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Dielectric and tunable properties of $Pb_{0.25}Ba_xSr_{0.75-x}TiO_3$ thin films fabricated by a modified sol–gel method

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Abstract

A modified sol–gel method was used to fabricate $(Pb_{0.25}Ba_x\ Sr_{0.75-x})TiO_3$ (PBST) thin films with $x=0.05,0.1,0.15$ and 0.2 on $Pt/TiO_2/SiO_2/Si$ substrate. The structure, surface morphology, dielectric and tunable properties of PBST thin films were investigated as a function of barium content (x). X-ray diffraction and scanning electron microscopy analysis showed that we could get pure PBST perovskite phase and relative fine density thin films with smooth surface. It was found that the crystal lattice constant, grain size, room temperature dielectric constant, dielectric loss and tunability of Ba solutionizing PST thin films increased with the increase in Ba content. For $(Pb_{0.25}Ba_{0.2}Sr_{0.55})TiO_3$ thin film, it had the highest dielectric constant of 1390 and the largest tunability of 80.6%. The figure of merit parameter reached a maximal value of 28.9 corresponding to the $(Pb_{0.25}Ba_{0.05}\ Sr_{0.7})TiO_3$ thin film, whose dielectric constant, dielectric loss and tunability measured at 1 MHz were 627, 0.024 and 69.4%, respectively.

Keywords: PST; Sol–gel; Scanning electron microscopy; X-ray diffraction; Dielectric properties; Tunability; Lead barium strontium titanate

1. Introduction

Lead strontium titanate $(Pb_xSr_{1-x})TiO_3$ (PST) have been receiving considerable attention recently. PST has the merits of the high dielectric constant of $PbTiO_3$ and the structural stability of $SrTiO_3$ [1] and its Curie temperature varies linearly with the content of Sr [2]. Moreover, the processing temperature is lower in lead-based materials compared to $(Ba_{1-x}Sr_x)TiO_3$ (BST), which offers an additional advantage over BST thin films [2]. Yoshitaka Somiya etc have studied $(Pb,Sr)TiO_3$ ceramics and found $Pb_{0.3}Sr_{0.7}TiO_3$ has extremely high dielectric tunability of 70% under 2 kV/cm at 1 kHz with very low dielectric loss value of less than 0.001 [3]. All these facts make PST thin films to be promising candidates for applications in room temperature tunable microwave elements [4–7].

To the present, PST thin films have been prepared by a variety of techniques involving pulsed laser deposition [8,9], radio frequency magnetron sputtering [7], metal-organic deposition [10] and sol–gel process [2,4,5,11–13]. Among these techniques, the sol–gel technique offers significant advantages over other film fabrication methods such as purity, better homogeneity, precision stoichiometry control, substrates with non-planer shapes, large area deposition and ease of doping. Especially, its lower processing temperature in the whole heat treatment avoids the problems of volatilization of Pb element by ordinary sintering. So it is fitter to prepare PST thin films.

We noticed that the dielectric properties of PST were highly dependent upon the composition ratio between the Pb and Sr in the compound. Earlier studies indicated that the Curie temperature of PST varied from −237 to 485 °C [14] and the composition range of tetragonal/cubic phase boundary at room temperature was about $0.5<Sr<0.55$ for the PST thin film system [11]. Also, the dielectric tunabilities of $(Sr_{1-x}Pb_x)TiO_3$ ($x=0.2$, 0.25, and 0.3) ceramics showed very large difference, which were 3, 15, and 70%, respectively, under 20 kV/cm bias field at room temperature [3]. Furthermore, increasing of Pb content led to simultaneous increasing of both dielectric constant and dielectric loss characteristics of PST films [5].

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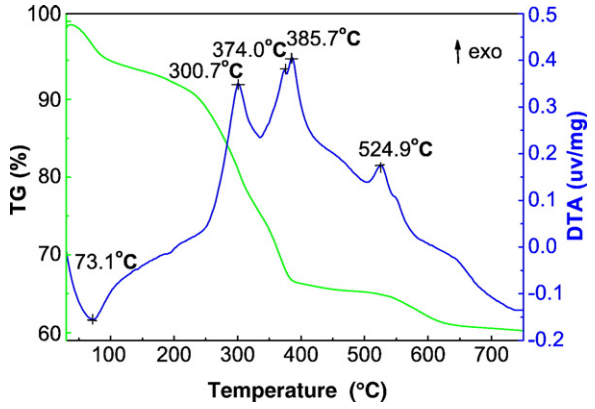

Fig. 1. TGA and DTA curves of $Pb_{0.25}Ba_{0.15}Sr_{0.6}TiO_3$ dry gel precursor.

The ratio of Ba/Sr showed similar effect on dielectric behavior of $Ba_xSr_{1-x}TiO_3$ system in paraelectric region [15–18]. Hence, we believe proper content of Ba solutionizing PST ($(Pb_{0.25}Sr_{0.75})TiO_3$) will have significant effect on the dielectric and tunable properties of $(Pb_{0.25}Ba_xSr_{0.75-x})TiO_3$ (PBST) with x=0.05,0.1,0.15 and 0.2. However, there are few studies regarding Ba solutionizing PST thin films.

In the present work, We synthesized precursor solution of Ba solutionizing PST ($(Pb_{0.25}Sr_{0.75})TiO_3$) without separately dissolving strontium acetate and lead acetate and need not to reflux at 110 °C for 1 h to remove the crystallization water [2]. Furthermore, the preparation of precursor solution of PBST can be finished effectively at a temperature of about 65 °C not for 24 h [11] but for 0.5 h. The PBST thin films were prepared by this modified sol–gel technique on $Pt/TiO_2/SiO_2/Si$. The effects of Ba content on the microstructure, surface morphology, dielectric and tunable properties of PBST thin films have been investigated.

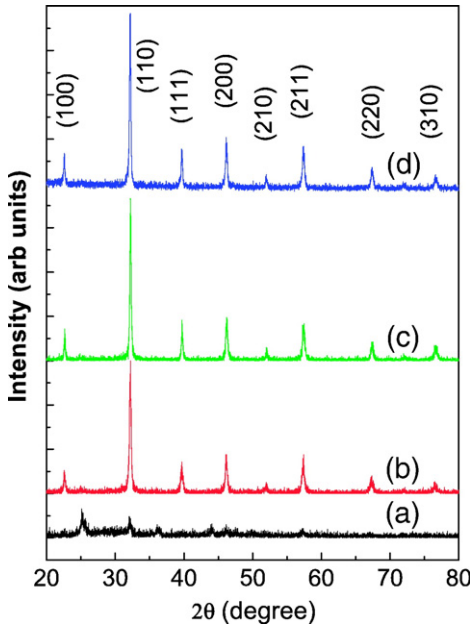

Fig. 2. XRD pattern of $Pb_{0.25}Ba_{0.15}Sr_{0.6}TiO_3$ powder calcined at different temperatures.

2. Experimental details

PBST thin films were prepared using lead acetate tri-hydrate $Pb(CH_3COO)_2{\cdot}3H_2O$, barium acetate $Ba(CH_3COO)_2$, strontium acetate $Sr(CH_3COO)_2{\cdot}1/2H_2O$ and titanium butoxide $Ti(OC_4H_9)_4$ as the starting materials. Glacial acetic acid, 2-methoxyethanol and ethylene glycol were selected as solvents. The lead acetate, barium acetate and the strontium acetate were dissolved in acetic acid above 90 °C with a ratio of $0.25{:}x{:}(0.75-x)$. The titanium butoxide with addition of about 10 V% (volume percent) 2-methoxyethanol was added into the above solution at 65 °C. Then about 2 V% ethylene glycol was added into the solution to reduce the tendency of cracking and the pH value of solution was adjusted using glacial acetic acid to remain about 4.1. At last, the solution was mixed and stirred at a temperature of about 65 °C for 0.5 h to obtain clear solution. The concentration of the final solution was adjusted to 0.5 mol/l. The precursor solution was coated on the $Pt/TiO_2/SiO_2/Si$ substrates. Spin coating was performed using a spinner rotated at a rate of 400 pm for 2 s. The as-deposited PBST thin films were pyrolyzed at 400 °C for 60 min and crystallized at about 750 °C in O_2 atmosphere for 60 min. The coating and firing sequence was repeated for several times to attain a film thickness of about 350 nm.

Thermogravimetry (TG) and Differential thermal analysis (DTA) (TG/DTA NETZSCH STA449C) analyses were carried out in air with a heating rate of 5 °C/min by a NETZSCH STA449C thermal analysis system. X-ray diffraction (XRD) profiles were obtained using a BSX3200 diffractometer with Cu Ka radiation to determine the phase formation and the crystallinity of PBST powders. The morphologies of the films were observed by field emission scanning electron microscopy (SEM, sirion FEG, FEI) using 2 kV operating voltage. Dielectric measurements were carried out using the metal-insulator–metal capacitor configuration. Cu top electrodes with 0.3 mm diameter were deposited on the film by direct current radio frequency magnetron sputtering. Dielectric constant, tunability and loss were measured using an Agilent 4294A precision impedance analyzer at room temperature (27 °C).

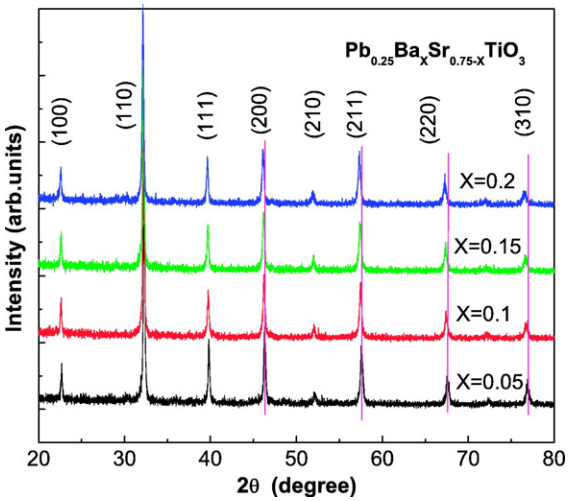

Fig. 3. XRD patterns of $Pb_{0.25}Ba_xSr_{0.75-x}TiO_3$ powder as a function of x.