Effect of Mg-doping on pyrolysis evolution and phase constitutes of Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ (BST) system derived from sol-gel

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Abstract. Gels and powders of dielectric Ba$_{0.7}$Sr$_{0.3}$(Ti$_{1-x}$Mg$_x$)O$_3$ (BST) were prepared by sol-gel technique. Effect of Mg-doping on the pyrolysis evolution and phase constitutes of BSTs was investigated using DSC-TG and XRD. Results show that Mg-doping leads to a remarkable change of crystallizing process of BSTs from a double phase-transformation of non-doping sample into a single phase-transformation and quickens the crystallizing reaction of formation of BST perovskite. The maximum Mg-doping level should be less than x=0.15 in Ba$_{0.7}$Sr$_{0.3}$ (Ti$_{1-x}$Mg$_x$)O$_3$ system. The amount of (Ba,Sr)CO$_3$ phase in the BST powders increases considerably with the Mg-doping level, indicating Mg atoms should occupy the A positions of ABO$_3$ structure of BST, instead of the B position.

1. Introduction

In recent years, barium strontium titanate (BST) has received considerable attention. Due to their high dielectric nonlinearity, high dielectric constant, good pyroelectric properties and composition-dependant Curie temperature adjustability, BST ferroelectric thin films have many potential applications, such as in tunable microwave devices, dynamic random access memories and pyroelectric far-infrared detectors etc [1-4]. The Cure temperature and electric properties of BST could be controlled by adjusting the Ba/Sr ratio. It has been reported [5-6] that the Cure temperature of BST is near room temperature when Ba/Sr is 7/3 and the best electric pyroelectric properties of it could be obtained operating d.c. bias voltages.

While the relatively high dielectric loss of BST thin films compared to their bulk counterparts limits its applications. Physics processes controlling leakage current density, resistance degradation, and dielectric loss of BST still need to be further studied to provide better performance. Doping with small amounts of dopants such as Mg, Ni, Mn, La, and Nb was found to suppress leakage current [7-10]. The changed electrical properties are attributed to the charged defects, which are created to maintain charge neutrality.

It has been thought that Mg-doping, as an acceptor-dopant occupying the B sites of the ABO3 perovskite structure in BST system [9,11-14], on the one hand, could restrain coarsening of grains and condense the surface microstructure, and on the other hand, of importance, could enhance the potential barrier at grain boundary and suppress the leakage current, and therefore decreases the dielectric loss [11,15,16]. Sol-gel technique is one of the best preparing processes of doped BST system. Adopting this method, Joshi et al [8], Yoon et al [9], Zhang et al [11] and Cole et al [17] investigated Mg-doping
effect on leakage current and its mechanisms of BSTs. Gel should be pyrolyzed and crystallized to produce BST ferroelectric thin films. It is well known that the pyrolyzing and crystallizing processes have an important influence on the microstructure and dielectric properties of BSTs [18-21]. However, the influence of dopants on pyrolysis evolution and phase constitutes of BST system, involving in Mg, Ni, Mn and B etc, has not been well established. In this paper, the aim is to have a highlight in the Mg-doping effect on pyrolysis evolution and phase constitutes of BST derived by Sol-gel technique.

2. Experimental Procedure

It has been thought Mg atoms into ABO₃ lattice of BST should occupy B sites (namely Ti site). But, substituting Ti by Mg during composition design of the precursor of BST did not be considered [16]. In this paper Ba₀.₇Sr₀.₃(Ti₁₋ₓMgx)O₃ (x=0, 0.05, 0.10 and 0.15) precursor solutions were confected using barium acetate, strontium acetate and Ti(OC₄H₉)₄ to form BST, acetic acid and 2-methoxyethanol as solvents, and magnesium acetate as the dopant precursor. Figure 1. shows the process of preparing Ba₀.₇Sr₀.₃(Ti₁₋ₓMgx)O₃ sol-gels. The wet gels were analyzed by DSC-TG (SDTQ600) among a temperature range from 25°C to 900°C with a rate of 20°C /min and high purity of N₂ gas as protecting atmosphere. According the results of DSC-TG analysis, the gels were heated at 210°C for 0.5 hour and 340°C for 2 hours for pyrolyzing, and then crystallizing-annealed at 750°C for 0.5 hour at air atmosphere to produce BST powder. Then BSTs crystallizing-annealed were analyzed by XRD (XD-3AX) for determining phase constitutes, with CuKα radiation (λ=0.154nm) at 40 kV and 30mA. The scanning range was 2θ=20°-60° and rate was 2°/min.

3. Results and discussion

3.1. Thermal analysis (DSC-TG)

Figure 2 shows the pyrolysis evolution of Ba₀.₇Sr₀.₃(Ti₁₋ₓMgx)O₃ (x=0, 0.05, 0.10 and 0.15) gels. It can be divided into three regions: evaporating (temperature about 25°C-250°C), pyrolyzing (temperature about 250°C-600°C) and crystallizing (temperature above 600°C). The first suggests evaporation of residual free organic solvents. In the pyrolyzing process, residual organic matters begin to burn. Perovskite BST begins to form in the last crystallizing process.

Pyrolyzing process of all gel samples is made up of exothermal peaks and endothermal peaks, as shown in Figure 2. Endothermal peaks indicate pyrolysis of organics, and exothermal peaks suggest the breaking-down of gels’ framework. From Figure 2, it is seen that Mg-doping has an obvious influence on the pyrolyzing process of BST gels, even the details occurred are not understood clearly now.

Of more interest, Mg-doping has a considerable influence on the crystallization of BSTs. With increase in the doping level of Mg, temperature of the last exothermic peak (crystallizing peak) forming perovskite BST first rises a little and then drops remarkably, and the intensity of heat flow, representing the reaction rate, increases from 1.25 W g⁻¹ of the sample with x=0 to larger than 2.0Wg⁻¹.
of the sample with $x=0.10$, although when $x=0.15$ the intensity of heat flow decreases down to 1.08 W g$^{-1}$. It indicates Mg-doping accelerates the crystallizing reaction of BST system. According to the regulation of International Union of Thermal Analysis and Calorimetry, the onset temperature of crystallizing reaction is the onset temperature of the last exothermic peak (crystallization peak). Therefore the onset temperatures of crystallizing reaction of Ba$_{0.7}$Sr$_{0.3}$ (Ti$_{1-x}$Mg$_x$)O$_3$ ($x=0$, 0.05, 0.10 and 0.15) are 662.7°C, 659.3°C, 627.3°C and 609.1°C respectively. It suggests that Mg-doping makes the crystallizing reaction occurred easily.

Figure 2b-c show the crystallizing process of Mg-doped BST samples has only one exothermal peak, namely one reaction occurring, and it is worth to note the exothermal peak of un-doped BST sample seems to be a superposition of two exothermal peaks, indicating there are two crystallizing reactions occurred in the crystallizing process, the first one feeble begun at 623.2°C and the latter strong and dominant. So it is rational to think that Mg-doping might lead to a remarkable change of the crystallizing process of BST system from a double phase-transformation of non-doping sample into a single phase-transformation.

**Figure 2.** DSC-TG curves of Ba$_{0.7}$Sr$_{0.3}$ (Ti$_{1-x}$Mg$_x$)O$_3$ gels a $x=0$, b $x=0.05$, c $x=0.10$, d $x=0.15$

### 3.2. XRD analysis

Figure 3 shows XRD patterns of Ba$_{0.7}$Sr$_{0.3}$ (Ti$_{1-x}$Mg$_x$)O$_3$ powders after same thermal history described above. The diffraction peaks of all curves in Figure 3 at $2\theta$ value of 22.4°, 31.8°, 39.2°, 45.6°, 51.3°, and 56.7° are corresponding to the crystal planes of (100), (110), (111), (200), (210) and (211) of perovskite BST. However, the peak intensity of undoped sample is very small, as shown in Fig.3a. It indicated the crystallinity of BST crystal was low and the crystallizing process had not been completed. Besides the diffraction peaks of perovskite BST, the characteristic peaks of (Ba,Sr)CO$_3$ phase were detected at $2\theta$ value of 24.2°, 34.7° and 42.7°; TiO$_2$ (rutile) phase was detected at $2\theta$ value of 27.2° and (Ba,Sr)$_2$TiO$_4$ phase were detected at $2\theta$ value of 27.8° and 47.7°, as marked on the figure. As described in the DSC-TG analysis, un-doped BST sample had two exothermal peaks during crystallizing process,
indicating there were two kinds of crystallizing paths taken place. It has been reported [18] that after pyrolyzing the precursor of barium titanate didn’t transform directly into perovskite phase but interim phase that finally form perovskite structure through solid reaction at high temperature. Gust et al [14] also found interim phase present in Ba_{0.5}Sr_{0.5}TiO_{3} thin film. (Ba,Sr)CO_{3}, TiO_{2} (rutile) and (Ba,Sr)_{2}TiO_{4} phases found simultaneously in the un-doped sample, on the one hand, suggests the crystallizing reaction of BST system annealed at 750°C for 0.5 hour has not finished, needing more time or at higher temperature to obtain well-perovskited BST phase, and on the other hand, of more importance, confirms the point of view that the crystallizing process of un-doped BST system is undergone by a double phase-transformation, namely, a decomposing reaction of (Ba, Sr)_{2}TiO_{4} and a solid reaction between (Ba,Sr)CO_{3} and TiO_{2}.

Figure 3. XRD patterns of of Ba_{0.7}Sr_{0.3} (Ti_{1-x}Mg_{x})O_{3} powders a x=0, b x=0.05, c x=0.10, d x=0.15

Compared the peak intensity of BST phase at curve-a with that at curve-b to -d in Figure 3, it was found that Mg-doping improved the crystallinity of BST crystal. When Mg were doped into the BST, neither TiO_{2} nor (Ba, Sr)_{2}TiO_{4} phase was detected, as shown at curves of b-d in Figure3. It suggested that the crystallizing reaction had finished in the Mg-doped samples through the same thermal history as the un-doped sample. Mg-doping quickens the crystallizing reaction of formation of BST perovskite, consistent with DSC analysis. The diffraction intensity of the BST crystal became lowered when Mg dopant concentration was x=0.15, as shown in Figure3d, and a flat peak appeared at 2θ = 27.5°. Considering the Joint Committee of Powder Diffraction Standard (JCPDS) data, this peak may be attributed to the formation of the MgO_{4} phase, indicating Mg-doping by this level was excessive. The redundant Mg did not enter into the lattice of ABO_{3} structure of BST but was present as oxide of magnesium. Cole et al [15] also reported MgO present in the Mg-doped BST by sol-gel technique. Additionally, there were no diffraction peak of Mg and MgO in doped BSTs with Mg dopant concentration of x=0.05 and 0.10, shown in Fig.3b-c, indicating Mg element had entered into the lattice of ABO_{3} structure of BST. So it could be concluded that the maximum Mg-doping level should be less than x= 0.15 in Ba_{0.7}Sr_{0.3} (Ti_{1-x}Mg_{x})O_{3} system.

However, there was a small quantity of (Ba,Sr)CO_{3} phase still detected in Mg-doped BST system, of which the peak intensity increased with the Mg-doping level. This indicated that the amount of (Ba,Sr)CO_{3} phase in the BST powder crystallized was increased with Mg-doping. It is known that the BST precursor solutions were confected by mol ratio of (Ba+Sr) and (Ti+Mg) of 1:1 assuming Mg...
atoms occupying Ti positions into ABO$_3$ structure [9,11-14]. (Ba,Sr)CO$_3$ phase detected means that Ti should exist as TiO$_2$ or other containing Ti. But there were no diffraction peak of TiO$_2$ or other containing Ti found in the Mg-doped samples. Therefore, a question emerges: who is with responsibility for the increased (Ba,Sr)CO$_3$ phase? Is the supposition of Mg atoms occupying Ti positions into ABO$_3$ structure wrong? If so, Mg atoms should occupy the A positions of ABO$_3$ structure, namely, substituting Ba or Sr atoms. And the mol of (Ba+Sr+Mg) should be more than that of Ti in the Mg-doped BST precursor solutions. As a result, excessive Ba and/or Sr would exist as (Ba,Sr)CO$_3$ phase, of which the amount would increase with the Mg-doping level as expected. So it is rational to think Mg atoms occupy the A positions of ABO$_3$ structure, instead of the B position. This supposition has been confirmed by XRD and XPS analysis on BSTs prepared by 1:1 mol ration of (Ba+Sr+Mg): Ti, which will be discussed in details in another paper.

4. Conclusion

(1) Mg-doping leads to a remarkable change of crystallizing process of BSTs from a double phase-transformation of non-doping sample into a single phase-transformation.

(2) With increase in the Mg-doping level, the onset temperature of crystallizing reaction of formation of perovskite BST first rose a little and then dropped down considerably, and the intensity of heat flow, representing the reaction rate, increases when the Mg-doping level was less than 0.15.

(3) The crystallinity of BST crystal by XRD analysis indicated Mg-doping quickens the crystallizing reaction of formation of BST perovskite, consistent with DSC analysis. The maximum Mg-doping level should be less than $x=0.15$ in Ba$_{0.7}$Sr$_{0.3}$Ti$_{1-x}$Mg$_x$O$_3$ system.

(4) The amount of (Ba,Sr)CO$_3$ phase in the BST powders increases considerably with the Mg-doping level, indicating Mg atoms should occupy the A positions of ABO$_3$ structure of BST, instead of the B position.

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