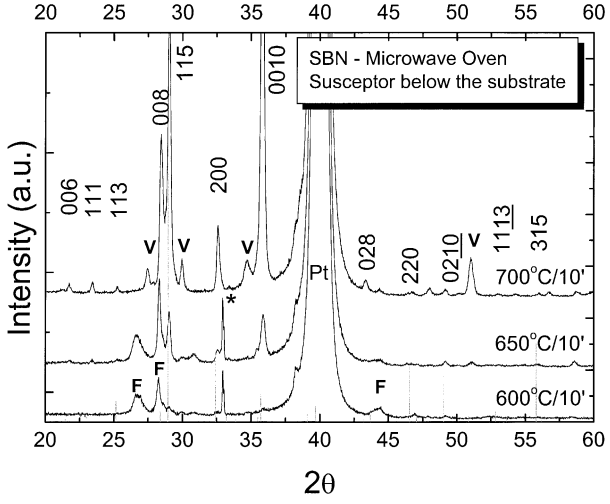

Fig. 2. XRD patterns for the films crystallized at 600, 650 and 700 °C for 10 min in a domestic microwave oven with the SiC susceptor placed below the substrate (F intermediate fluorite phase; Vunidentified phase, *substrate).

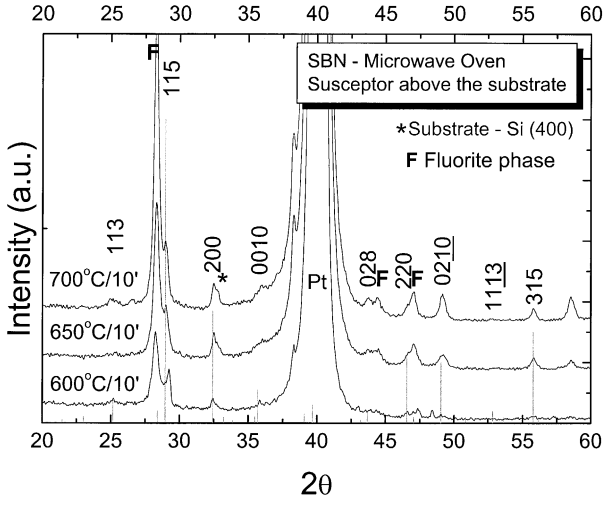

Fig. 3. XRD patterns for the films crystallized at 600, 650 and 700 °C for 10 min in a domestic microwave oven with the SiC susceptor placed above the substrate.

incipient 0010 preferential orientation. For the film treated at 700 °C, the high intense 0010 peak, denoting preferential orientation, is clearly seen. This result is not satisfactory for SBN films from a ferroelectric point of view, since the polarization occurs mainly in the *a–b* plane, but it is still a very interesting effect. In this case, the thermal treatment was done with the SiC-susceptor placed below the films, suggesting that the crystallization initiates at the film-substrate interface. For the film treated at 700 °C, some unknown extra peaks were observed.

When the SiC-susceptor is placed above the films (Fig. 3), the superficial crystallization is induced and the films presented polycrystalline nature as well as the films obtained in the conventional furnace. At 600 °C it is observed the intermediate fluorite phase as verified also for the conventional treatment. At 650 °C the fluorite phase coexists with the incipient perovskite phase. However, the time is very short for the complete

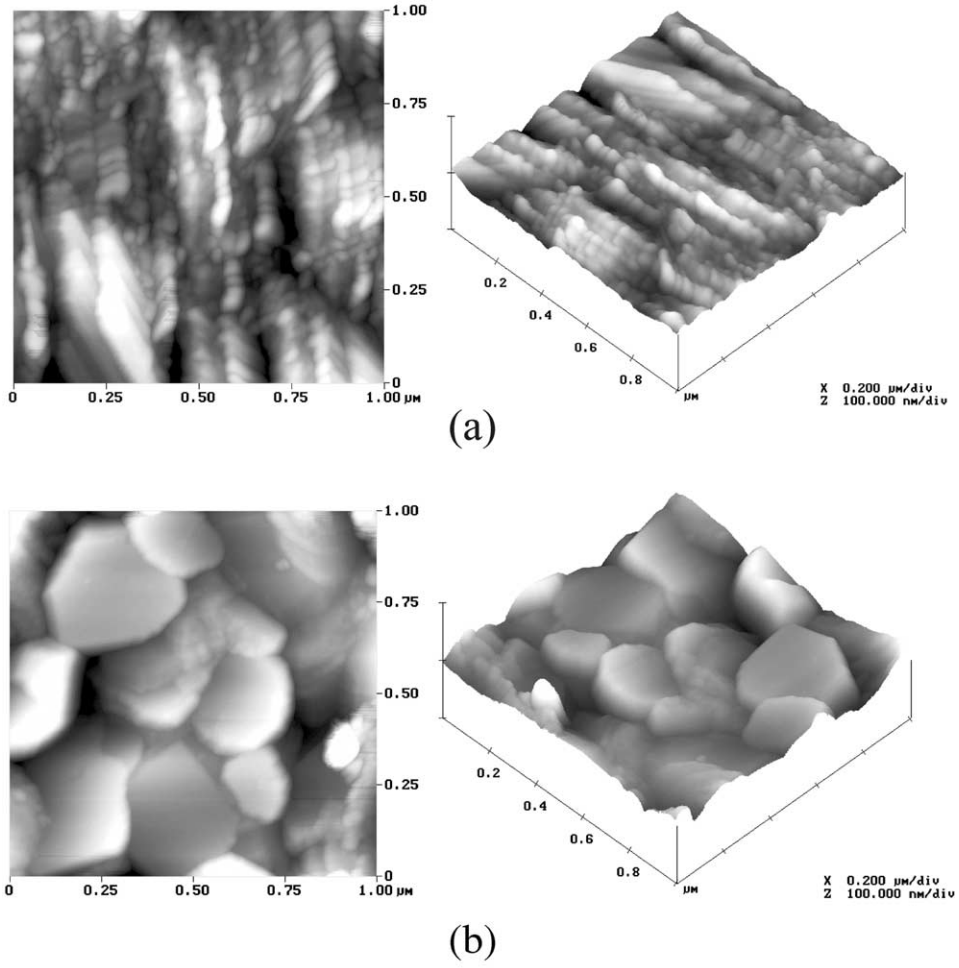

Fig. 4. AFM images of the films crystallized in a microwave oven for 10 min, at (a) 600 °C and (b) 700 °C (susceptor placed below the substrate).

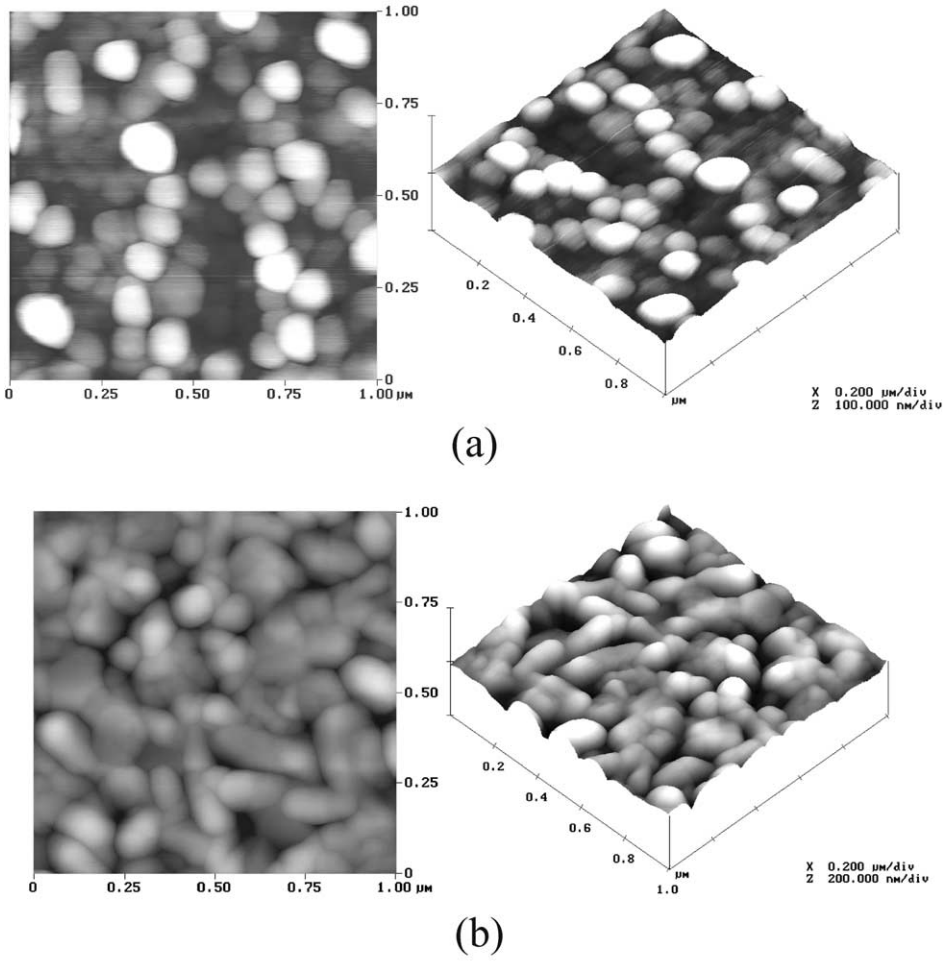

Fig. 5. AFM images of the films crystallized in a conventional furnace for 2 h, at: (a) 600 °C and (b) 700 °C.

crystallization of the perovskite phase and at 700 °C the fluorite phase is yet predominant. It can be observed that the XRD patterns are very similar to those depicted in Fig. 1. These results enhance the versatility of the microwave treatment, since the structure of the films may be modulated according to the conditions of the thermal treatment in the microwave oven.

The changes in the surface morphology of the films submitted to microwave oven at different temperatures were followed by AFM measurements. Fig. 4 depicts the micrographs for the films treated at 600 and 700 °C in microwave oven for 10 min, with the susceptor placed below the substrate.

It can be observed that the film treated at 600 °C for 10 min presents clusters of elongated grains coexisting with very small spheroid grains. These small grains probably are the intermediate fluorite phase, already described in literature by Rodriguez et al.[22] As the temperature increases, the clusters of elongated grains turn into plate-like grains, typical of the bismuth-layer compounds and when the film was treated at 700 °C big oriented plate-like grains of around 250 nm were formed. These results are in agreement with the XRD patterns.

The AFM images of the films treated at 600 and 700 °C in a conventional furnace are showed in Fig. 5. The films treated at 600 °C presented a microstructure with small spheroid grains due to the presence of the intermediate phase, according to the XRD results. The increase in the temperature to 700 °C provokes an increase in the mean grain size, also their shape turned into elongated grains.

When the films are crystallized in the microwave oven with the susceptor placed above the films, the

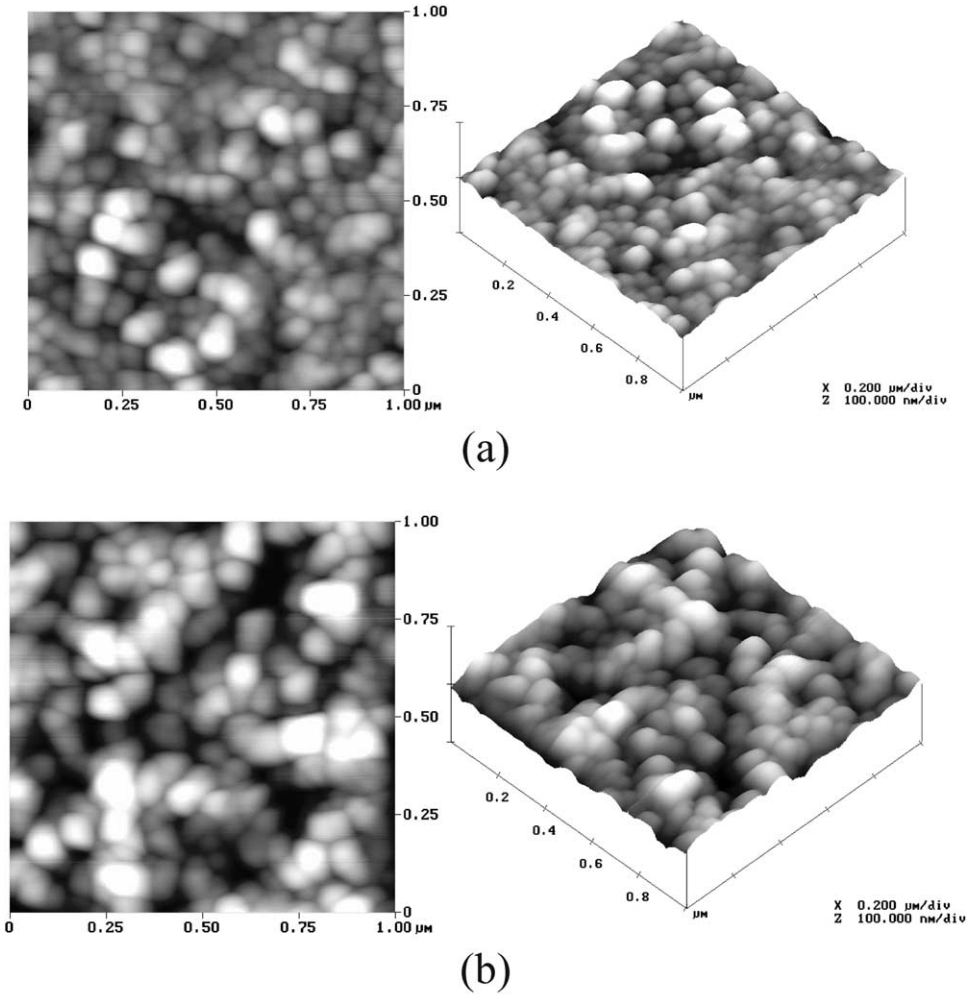

Fig. 6. AFM images of the films crystallized in a microwave oven for 10 min, at: (a) 600 °C; (b) 700 °C (susceptor placed above the film).

microstructure is very similar to that obtained in the conventional furnace. The AFM micrographs are depicted in Fig. 6. It can be observed that the films present a dense microstructure with small spheroid grains related to the fluorite phase at 600 °C. Increasing the temperature leads to an increase in the mean grain size, but the shape of the grains is maintained. The mean grain size is smaller than for the films crystallized in the conventional furnace, probably due to short time treatment, only 10 min and also due to the superficial nucleation, favored when the susceptor is placed above the substrate.

The surface roughness was measured by AFM and the data are summarized in Table 1. It worth emphasizing that the microwave treatment leads to films with higher superficial roughness. This is not surprising since the films crystallized in a microwave oven present some preferential orientation in the 0010 direction, with sharper grains than those obtained in a conventional furnace, normally rounded grains.

Electrical measurements were performed for the films treated in a microwave oven with the susceptor placed below the substrate, but a very small remnant polarization was obtained. This result was expected since these films presented a 0010 orientation and there is no appreciable polarization in the *c*-direction.

Table 1
Surface roughness measured by AFM for films treated in a microwave oven and in a conventional furnace

Temperature (°C)	Roughness (nm)		
	Microwave oven (time = 10 min)		Conventional furnace (time = 2 h)
	Susceptor below	Susceptor above	
600	9.8	4.8	4.9
650	14.6	8.4	3.7
700	21.9	9.5	16.2

4. Conclusions

A domestic low power microwave oven was used for crystallization of SBN films prepared by the polymeric precursor method. The films obtained are well-adhered and homogeneous even when treated at 600 °C for 10 min. The microstructure of the films can be tuned by adjusting the crystallization conditions. This method allows to obtain oriented films with big plate-like grains (when the susceptor is placed below the substrate) as well as polycrystalline films with spheroid grains (when the susceptor is placed above the substrate). The time required for well crystallized films is drastically reduced (10 min) compared with the conventional way (normally 2 h). This is of great advantage for preventing undesired reactions between the film and the substrate and loss of stoichiometry of the film.

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