

Effect of excess TiO_2 on the phase evolution and densification of sol-gel derived $(\text{Ba,Sr})\text{TiO}_3$ powders

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Abstract Nanoscaled $(\text{Ba}_{2/3}\text{Sr}_{1/3})\text{Ti}_{1+x}\text{O}_3$ powders have been prepared by sol-gel technique. Their phase evolution and densification behaviors have been studied by differential thermal analysis (DTA) and high temperature dilatometer, respectively. It is found the addition of 2 mol%-excess amount of TiO_2 lowers the activation energy required for the formation of the perovskite phase by about 130 kJ/mol and thus lowers the crystallization temperature of BST powders. However, the excess amount of TiO_2 makes the nano-powder difficult to sinter. Transmission electron microscopy reveals that a metastable nano-porous layer has formed on the surface of TiO_2 -excess nanopowder and this may account for the slow densification rate.

Keywords BST · Sol-gel · Microstructure

1 Introduction

Barium strontium titanate (BST) has in the past few decades aroused many research activities around the world since it is the material of choice in a variety of applications, such as, dynamic random access memory devices (DRAMs), hydrogen

gas sensors, pyroelectric detector, tunable microwave devices and positive temperature coefficient of resistance devices. Among the many synthesis methods, sol-gel offers good compositional control on the nanoscale range and a low synthesis temperature. By using a sol-gel acetate method, Zhu, et al. has demonstrated a novel type of hydrogen gas sensor made of BST thin films [1–3]. At a hydrogen level of about 1000 ppm in air, the H_2 -induced polarization potential can be as large as 4.5 V, a value about seven times larger than the best silicon based gas sensor.

Recently, Beck et al. [4, 5] has compared the various sol-gel processes such as acetate, hydroxide, alkoxide and alkoxide decomposition methods and has pointed out that the compositional homogeneity of the nanoscaled BST powders may well be destroyed by the formation of intermediate compounds. For acetate method, BaCO_3 is the major type of intermediate compounds [5]. Other phases could be Ba_2TiO_4 and BaTi_2O_5 depending on the Ba/Sr ratio in BST [5]. However, BaCO_3 was not identified in the report by Chen et al. [6]. Instead, an intermediate oxycarbonate phase $(\text{Ba,Sr})_2\text{Ti}_2\text{O}_5\text{CO}_3$ was suggested [6–8]. In their reports [6–8], no thermal gravimetric results were shown to support the existence of the $(\text{Ba,Sr})_2\text{Ti}_2\text{O}_5\text{CO}_3$ phase. Alternatively, Gust et al. [9] suggested the intermediate phase be $\text{BaTiO}_2\text{CO}_3$ to account for the large weight loss of the sol-gel derived powder at a temperature around 600°C.

In view of the above-mentioned controversies in literature, it is therefore necessary to revisit the structural and phase evolution of nano BST powder prepared by sol-gel method. More specifically, the effect of excess TiO_2 on the phase evolution will be studied in the present work since excess TiO_2 is beneficial to the hydrogen gas sensitivity [1–3].

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2 Experiments

The nominal composition chosen was $(\text{Ba}_{2/3}\text{Sr}_{1/3})\text{Ti}_{1+x}\text{O}_3$ ($x = 0$ and 0.02). The BST nano-powders were synthesized through a conventional sol-gel route. The precursors used were barium acetate, strontium acetate, and titanium (IV) butoxide. Acetylacetonone was used as a chelating agent to form a stable complex. Detailed processing procedure can be found elsewhere [10]. The clear stock solution with a concentration of 0.25 M was dried at 90°C for over 12 hours and the dried gel powders were ground in a zirconia grinding media. A Perkin Elmer thermogravimetric analysis (TGA-7) and a differential thermal analysis (DTA-7) were used to study the thermal decomposition and crystallization behaviors of the dried gel powders. The scanning of DTA and TGA was conducted in air at different heating rates. The formation of perovskite phase was verified by Bragg-Brentano X-ray diffraction (Rigaku, Dmax 2200) method using $\text{Cu K}\alpha$ radiation at a scanning rate of $3^\circ/\text{min}$. For the microstructure study, the nanosized powders were first ultrasonically dispersed in acetone and then collected by a copper-mesh holder mounted with amorphous carbon film. The dried powders were observed under a 200 keV transmission electron microscope (TEM, JEOL JEM-2010). The densification and sintering behaviors were characterized by a vertical high temperature dilatometer (Setaram, Setsys 16/18). The pellets used for the densification and sintering study have a diameter of 10 mm and a thickness of $2\text{--}3\text{ mm}$. They are formed by uniaxial cold pressing at a pressure of 250 MPa .

3 Results and discussions

The thermal decomposition and crystallization behaviors of BST dried gel powder were studied by DTA and TGA (Fig. 1) under a heating rate of $2^\circ\text{C}/\text{min}$. The endothermic peak at around 70°C is due to the loss of liquid residue such as water and solvent, etc., which corresponds to a weight loss in the TGA curve. The two exothermic peaks at around 250°C and 325°C result from the burnt out of the organic compounds and the decomposition of acetate. Corresponding to the two exothermic peaks there exist a huge weight loss. The exothermic peak between $380\text{--}500^\circ\text{C}$ is associated with the further combustion of organics, such as $(\text{Ba,Sr})_2\text{Ti}_2\text{O}_5\text{CO}_3$ [10], which is accompanied by a gradual loss of weight. It might also be related to the formation of amorphous TiO_2 since it is very similar to the DTA curve of TiO_2 gel derived from titanium (IV) butoxide [11]. Indeed, as can be seen from Fig. 1, this exothermic peak is more significant for gels with excess TiO_2 . A flat region in TGA persists up to a temperature of 520°C above which a step is found in the TGA curve. From Fig. 1 it can be calculated that the corresponding weight loss during the decomposition reaction at around 600°C is about

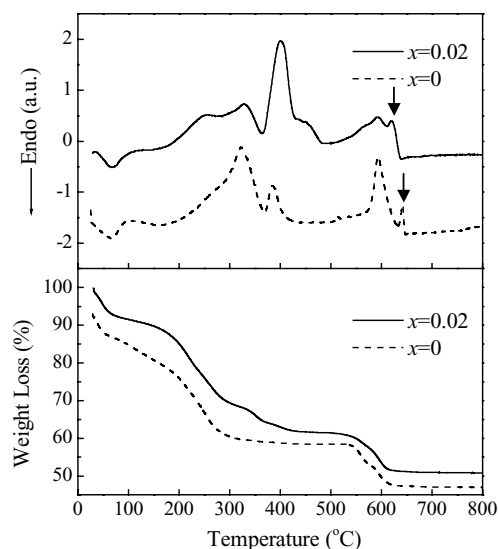
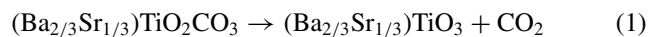


Fig. 1 DTA (top) and TGA (bottom) curves of the $(\text{Ba}_{2/3}\text{Sr}_{1/3})\text{Ti}_{1+x}\text{O}_3$ gel powders under a heating rate of $2^\circ\text{C}/\text{min}$. The curves for $x = 0$ are shifted vertically for clarity. The temperature T_m at which the perovskite phase is formed is indicated by an arrow in the DTA curves for two different compositions

17% for both stoichiometric and TiO_2 excess gel powders. It agrees well with a theoretical weight loss of 16.9% for the decomposition of the following carbonate.



The intermediate phase $(\text{Ba,Sr})_2\text{Ti}_2\text{O}_5\text{CO}_3$ as proposed previously by other researchers [6, 7], however, cannot account for the large weight loss experimentally observed. Our result is consistent with the conclusion drawn by Gust et al. [9]. TG-MS measurement by Beck et al. [5] has also proven that at around 600°C , the gaseous product due to the decomposition has a mass number of 44, which is the molecular weight of CO_2 . It can thus be concluded that the decomposition at around 600°C is due to the above reaction Eq. (1).

In the DTA curves (Fig. 1) there are two exothermic peaks at around 600°C . The first peak at around 593°C is due to the decomposition reaction of Eq. (1). The decomposition temperature is the same for both stoichiometric and TiO_2 -excess powders. The second peak at higher temperature, which corresponds to little weight loss, is related to the formation of perovskite phase. The phase formation temperature for TiO_2 -excess BST powder is about 20°C lower than that of the stoichiometric BST powder. It is well known that titanium oxide acts as nucleation site in the growth of BST thin films [12]. In the present case, the excess TiO_2 also acts as nucleation site for the perovskite phase and thus reduce the phase formation temperature.

The activation energy E_a for the formation of the perovskite phase can be estimated from DTA curves with various

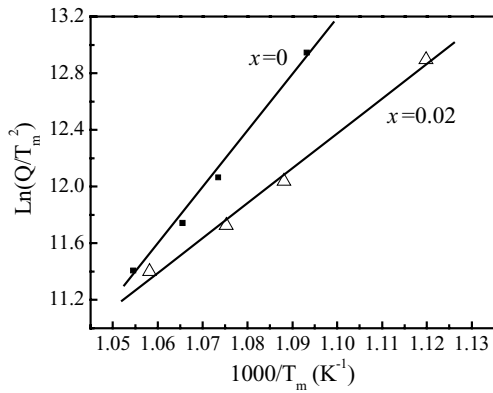


Fig. 2 Kissinger plot for the formation of perovskite phase in $(\text{Ba}_{2/3}\text{Sr}_{1/3})\text{Ti}_{1+x}\text{O}_3$ gel powder. The linear line is the best fitted one for the discrete experiment data points

heating rates by using the Kissinger equation [13],

$$d\left(\ln\frac{Q}{T_m^2}\right)/d\left(\frac{1}{T_m}\right) = -\frac{E_a}{R} \quad (2)$$

where R is the universal gas constant, T_m is the temperature for maximum rate of phase transformation and Q is the heating rate. In the present case, T_m is determined as the exothermic peak temperature in a DTA curve at about 600°C and above. By plotting the $-\ln(Q/T_m^2)$ versus $1/T_m$, the activation energy E_a can be obtained from the slope of the linearly fitted line (Fig. 2). The activation energy E_a thus obtained is about 204 kJ/mol for TiO_2 -excess powder and 334 kJ/mol for stoichiometric BST powder, respectively. The excess amount of TiO_2 reduces the energy barrier required for the formation of the perovskite phase.

According to Jang et al. [14], the growth of the BST perovskite phase is a diffusion-controlled process. The formation of the perovskite phase is therefore time-dependent. In

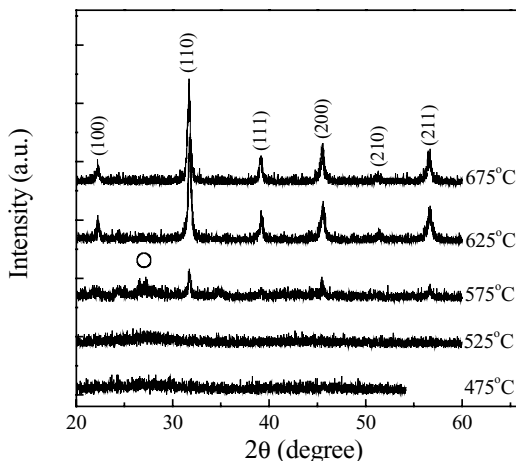
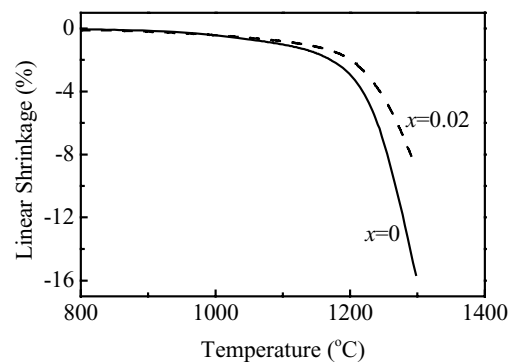


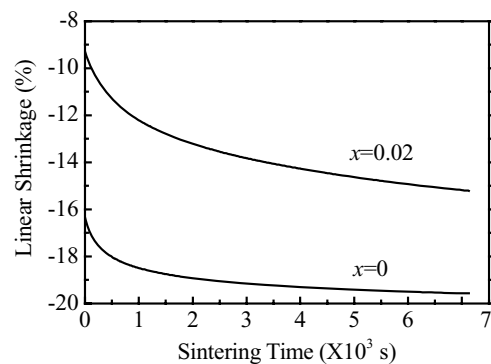
Fig. 3 XRD of $(\text{Ba}_{2/3}\text{Sr}_{1/3})\text{Ti}_{1.02}\text{O}_3$ gel powders annealed for one hour at different temperatures. An intermediate phase $(\text{Ba,Sr})\text{TiO}_2\text{CO}_3$ is indicated by a circle

our case, for the TiO_2 -excess gel powder, a small amount of perovskite phase has already been formed together with the intermediate phase after one hour's annealing at 575°C as judged from the XRD pattern (Fig. 3). The intermediate phase could be the one appeared in left hand side of Eq. (1). When the temperature is raised to 625°C , it can be seen from Fig. 3 that, after one hour's annealing, the formation of the perovskite phase is complete and no intermediate phase is left. This result agrees well with the conclusion drawn from the TGA curve of Fig. 1. As illustrated in Fig. 3, at temperatures below 575°C , no perovskite phase is formed while at a temperature of 675°C the perovskite phase is well crystallized showing strong diffraction intensities.

The linear shrinkage of BST powder under a constant heating rate and that at a fixed temperature are shown in Fig. 4. Before the sintering study, the starting powders were annealed at 625°C for one hour so that according to Fig. 3 all the powders were perovskites already. Figure 4 shows that stoichiometric BST powder starts to shrink at a lower temperature than TiO_2 -excess BST powder. Derivative of the linear shrinkage curve shows that the maximum shrinkage rate of stoichiometric BST powder has been reached at about 1280°C while that of the TiO_2 -excess powder should be well above 1300°C . Under a constant heating rate of 5°C/min the



(a)

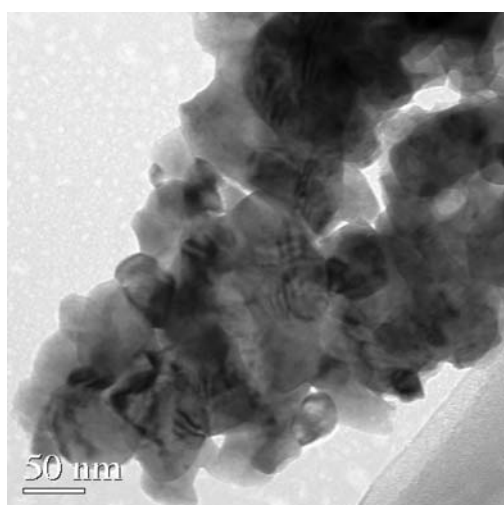


(b)

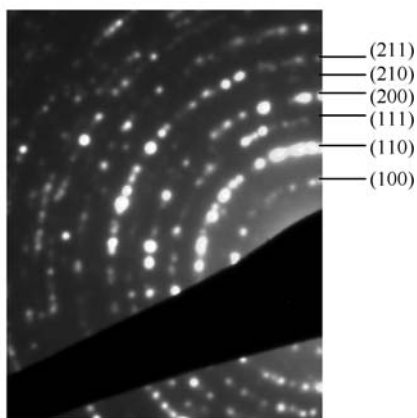
Fig. 4 Sintering behavior of sol-gel derived $(\text{Ba}_{2/3}\text{Sr}_{1/3})\text{Ti}_{1+x}\text{O}_3$ nanopowder. (a) Linear shrinkage under a constant heating rate of 5°C/min ; (b) Isothermal linear shrinkage at 1300°C

linear shrinkage for stoichiometric BST reaches 16%, which is about twice the shrinkage for the TiO_2 -excess BST when the temperature goes up to 1300°C . During the isothermal sintering process at 1300°C , the dimension of stoichiometric BST almost stops changing after 2 hours while it keeps on decreasing for TiO_2 -excess BST. A higher temperature or a longer dwell time is needed for the full densification of TiO_2 -excess BST.

TEM microstructure study of the 625°C annealed gel powders shows that the stoichiometric BST powder has a polycrystalline nature (Fig. 5). The corresponding electron diffraction pattern of the polycrystalline BST can be well indexed according to a pseudo-cubic perovskite structure. However, the TiO_2 -excess BST powder shows two types of morphology. One type of the morphology is similar to that of the stoichiometric BST powder observed in Fig. 5(a). The



(a)



(b)

Fig. 5 Morphology (a) and electron diffraction pattern (b) of stoichiometric BST gel powders annealed at 625°C for one hour

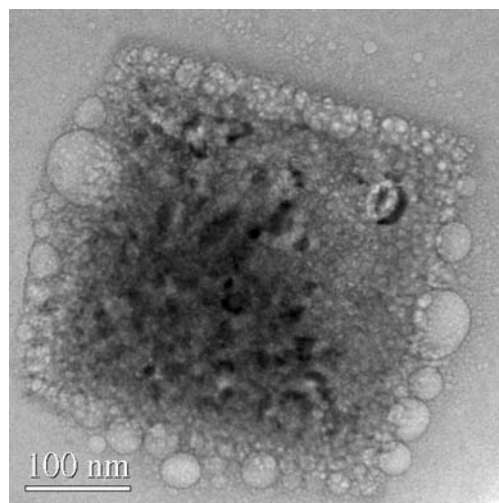


Fig. 6 Cubic particles of TiO_2 -excess BST powder

agglomerated particles are well-crystallized perovskites. Another type of morphology has a cubic shape as shown in Fig. 6. The outer surface of the particle has a nanoporous structure. It is believed that the nano-porosities are left behind after the evaporation of the organic compounds. The nano-porosities are stable even if the powder is heated up to 800°C . There is some amorphous nature of the cubic particle, which can be identified from the electron diffraction pattern. But it can be fully crystallized *in-situ* in the TEM chamber under the strong irradiation of electron beam. The nano-porosities disappeared after the irradiation of focused electron beam for a few minutes.

The microstructure of the BST gel powder helps to understand its sintering behavior. For the TiO_2 -excess powder, the metastable nano-porosities increase the distance for mass transportation and result in a low densification in the early stage of sintering. Although usually a small amount of TiO_2 is used as a sintering aid for barium titanate based materials, in the present study, the sintering temperature of 1300°C is below the eutectic temperature so that the normal grain growth prevails rather than the discontinuous or abnormal one. It has been reported that the normal grain growth of BaTiO_3 containing excess TiO_2 is extremely slow [15]. One possible reason is that the excess Ti-O_2 bond formed at the faceted surface of BaTiO_3 grain will retard the normal grain growth [16].

4 Conclusion

The phase formation and densification behaviors of $(\text{Ba}_{2/3}\text{Sr}_{1/3})\text{Ti}_{1+x}\text{O}_3$ sol-gel powders were studied. It is found that the 2 mol% excess TiO_2 promotes the formation of the perovskite phase by reducing the activation energy. However,

it results in a low densification rate in the sintering process of the powders due to the formation of the metastable nanoporous surface layers.

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