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Chemical Fabrication $SrBi_4Ti_4O_{15}$ Thin Films

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Abstract

The ferroelectric compound $SrBi_4Ti_4O_{15}$ that belongs to the so-called Aurivillius family could be promising for the fabrication of ferroelectric thin film memories. Pure $SrBi_4Ti_4O_{15}$ powders were obtained after heating adequate sols (bismuth and strontium 2-ethylhexanoates in 2-ethylhexanoic acid and appropriate amount of titanium isopropoxide) at 350°C for 12 h and subsequently putting the samples directly in an electric oven at 700–900°C for 3 h. When spin-coated on silicon wafers and submitted to a similar process, the same sols always led to a mixture of SBT and the pyrochlore phase $Bi_2Ti_2O_7$. In order to avoid the presence of this impurity, extra bismuth content (0–40 mol%) was added during the preparation of the sols. The pyrochlore formation was completely eliminated when using 20% bismuth excess and the following process: (spin-coating 250°C/5 min–750°C/1 min)/10 times + final annealing at 800°C/1 h © 1999 Elsevier Science Limited. All rights reserved

Keywords: films, sol–gel processes, X-ray methods, titanates, Aurivillius phases.

1 Introduction

The bismuth layered structure ferroelectrics are promising candidates for non-volatile memory devices.[1,2] They belong to the family of the so-called Aurivillius phases generally formulated as $Bi_2A_{m-1}B_mO_{3m+3}$. Their crystal structure can be regarded as a regular intergrowth of $(Bi_2O_2)^{2+}$ layers and $(A_{m-1}B_mO_{3m+1})^{-2}$ perovskite-like slabs.[3,4] In these compounds, A is a mono-, di- or trivalent element allowing dodecahedral coordination, B is a transition element suited to octahedral coordination and m is an integer ($1 \leq m \leq 5$) which represents the number of perovskite-like slabs intercalated between the $(Bi_2O_2)^{2+}$ layers. A number of them, e.g. $SrBi_2Nb_2O_9$ ($m=2$), $Bi_4Ti_3O_{12}$ ($m=3$), $BaBi_4Ti_4O_{15}$ ($m=4$), have been thoroughly investigated from the point of view of both structural and electric properties.[5–9] Recently, thin films made from materials with $m=2$ and, in a less extent with $m=4$, have been found to show low fatigue of the remnant polarisation under cycling.[10] If $SrBi_2(Nb,Ta)_2O_9$ ($m=2$) thin films have been prepared either by physical (e.g. sputtering, laser ablation) or by chemical (metal–organic chemical vapour deposition, sol–gel spin-coating) techniques very few data have been published devoted to the chemical preparation of $SrBi_4Ti_4O_{15}$ films.[11] The aim of this paper is to present the results of investigations about the preparation of $SrBi_4Ti_4O_{15}$ precursors as well as the fabrication of thin films by spin-coating and their structural characterisation by X-ray diffraction.

2 Experimental

The $SrBi_4Ti_4O_{15}$ precursor solution was prepared by mixing bismuth 2-ethylhexanoate $Bi(C_7H_{15}COO)_3$ and strontium 2-ethylhexanoate $Sr(C_7H_{15}COO)_2$ in 2-ethylhexanoic acid $C_7H_{15}COOH$ and adding appropriate amount of titanium isopropoxide $Ti(OC_3H_7)_4$. The mixture was then continuously stirred for 2 h at 200°C. After cooling to room temperature a homogeneous clear sol was obtained and can be stored unchanged for several weeks. Such sols will be used subsequently for preparing either powders by controlled calcination or thin films by spin coating on Si substrates placed in a Sulzer photoresist spinner. The flow chart of the whole process is shown in Fig. 1.

The thermal behaviour of the solution was checked by TGA/DSC using a Netzsch STA 409

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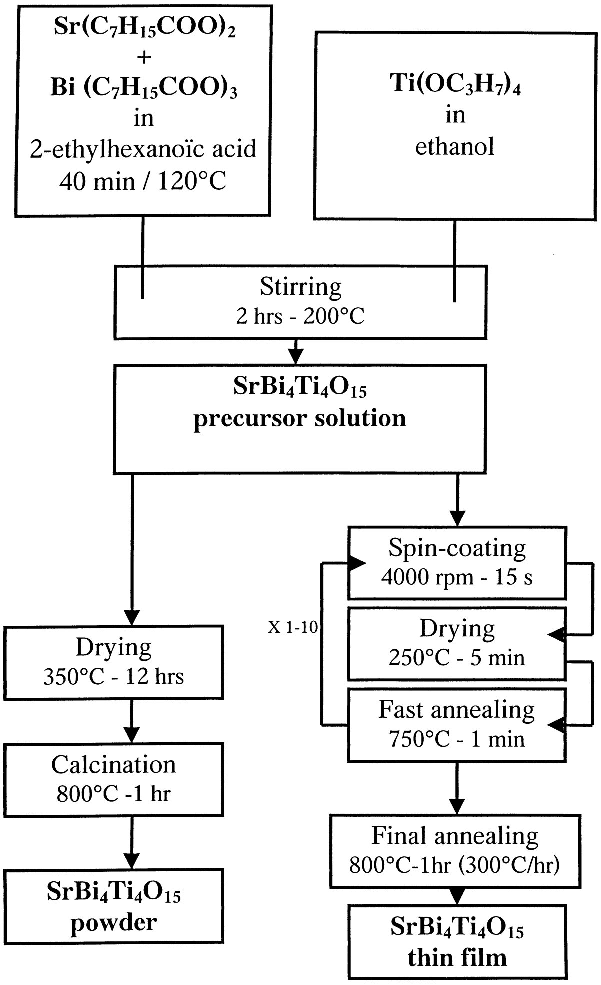


Fig. 1. Flow chart of the fabrication process.

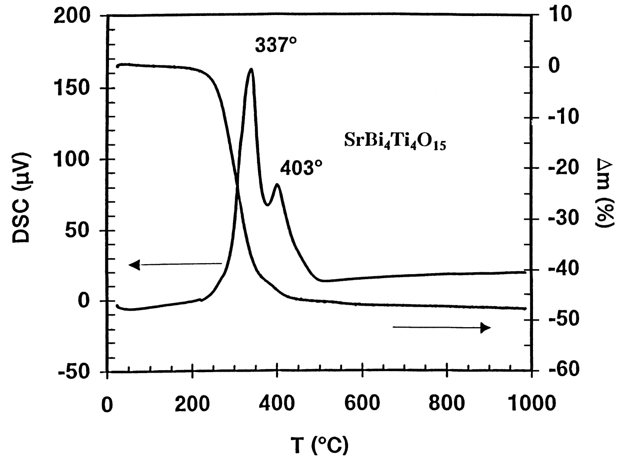


Fig. 2. TGA/DSC traces of the $SrBi_4Ti_4O_{15}$ precursor.

device. Crystallisation processes and phase analyses were performed using a Siemens D5000 powder diffractometer fitted with an Anton Parr HTK variable temperature attachment. The morphology of powders was observed with a Philips XL30 scanning electron microscope.

3 Results and Discussion

3.1 Thermal behaviour of the precursor solution

After drying at 250°C for 20 h, the precursor solution transforms into a xerogel which was studied by simultaneous TGA/DSC between room temperature and 1000°C at an increasing temperature rate of 10° min^{-1}. As shown in Fig. 2, the weight loss becomes significant at 250°C where it steeply increases to completion achieved at about 500°C. The strong exothermic lines observed at 337 and 403°C in the DSC trace would be assigned to the onset of crystallisation. The mechanisms associated with the crystallisation are somewhat complex. As a matter of fact, the Aurivillius phase $SrBi_4Ti_4O_{15}$ does not crystallise at these temperatures. As shown by X-ray diffraction patterns recorded at several rising temperatures (Fig. 3), the phases that appear first would certainly be bismuth titanates like $Bi_2Ti_2O_7$ (or $Bi_2Ti_4O_{11}$) as well as $SrTiO_3$ which are the most stable phases of the system: such a behaviour has been already observed during the first steps of the crystallisation of precursors of $Bi_4Ti_3O_{12}$.[12] At the highest temperatures reached in the high temperature attachment, no significant change will occur.

To avoid the initial formation of undesirable stable phases, rapid thermal heating was performed on the powder previously dried at 300°C. The powder put on the platinum heating element of the high temperature X-ray device was heated up to 700°C at 10°C s^{-1} and the patterns were recorded every 50°C from 700 to 900°C (10 min between each record). The results are given in Fig. 4. The Aurivillius phase $SrBi_4Ti_4O_{15}$ actually forms at 700°C and show no modification up to 900°C. After cooling to room temperature, the diffraction pattern remains unchanged and fits well with the 43-0973 JCPDS file.

When the xerogel was heated directly at 700°C for 3 h, the $SrBi_4Ti_4O_{15}$ powder is made of grains of about 10 μm in which one can observe smaller coalescent particles (0·2 μm). After heating up to 900°C, the microstructure has changed significantly: the shape of the smaller grains is more defined and the micrographs show the beginning of the sintering process (Fig. 5).

3.2 Fabrication and structural characterisation of thin films

The conditions used for deposition by spin-coating were determined from previous experiments. Owing to both the viscosity and the concentration of the stock solution, the films were spin-coated at 4000 rpm (initial acceleration 7 rpm s^{-1}) for 15 s followed by drying at 250°C for 5 min to remove most of the organics and then rapidly annealed at

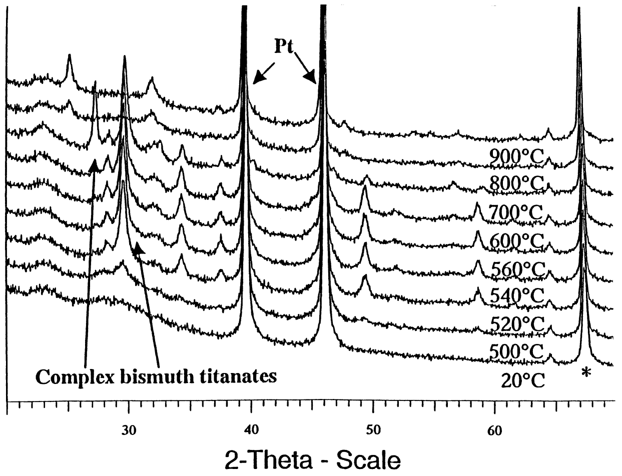


Fig. 3. X-ray diffraction patterns of the $SrBi_4Ti_4O_{15}$ precursor at several rising temperatures.

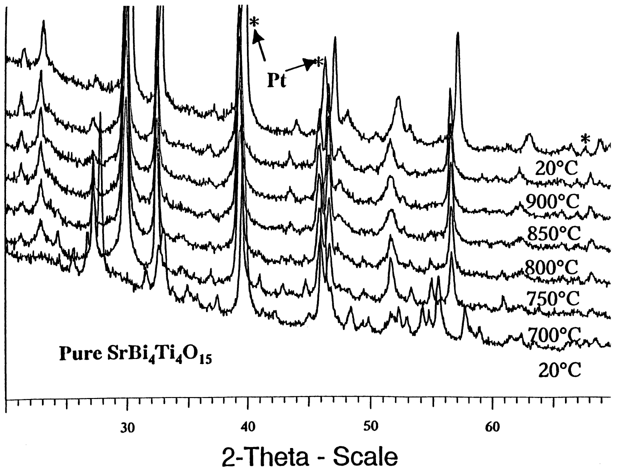


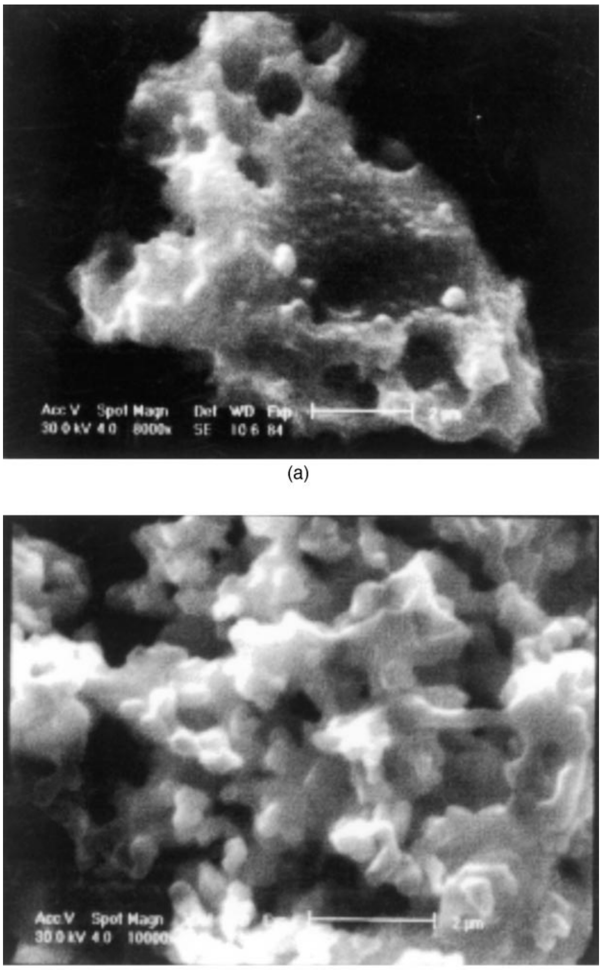
Fig. 4. X-ray diffraction patterns of the $SrBi_4Ti_4O_{15}$ precursor recorded every 50°C from 700 to 900°C.

750°C for 1 min. This process generally led to a dry film with thickness in the range 20–30 nm. To reach the required thickness for subsequent electrical characterisation, the procedure was repeated one to 10 times. The films underwent a final annealing at 800°C for 1 h to insure full crystallisation.

As already observed by several authors, films made with lead or bismuth containing materials sometimes show understoichiometric composition due to loss of lead or bismuth during annealing at high temperature.[11] In the case of the Aurivillius phases, this phenomenon is generally accompanied by the formation of extra phases with not well defined compositions. To insure stoichiometric composition, the simplest way consists in adding excess bismuth into the precursor solution. So some precursor solutions were prepared with various bismuth excess (0, 15, 18, 20, 23, 30 and 40 mol%).

For no bismuth excess, the XRD patterns of the films always show the presence of the pyrochlore phase $Bi_2Ti_2O_7$ (Fig. 6). Attempts to eliminate this undesirable impurity by changing the concentration or the viscosity of the solution as well as the nature of the solvent were unsuccessful. A plausible explanation of this phenomenon would be based on the relative stability of the principal binary or ternary phases occurring in the $SrO–Bi_2O_3–TiO_2$ system. In both phases $Bi_2Ti_2O_7$ and $SrBi_4Ti_4O_{15}$, the Bi/Ti ratio is the same. Nevertheless the former is known to be one of the more stable phase in the $Bi_2O_3–TiO_2$ system and so will preferentially form during the early stage of the thermal process. So the residual Bi_2O_3 content, which is quite far from the stoichiometry due to some evaporation, would not be large enough to insure further reaction with the remaining oxides (native SrO and TiO_2) to get the desired $SrBi_4Ti_4O_{15}$ phase.

When the bismuth excess increases the $Bi_2Ti_2O_7$ content decreases and there is an optimal excess about 20–23 mol%, which leads to pure $SrBi_4Ti_4O_{15}$. For this specific excess, the Bi_2O_3 evaporation allows the initial mixture to reach the actual composition $SrO–2Bi_2O_3–4TiO_2$ at the temperature of thermal treatment so that $SrBi_4Ti_4O_{15}$ phase can be obtained as a pure phase. As the Bi excess is increased above 23%, the Bi_2O_3 evaporation is no longer compensated and $Bi_2Ti_2O_7$



(a)

(b)

Fig. 5. Scanning electron microscope micrographs of $SrBi_4Ti_4O_{15}$ powders.

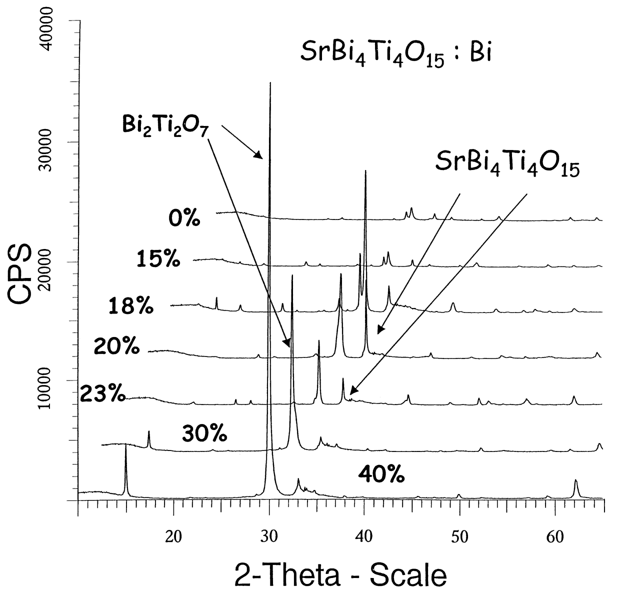


Fig. 6. Influence of the Bi excess on the X-ray diffraction patterns of $SrBi_4Ti_4O_{15}$ films after final annealing at 800°C for 1 h.

appears again together with the Aurivillius phase. Increasing further the Bi excess made the amount of $Bi_2Ti_2O_7$ to be so large that its main diffraction line (close to $2\theta = 30°$) masks those of $SrBi_4Ti_4O_{15}$.

4 Conclusion

Powders and thin films of the Aurivillius phase $SrBi_4Ti_4O_{15}$ have been prepared by the metal-organic decomposition route. The obtention of single phase thin films needs 20–23% Bi_2O_3 excess in the precursor solution and a final annealing at 800°C. Further investigations will be concerned with the deposition of films on $SrTiO_3$ single crystals to study the occurrence of preferred orientation and the associated electrical properties.

Acknowledgements

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