Effect of excess TiO$_2$ on the phase evolution and densification of sol-gel derived (Ba,Sr)TiO$_3$ powders

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Abstract Nanoscaled (Ba$_{2/3}$Sr$_{1/3}$)Ti$_{1+x}$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$_2$TiO$_4$ and BaTi$_2$O$_5$ 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 oxy-carbonate phase (Ba,Sr)$_2$Ti$_2$O$_5$CO$_3$ was suggest [6–8]. In their reports [6–8], no thermal gravimetric results were shown to support the existence of the (Ba,Sr)$_2$Ti$_2$O$_5$CO$_3$ phase. Alternatively, Gust et al. [9] suggested the intermediate phase be BaTiO$_2$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].
2 Experiments

The nominal composition chosen was \((\text{Ba}_{2/3}\text{Sr}_{1/3})\text{Ti}_{1+x}\text{O}_3\) \((x = 0 \text{ and } 0.02)\). The BST nano-powders were synthesized through a conventional sol-gel route. The precursors used were barium acetate, strontium acetate, and titanium (IV) butoxide. Acetylacetone 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 Cu Kα radiation at a scanning rate of 3°/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 2–3 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°C/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 380–500°C is associated with the further combustion of organics, such as \((\text{Ba},\text{Sr})_2\text{Ti}_2\text{O}_5\text{CO}_3\) [10], which is accompanied by a gradual loss of weight. It might also be related to the formation of amorphous TiO2 since it is very similar to the DTA curve of TiO2 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 TiO2. 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 17% for both stoichiometric and TiO2 excess gel powders. It agrees well with a theoretical weight loss of 16.9% for the decomposition of the following carbonate.

\[
(\text{Ba}_{2/3}\text{Sr}_{1/3})\text{Ti}_2\text{CO}_3 \rightarrow (\text{Ba}_{2/3}\text{Sr}_{1/3})\text{TiO}_3 + \text{CO}_2 \quad (1)
\]

The intermediate phase \((\text{Ba},\text{Sr})_2\text{Ti}_2\text{O}_5\text{CO}_3\) 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 CO2. It can thus be concluded that the decomposition at about 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 TiO2-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 TiO2-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 TiO2 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

\[
\begin{align*}
\text{Weight Loss (m%)} & \\
\text{Temperature (°C)} & \\
\text{Exotherm (mJ)} & \\
\text{Temperature (°C)} & \\
\end{align*}
\]