Sintering and dielectric characteristics of CuO-Bi$_2$O$_3$ doped (Ba$_{1-x}$Sr$_x$)TiO$_3$ ceramics

Chao-Chin Chan$^1$, Cheng-Fu Yang$^2$, Chien-Min Cheng$^3$, and Chien-Jau Huang$^3$. 

Dept. Chemical Eng., Kao Yuan Institute of Technology, Kaohsiung, Taiwan, R.O.C.$^1$
Dept. Chemical & Materials Eng., National University of Kaohsiung, Kaohsiung, Taiwan, R.O.C.$^2$
Dept. Electronic Eng., Southern Taiwan University of Technology, Tainan, Taiwan.$^3$

* lecturer

Corresponding author. Email: cfyang@nuk.edu.tw

Abstract

The sintering characteristics of (Ba$_{1-x}$Sr$_x$)TiO$_3$ (x=0, 0.1, and 0.2) were investigated for using 1 wt% CuO/Bi$_2$O$_3$ (molar ratio, CuO/Bi$_2$O$_3$= 1) mixture as liquid phase sintering aid. Sintering in air for 2h form 1050$^\circ$C to 1200$^\circ$C was studied. The grain growth of (Ba$_{1-x}$Sr$_x$)TiO$_3$ ceramics was a function of sintering temperatures and SrO content. The grain size increased with the increase of sintering temperatures and decreased with the decrease of SrO content. The crystal characteristics of (Ba$_{1-x}$Sr$_x$)TiO$_3$ ceramics were developed. For the (Ba$_{1-x}$Sr$_x$)TiO$_3$ ceramics, as the SrO content decreased, the crystal phase of (Ba$_{1-x}$Sr$_x$)TiO$_3$ ceramics would change from a pseudo cubic phase to a tetragonal phase. In this study, the dielectric characteristics of CuO/Bi$_2$O$_3$ mixture-fluxed (Ba$_{1-x}$Sr$_x$)TiO$_3$ ceramics are also developed.

Keywords: (Ba$_{1-x}$Sr$_x$)TiO$_3$, liquid phase sintering, grain size, pseudo cubic

1. Introduction

Sintering in the presence of a liquid phase is one processing technique which had been applied to enhance the densification and the grain growth of BaTiO$_3$-based ceramics as well as for several other ceramic systems. In the past, many oxides could be used as the sintering aids for BaTiO$_3$-based ceramics, including Bi$_2$O$_3$, Bi$_2$O$_5$, SiO$_2$, and LiF [1-4]. The mixtures of CuO with TiO$_2$ and ZrO$_2$ can also be used to reduce the sintering temperatures of BaTiO$_3$-based ceramics [5]. Roth et al. [6] revealed a tentative diagram for the CuO-BaO system involving two binary compounds BaCuO$_2$ and Ba$_2$CuO$_3$, this last being apparently unstable above 800$^\circ$C [7]. BaCuO$_2$, originally synthesized by Arjomand and Machin [8], melted incongruently around 1000$^\circ$C in air. In addition, there was a eutectic between BaCuO$_2$ and CuO at around 900$^\circ$C. Because of the low melting point of the binary BaO-CuO system (or BaCuO$_2$-CuO), we had used the different CuO-BaO mixtures (CuO/BaO=1, 2, and 2.5, mole ratio) as a sintering aid for different amount addition [9,10]. The need sintering temperatures of BaTiO$_3$ ceramics were a function of CuO/BaO ratio and CuO-BaO mixtures amount, and the addition of 1wt% CuO-BaO mixtures to BaTiO$_3$ ceramics has significantly reduced the sintering temperatures of BaTiO$_3$ ceramics to around 1100$^\circ$C [9,10].

The CuO-BaO mixtures could be used as a sintering aid to lower the sintering temperatures of BaTiO$_3$ ceramics, but the grain growth was hard to control for the multi-layer ceramics capacitor used. In this study, the SrO was used to substitute the site of BaO in order to shift the Curie temperatures (the temperatures to reveal the maximum dielectric constant) to close room temperature. And the (Ba$_{1-x}$Sr$_x$)TiO$_3$ ceramics (x=0, 0.1, and 0.2) compositions were used as the precursors. However, we would find another composition, CuO-Bi$_2$O$_3$ mixture, as a new sintering aid of the (Ba$_{1-x}$Sr$_x$)TiO$_3$ ceramics. Attempts had been made to study the effect of 1 wt% of CuO-Bi$_2$O$_3$ mixture (molar ratio, CuO/Bi$_2$O$_3$=1) on the densities, the microstructure, the crystal structures, and the dielectric characteristics of the (Ba$_{1-x}$Sr$_x$)TiO$_3$ ceramics.

2. Experimental Procedures

BaCO$_3$, SrCO$_3$, and TiO$_2$ with purities of 99.8% were used as the raw materials and weighted in accordance with the compositions (Ba$_{1-x}$Sr$_x$)TiO$_3$ + 0.5 mol% TiO$_2$, for x=0.0, 0.1, and 0.2, respectively. Then the powders were mixed with distilled water, dried, and ground. In the past, adding a liquid-phase former may be accompanied by a significant decrease in dielectric constant. This was mainly caused by the dilution of high dielectric constant ceramics with low dielectric constant flux or glass and the formation of low dielectric constant compounds by the reaction of the ceramics with low-melting oxide. The low dielectric compound could be prevented by using high calcining temperature to form ABO$_3$ phase completely. The ground powder was calcined in air at 1150$^\circ$C for 2h. The calcined materials was again ground to -325 BBS mesh. X-ray diffraction pattern (XRD) analysis was carried out on the calcined (Ba$_{1-x}$Sr$_x$)TiO$_3$ powder.

In the calcined powder only the tetragonal (or pseudo Cubic) (Ba$_{1-x}$Sr$_x$)TiO$_3$ phase was observed in XRD patterns. CuO-Bi$_2$O$_3$ mixture with the CuO/Bi$_2$O$_3$ ratio 1 was prepared. 1wt% CuO/Bi$_2$O$_3$ mixture were added to calcined (Ba$_{1-x}$Sr$_x$)TiO$_3$ powder by wetting mixing. After drying and grinding, the products were pressed into pellets using distilled water as binder. The pellets were sintered at temperatures varying from 1050 to 1200$^\circ$C, the sintering duration was fixed for 2h to study the effect of sintering temperatures on the morphology and densities of CuO/Bi$_2$O$_3$ mixture fluxed (Ba$_{1-x}$Sr$_x$)TiO$_3$ ceramics. Bulk densities were calculated by using the
Archimedes method. The microstructural observations of the surfaces of sintered samples were directly observed from the SEM (scanning electronic micrograph). The Ag-Pd paste were printed at both side and sintered at 700°C for 15min. The dielectric properties of liquid phase fluxed (Ba_{1-x}Sr_{x})TiO_{3} ceramics were measured at 1MHz with Agilent-4294A impedance/gain phase analyzer.

3. Results and Discussion

The sintered morphologies will prove that CuO/Bi_2O_3 mixture can be used as a sintering aid and improve the grain grow of (Ba_{1-x}Sr_{x})TiO_3 ceramics. Fig.1 shows the photomicrographs of (Ba_{1-x}Sr_{x})TiO_3 ceramics with 1wt% CuO/Bi_2O_3 mixture addition and fired at different temperatures. For (Ba_{1-x}Sr_{x})TiO_3 ceramics without CuO/Bi_2O_3 mixture addition, the grain growth is found to be negligible as when 1300°C is used as sintering temperature (not shown here). For (Ba_{1-x}Sr_{x})TiO_3 ceramics with 1wt% CuO/Bi_2O_3 mixture addition and sintered at 1100°C, the grain growth was not found and the sintered (Ba_{1-x}Sr_{x})TiO_3 ceramics show a densified morphologies, and less pores are observed. Sintering at 1150°C, the (Ba_{1-x}Sr_{x})TiO_3 ceramics reveal a densified and uniform-grain-growth surface. As the results shown in Figs.1(d)−1(f) are compared, it is found that the grain sizes of (Ba_{1-x}Sr_{x}) TiO_3 ceramics increase with the increase of SrO content.

Fig.1 The photomicrographs of 1wt% CuO/Bi_2O_3-added (Ba_{1-x}Sr_{x})TiO_3 ceramics. Sintered at 1100°C for (a) x=0, (b) x=0.1, and (c) x=0.2. Sintered at 1150°C for (d) x=0, (e) x=0.1, and (f) x=0.2.
Fig. 2 shows the X-ray diffraction patterns of (Ba$_{1-x}$Sr$_x$)$_3$TiO$_3$ ceramics as a function of sintering temperature and SrO content. As Fig. 2 shows, for $x=0$ and 0.1 the (0,0,10) plane $\{\overline{1}1\overline{1}\}$ shows an apparent splitting. This result suggests that the CuO/Bi$_2$O mixture fluxed (Ba$_{1-x}$Sr$_x$)$_3$TiO$_3$ ceramics reveal a tetragonal ($x=0$ and 0.1) or pseudo-cubic structure ($x=0.2$). The 2$\theta$ values of (Ba$_{1-x}$Sr$_x$)$_3$TiO$_3$ ceramics are shifted to higher values as the SrO content increases, this result suggests that the lattice constants of (Ba$_{1-x}$Sr$_x$)$_3$TiO$_3$ ceramics will decrease with the increase of SrO content.

The bulk densities of (Ba$_{1-x}$Sr$_x$)$_3$TiO$_3$ ceramics as a function SrO content and sintering temperatures are presented in Fig. 3. The unfluxed (Ba$_{1-x}$Sr$_x$)$_3$TiO$_3$ ceramics will be densified at about 1400°C-1450°C, and the densities of (Ba$_{1-x}$Sr$_x$)$_3$TiO$_3$ ceramics are about 94%TD of (Ba$_{1-x}$Sr$_x$)$_3$TiO$_3$ ceramics (not shown here). The densification curves of CuO/Bi$_2$O mixture fluxed (Ba$_{1-x}$Sr$_x$)$_3$TiO$_3$ ceramics are shifted about 300°C lower than those of unfluxed (Ba$_{1-x}$Sr$_x$)$_3$TiO$_3$ ceramics. The CuO/Bi$_2$O mixture fluxed (Ba$_{1-x}$Sr$_x$)$_3$TiO$_3$ ceramics start to densify at around 1000°C, and the densified process is essentially saturated at about 1100°C. As the lattice constants of (Ba$_{1-x}$Sr$_x$)$_3$TiO$_3$ ceramics decrease with the increase of SrO content, the saturated bulk densities decrease with the increase of SrO content. The Ba atom being heavier than that of Sr atom would cause this result. Sintered at 1150°C, a density higher than 95%TD of (Ba$_{1-x}$Sr$_x$)$_3$TiO$_3$ ceramics is consistently obtained. And these results (Fig. 1 and Fig. 3) confirm that the addition of CuO/Bi$_2$O mixture can effectively lower the need temperatures for densification of (Ba$_{1-x}$Sr$_x$)$_3$TiO$_3$ ceramics.
Fig.5 The maximum dielectric constants of \((\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3\) ceramics as a function of Sr content and measured temperatures.

Fig.6 shows the temperature-dielectric constant curves as a function of SrO content, the measured frequency is 1 MHz. As Fig.6 shows, the T-\(\varepsilon_r\) values curves are shifted to lower temperatures as the SrO content increases, the Curie temperatures shifting effect of SrO is obvious.

![Diagram](image)

Fig.6 The dielectric constants of \((\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3\) ceramics as a function of Sr content and measured temperatures.

4. Conclusions

(1) Using CuO/Bi\(_2\)O mixture as the sintering aid will low down the sintering temperatures of \((\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3\) ceramics to about 1150\(^{\circ}\)C.

(2) Sintered at 1150\(^{\circ}\)C, normal grain growth are observed, and the grain sizes increase with the increase of SrO content.

(3) The CuO/Bi\(_2\)O mixture fluxed \((\text{Ba}_{1-x}\text{Sr}_x)\text{TiO}_3\) ceramics will reveal a tetragonal phase or a pseudo-Cubic phase.

(4) The saturated density values will decrease, the maximum \(\varepsilon_r\) values (revealed at Curie temperatures) will increase, and the Curie temperatures are shifted to lower temperatures as the SrO content increases.

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References: