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Thermochimica Acta 360 (2000) 57–62

thermochimica acta

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Synthesis and analyses of thermal decomposition and microstructure of Sr-doped barium titanate alkoxide derived precipitates and thin films

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Received 4 January 2000; received in revised form 17 April 2000; accepted 25 April 2000

Abstract

The structure and thermal decomposition process of $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) powders and thin films, which were prepared from a precursor of Sr-doped barium titanate alkoxides, were investigated by means of differential thermal/thermogravimetric analyses (DTA/TGA), X-ray diffractometer (XRD), AFM, and Fourier transform infrared spectroscopy (FTIR) measurements. From the FTIR spectra, it has been possible to observe that gel powders pyrolyzed and crystallized by analyzing the bands of organic functional groups and inorganic oxides. For further determination of the temperature of decomposition and crystallization, DTA/TGA technique was used. The thin films of $Ba_{0.8}Sr_{0.2}TiO_3$ were prepared by spin-on sol–gel process on Si (1 0 0) substrates, the films were crystallized above 600°C, and formed complete perovskite structure around 700°C. The morphology was investigated by atomic force microscope. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: $Ba_{0.8}Sr_{0.2}TiO_3$; Sol–gel; DTA/TGA; FTIR spectroscopy; AFM

1. Introduction

High permittivity perovskite ceramic thin films have been intensively investigated during recent years as high dielectric constant materials for high density dynamic random access memory devices (256MB/1GB) as well as for millimeter microwave integrated circuits (MMICs) [1–3]. Among these materials, $Ba_xSr_{1-x}TiO_3$ (BST) is paid more attention because of its unique combination of large dielectric constant, low dc leakage, low loss tangent, and stable operation at high temperatures [4–6]. The sol–gel method or MOD is one of the most important approaches, which is being extensively used for the preparation of complex oxide thin films. The sol–gel processing and MOD show attractive advantages due to the fact that films with extremely uniform composition over large areas can be obtained with simple non-vacuum equipment. A key issue of any chemical solution deposition (CSD) thin films processing is the chemistry of precursor solution, which governs the properties of the final oxide layer. Thermogravimetric/differential thermal analyses (TGA/DTA) is very popular and relatively simple equipment to determine the decomposition process. The solution system often shows complex TGA mass/temperature curves in which multiple decomposition products correspond with the weight change observed. Sawada et al. [7] and Sawada and Ito [8] had investigated the formation process of ceramic films by thermal analysis of the

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PII: S0040-6031(00)00530-X

precursor materials. The Fourier transform infrared spectroscopy (FTIR) is better suited for quantitative determination [9]. X-ray diffraction is a phase selective method and can be used advantageously for investigating phase transition phenomena.

The purpose of the present work is to obtain information about the mechanism of its thermal decomposition and to determine the optimum conditions for obtaining crystalline BST thin films.

2. Experimental methods

In this experiment, barium acetate $Ba(CH_3CO_2)_2$, strontium acetate $Sr(CH_3CO_2{\cdot}(1/2)H_2O)_2$ and tetrabutyl titanate $Ti(OC_4H_9)_4$ were used as starting materials. Acetic acid and methanol were selected as solvents, ethylene glycol dimethyl ether as additives. To eliminate the water associated with strontium acetate completely, 99.0% pure $Sr(CH_3CO_2{\cdot}(1/2)H_2O)_2$ was dried about 70°C for 24 h, and then dissolved in glacial acetic acid. Acetylacetone (acac) was used to stabilize tetrabutyl titanate, and then the modified tetrabutyl titanate was added to the above solution with constant rate stirring at room temperature. The ethylene glycol dimethyl ether was added to the solution under ultrasonic agitation to adjust viscosity, surface tension of the precursor. pH value was adjusted using glacial acetic acid to remain in the range 2–4. The resultant solution was filtered to form the stock solution. The solution was in yellow and transparent. Part of the solution was slowly evaporated and dried under an infrared lamp at approximately 70°C to form BST gel powders.

The solution was then spin-coated on the Pt/Ti/SiO_2/Si and Si (1 0 0) substrates. The as-deposited BST thin films were heated by a four-step heating procedure: first heated at a low temperature of 250°C for 30 min to dry the gel, then pyrolyzed at 390–450°C in air for 30 min and crystallized the films at about 700°C by rapid annealing in an oxygen ambient (flow rate was 3 l min^{-1}) for 15 min. To gain the crack-free films, an additional pre-annealing was used at 600°C before rapid thermal annealing. Thicker films were obtained by multiple repetition of the deposition/pyrolysis processing. Then the films were heated for 15 min at 500, 600 and 700°C, respectively. For comparison, part of the gel powder was heated at 950°C for 1 h to obtain BST crystallized powders. FTIR spectroscopic experiments were carried out with NIC 7199-C (Nicolet Instrument Corp.) spectrophotometer. FTIR spectra were recorded over 400–4000 cm^{-1} spectral range using the KBr method. One milligram of the sample was rapidly mixed with 300 mg of KBr and pressed. A transparent pellet was then obtained. Sixty-four scans, with a resolution of 2 cm^{-1} were recorded for each resulting spectrum. The corresponding background was subtracted from each spectrum.

Simultaneous thermal analyzer (Netzsch-STA 429, Germany) was used for TGA/DTA. The weight of the sample was 100 mg. The region in which temperature increased was 20–900°C. The full scale of DTA was 0.2 mV and the full scale of TG was 25 mg. The measurement was made in air with the heating rate 10°C min^{-1}. The crystalline phase of the BST thin films at room temperature was characterized by X-ray diffractometer (XRD) with Cu Kα (λ=0.1542 nm) radiation. The surface morphology was observed by atomic force microscope (SPM-9500J, Japan).

3. Results and discussion

The fabrication process from the precursors to the polycrystalline BST ferroelectric thin films can be divided into transformations: precursor→sol→gel→crystals. The structural changes occurring during these transformations can be monitored by using FTIR spectroscopy. The IR-spectra during the formation of the alkoxide complex are indicated in Fig. 1. Curves (a) and (b) show the IR-spectra of the sol and gel dried at 70°C of BST, respectively. The band around 3422 cm^{-1} is due to O–H stretching vibrations of hydroxyls presented in this system; the intensity of the sol is weaker than that of the gel. It is possibly because O–H bonds form chelation organic complex in the sol solution. The IR-absorption bands at 2800–3000 cm^{-1} are due to C–H stretching vibrations; the decreasing intensity of the BST from sol to gel is due to the evaporation of the methanol and other organic solvent in our samples. There are four main bands between 1200 and 1720 cm^{-1}, these bands are almost similar in sol and gel; 1704 cm^{-1} bands are due to symmetric and asymmetric stretching vibrations of the carboxylate functional group ($-COO^-$). The bands at

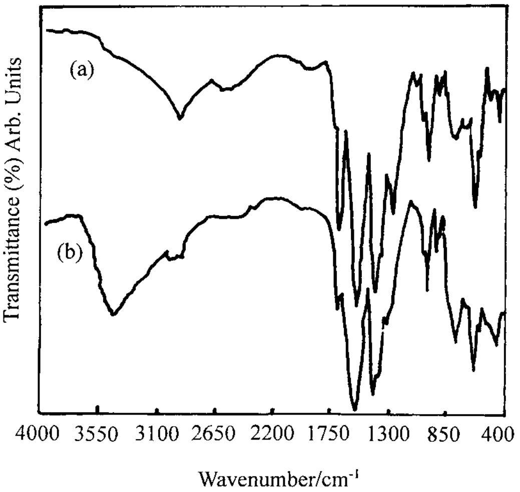
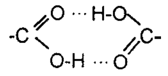


Fig. 1. IR-spectra of (a) sol and (b) gel dried at 70°C of $Ba_{0.8}Sr_{0.2}TiO_3$.

1557 cm^{-1} are due to acac bonded to titanium. Kamalasan et al. [10] have investigated that the spectrum of $BaTiO_3$ bands due to the titanium–acac complex are overlapped by carboxylate bands. Acetylacetone molecules are bonded to titanium ions bidentately to form a chelated structure as shown in Fig. 2. Yi and Sayer [11] had analyzed the chelating effect; the ring structure of the acetylacetonate ligands is very stable. The reduction of the number of functional groups and presence of the bulky acac ligands of the titanium ions prevent the condensation of the molecules of titanium acac.

The 1423 cm^{-1} bands are due to CH_2–CO bending vibrations, or –COOH bands which are coupled by O–H bending vibrations and C–O stretching vibrations. The structure of the coupled bonds is given below:



The 1287 cm^{-1} bands are due to –COOH group vibrations. It is obvious that the two bands of 1705 and 1287 cm^{-1} become weaker in the gel. It is probably because the –CO– and –COOH bonds broke up to form metal complex. There are three bands between 900 and 1100 cm^{-1} (1039, 1021, 1021 cm^{-1}). The 930 cm^{-1} bands are due to asymmetric vibrations of C–O–C bonds, and 1021 cm^{-1} bands are probably due to characteristic bands where metal ions combined with acetic radical (M–CH_3COO). The bands between 800 and 400 cm^{-1} are mainly due to the formation of metal oxides (M–O: Ba–O, Sr–O, Ti–O).

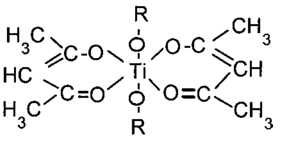


Fig. 2. Structure of titanium acetylacetone [11], R=alkyl radical.

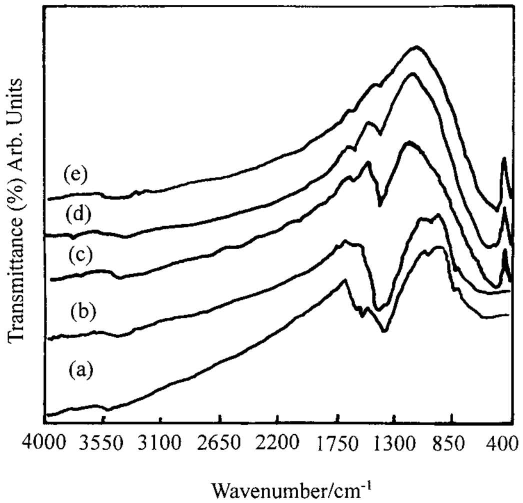


Fig. 3. IR-spectra of the gel powders dried at (a) 350; (b) 500; (c) 600; (d) 700 and (e) 800°C for 1 h.

Fig. 3a–e shows the IR-spectra of the gel powders dried at 350, 500, 600, 700, and 800°C for 2 h, respectively. The spectra in this case have much lower intensity of the O–H stretching vibration bands around 3420 cm^{-1}; the intensity becomes weaker as increasing temperature. The C–H stretching vibration bands in the range of 2800–3000 cm^{-1} are considerably less intense corresponding to the much lower content of organics in these dried gel powders. There are four main bands between 1400 and 1800 cm^{-1} in sol and gel powder dried at 70°C; the intensity of these bands becomes weaker or broader. For example, the 1423 and 1377 cm^{-1} are two distinct bands belonging to CH_2–CO– bending vibrations or –COOH bands that are coupled by O–H bending vibrations and C–O stretching vibrations. The 1422 cm^{-1} bands of the samples dried at 600°C become sharper, while these bands become broader and weaker as temperature increased to 700 and 800°C. Moreover, the bands shifted higher bands, e.g. 1435 cm^{-1} (700°C) and 1453 cm^{-1} (800°C), respectively. Only one band was observed between 900 and 1100 cm^{-1} in samples dried at 350 and 500°C. It means the C–O–C bonds have broken up, i.e. hydroxyls and organic presented in the precursors were removed. The bands around 855 cm^{-1} of the samples dried at 350 and 500°C are due to formation of carboxylate during oxidative decomposition of the alkoxide radicals. The results are different from that of the BST thin films prepared alkoxide solutions and alkoxide solutions modified by 2-ethylhexanoic acid, which were investigated by Vasiljev et al. [12]. They noted quite an intense band at 1580 cm^{-1} due to formation of carboxylate. When temperature was increased up to 600°C, the carboxylate disappeared, due to the crystallization of BST. The bands between 400 and 800 cm^{-1} are due to the formation of metal oxide bonds (M–O), these bands are wider and flatter in curves (a) and (b), while the bands become sharper and narrower as increasing temperature. Owing to the decreasing number of vibration molecules with the transformation of amorphous TiO_2 to the TiO_6-octahedra of the perovskite lattice, the bands shifted to lower wavelength (e.g. red-shift). The results are similar to $BaTiO_3$ thin films from the propionate precursor which were investigated by Hasenkox et al. [13].

The thermal analysis results of barium strontium titanate ($Ba_{0.8}Sr_{0.2}TiO_3$) gel powders are shown in Fig. 4. It is seen from curve of the DTA that there are two endothermic peaks at 106 and 307°C and five exothermic peaks at 370, 390, 429, 500, and 727°C, respectively. Combined with TGA data, it is obvious that the endothermic peaks are due to the evaporation of methanol and acetic acid used in the sol–gel solution. Whereas the five exothermic peaks, the first three peaks at 370, 390 and 429°C are accordingly correlated with the decomposition of the alkoxide redicals, which correspond to the bands around 855 cm^{-1} of the samples dried at 350–500°C. The peaks at 500 and 727°C are attributed to the decomposition of the intermediate complex carbonate phase and crystallization temperature, respectively. Some authors had investigated the preparation of the $BaTiO_3$ and $SrTiO_3$ thin films derived from the metal alkoxides; they indentified the intermediate phase as complex carbonate phase by analyzing the reaction process of the decomposition. Hennings et al. [14] and Hoffmann and Waser [15] suggested the composition of the intermediate phase as $Ba_2Ti_2O_5CO_3$ and $Sr_2Ti_2O_5CO_3$. Zhu et al. [16] suggested that the peaks at 340 and 361°C are attributed to the decarbonization of $BaCO_3$ and $SrCO_3$, which may easily form at relatively low temperature in the heating process. However, the XRD results that matched $BaCO_3$ and $SrCO_3$ were never observed during the heating from 350 to 700°C in our work. The exothermic peak at 727°C is attributed to the crystallization of (Ba,Sr)-TiO_3. One can presume that the overall reaction at this region is the reaction of $BaCO_3$+$SrCO_3$+TiO_2 to form crystallized BST by elimination of CO_2. It also demonstrates that the weight loss takes place in the endothermic processing, between 100 and 350°C, which is 27.3%. It has almost no weight loss (nearly 2 mg per 100°C) from 350 to 650°C, while there is second large weight loss (about 13 mg per 100°C) beginning at 650°C and ending at 700°C. The weight loss of the BST gel powder was illustrated in Fig. 5.

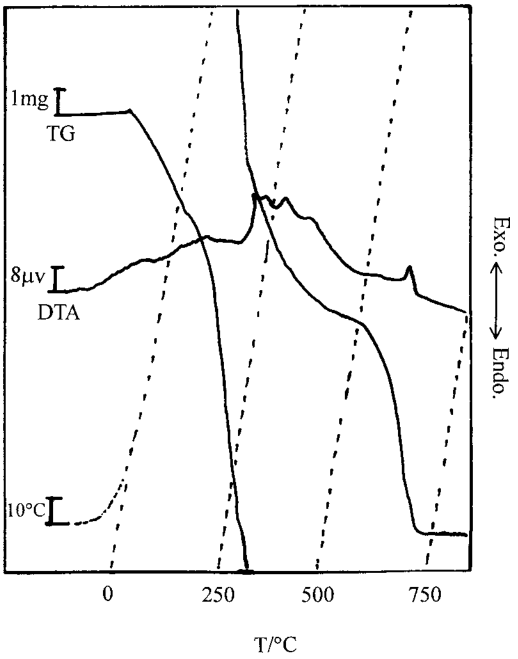


Fig. 4. TGA/DTA curves of $Ba_{0.8}Sr_{0.2}TiO_3$ gel powders dried at about 70°C.

The films start to crystallize at 600°C, and perovskite structure could be established above this temperature. A further increase in temperature will promote crystallization of the thin films [17]. The results are

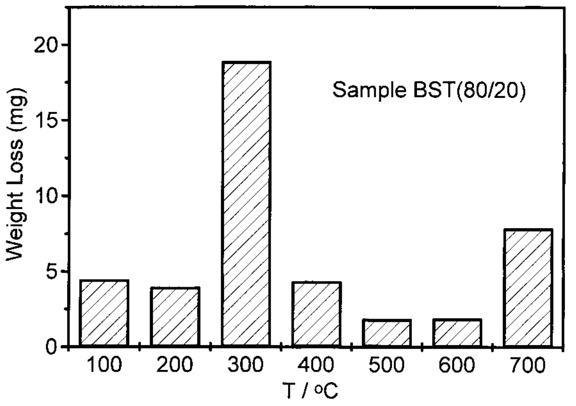


Fig. 5. Weight loss of $Ba_{0.8}Sr_{0.2}TiO_3$ gel powders.

well consistent with the information of the XRD patterns.

The crystalline phase of the BST thin films at room temperature was characterized by XRD with Cu Kα (λ=0.1542 nm) radiation. Fig. 6a–c shows the XRD spectra of the BST thin films on Si (1 0 0) substrate and annealed at 500, 600, 700°C, respectively. The spectrum of the sample annealed at 500°C shows no clear peaks belonging to BST crystalline and demonstrates the amorphous nature of the films. At 600°C, the films were inferior crystallinity suggesting an incomplete perovskite phase formation. As the annealing temperature increased, the peaks in the X-ray diffraction pattern became sharper indicating that the formation of BST was better at high annealing temperature. The XRD patterns also revealed that the BST thin films were crystallized at above 600°C and consisted of a pseudo-cubic, or perovskite phase, while having no preferred orientation. The intermediate phase $(Ba,Sr)_2Ti_2O_5CO_3$ was found below 700°C. Hoffmann and Waser [15] had reported the intermediate phase in the acetate-based CSD-prepared thin

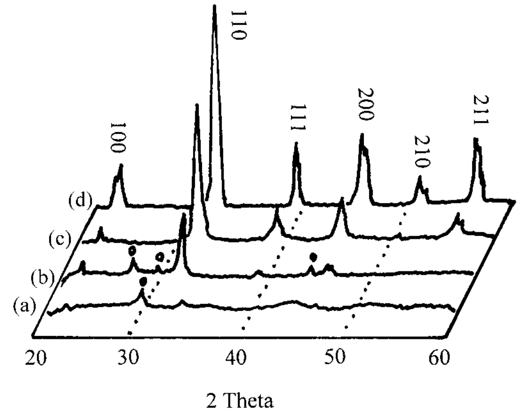


Fig. 6. X-ray diffraction patterns of the BST thin films at: (a) 500; (b) 600; (c) 700°C and (d) pattern of BST powder fired at 950°C. Intermediate phase marked with a hollow circle.

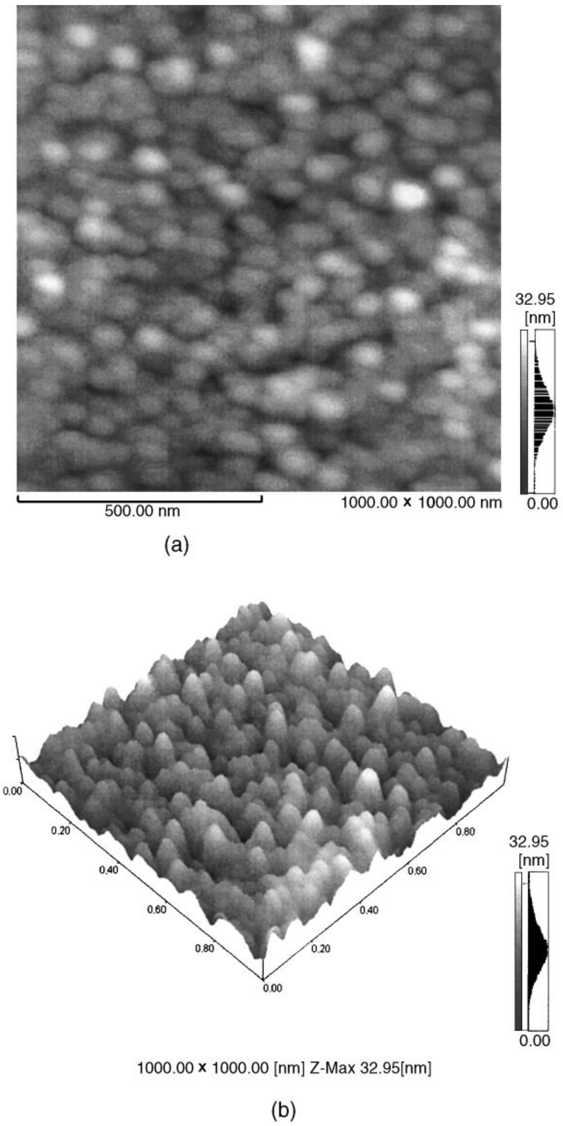


Fig. 7. (a) Two-dimensional and (b) corresponding three-dimensional AFM images of the surface of the BST thin film.

films. Hasenkox et al. [13] had found that a thin film of $Ba_{0.7}Sr_{0.3}TiO_3$ prepared at 550°C from the acetate precursor reveals similar peaks at 2θ values 27.18, 35.03 and 45.14°, while our results demonstrated that the intermediate phase (marked with a hollow circle in Fig. 6) appeared below 700°C and disappeared above 700°C. These peaks were at $2\theta=29.5°$(500°C), 27, 29.3 and 43.8°(600°C). Fig. 6d is the XRD spectrum of the BST powder fired at 950°C for 1 h in a muffle furnace, which shows a tetragonal phase structure. The average grain size of the BST films determined from the full width at half maximum [FWHM] of the X-ray diffraction (1 1 0) peak using Scherrer's equation was in the range of 40–60 nm [18]. A slight increase in the grain size of BST films was observed as heating temperature is increased. Fig. 7 shows (a) the two-dimensional and (b) corresponding three-dimensional AFM images of the BST thin films. The dominant surface feature observed is cone-like protrusion. The average size was 50 nm.

4. Conclusion

This study has shown that a semi-quantitative analysis can be carried out on the drying process of Sr-doped barium titanate alkoxides. By using FTIR and DTA/TGA techniques, the temperatures of decomposition and crystallization were determined at 350–450 and 700°C, respectively. The XRD spectra of the BST thin films on Si (1 0 0) substrates demonstrates the amorphous nature of the films dried at 500°C and the films were inferior crystallinity suggesting an incomplete perovskite phase formation at 600°C. The intermediate phase $(Ba,Sr)_2Ti_2O_5CO_3$ was found below 700°C. The XRD spectrum of the BST powder fired at 950°C showed a tetragonal phase structure. The average grain size of the BST films was in the range of 40–65 nm. A slight increase in the grain size of BST films was observed as the heating temperature is increased.

Acknowledgements

The authors would like to thank Dr. Xingui Tang for many useful discussions and financial support by the National Natural Science Foundation of China (No. 59995520) and the Laboratory of Functional Inorganic Materials of Chinese Academy of Sciences.

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