Grain Growth Control of $BaTiO_3$ Ceramics
with CuO/BaO=2.5 Mixture Addition

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Grain growth of $BaTi_{1.005}O_{3.01}$ during liquid-phase sintering of $BaTiO_3$ ceramics was investigated for CuO-BaO (molar ratio, CuO/BaO=2.5) mixture additions from 0.5wt% to 2wt%. Sintering in air for 2h at 1050^oC to 1250^oC was investigated to study the densification process, while sintering in air for 1 to 16h at 1150^oC to 1250^oC was investigated to study the grain growth. The sintered grain morphologies (no grain growth, abnormal grain growth, and normal grain growth) of $BaTi_{1.005}O_{3.01}$ ceramics depend on the amount of CuO-BaO mixture, the sintering temperature, and sintering time. The results were discussed in terms of the phenomenological kinetic grain growth expression: $G^n - G_o^n = K_o\ t\ exp(-Q/RT)$. The average grain growth exponents of $BaTiO_3$ with 0.5wt%, 1wt%, 1.5wt%, and 2wt% CuO-BaO mixture addition were 5.193, 4.307, 5.773, and 9.182, respectively. The activation energy for grain growth of $BaTiO_3$ with 0.5wt%, 1wt%, 1.5wt%, and 2wt% CuO-BaO mixture addition were 502 ± 25 kJ/mol, 314 ± 40 kJ/mol, 448 ± 53 kJ/mol, and 392 ± 48 kJ/mol.

Keywords: grain growth, liquid phase sintering, phenomenological kinetic

1. Introduction

The ZnO grain-growth process can be analyzed in terms of the phenomenological kinetic grain-growth equation :[1-3]

$$G^n - G_o^n = K_o\ t\ exp(-Q/RT) \qquad (1)$$

n is the grain growth kinetic exponent (used to indicate the grain growth rate), K_o is a preexponential constant, Q is the apparent activation energy (the magnitude of energy supplies for atoms to overcome barrier to moving from one site to another), and T is the absolute temperature. When the initial grain size, G_o, is small compared with the average grain size, G, at the time t, the factor G^n can be neglected relative to G^n, and Eq. (1) can be simplified to :[4]

$$G^n = K_o\ t\ exp(-Q/RT) \qquad (2)$$

The grain-growth exponent (or n value) can be determined from the slope of a log(G) vs log(t) plots. The n value then can be applied to determine the activation energies from the slope of the Arrhenius plots of $log(G^n/t)$ vs 1/T. The reported activation energies of grain growth in pure ZnO were in the range from 213 to 409 KJ/mol. The technique can be applied to investigate the activation energies of grain growth in $BaTiO_3$.

In the past, many oxides could be used as the sintering aids of $BaTiO_3$-based ceramics, including

B_2O_3, Bi_2O_3, and LiF [5-7]. The mixtures of CuO with TiO_2 and ZrO_2 can be also used to reduce the sintering temperature of $BaTiO_3$ [8] The binary phase relations of BaO-CuO were complicated as reported in the Eu-Ba-Cu-O system. Roth ea al. revealed a tentative diagram for the BaO-CuO system involving two binary compounds $BaCuO_2$ and Ba_2CuO_3 [9], the latter apparently being unstable above 800^oC [10]. $BaCuO_2$, originally synthesized by Arjomand and Machin [11], melts incongruently around 1000^oC in air. In addition, there was a eutectic between $BaCuO_2$ and CuO at around 900^oC. Because of the low melting point of the binary BaO-CuO system (or $BaCuO_2$-CuO), so we used to use the mixtures as a new potential candidate for lowering the firing temperature of $BaTiO_3$ ceramics. In this study, attempts had been made to study the effect of different amount of CuO-BaO mixture (molar ratio, CuO/BaO=2.5) on microstructure and grain size. We also attempted using Eq. (1) to analyze the grain growth with regard to the kinetic exponents and activation energies. It was also necessary to quantitatively describe the kinetic of $BaTiO_3$ grain growth in liquid-phase-sintering $BaTiO_3$/CuO-BaO systems. The grain growth of $BaTiO_3$ with systematic CuO-BaO addition has been undertaken to address the issues.

2. Experimental Procedures

$BaCO_3$ and TiO_2 with purities of 99.8% were used as the raw materials, and were weighted in accordance with the composition $BaTi_{1.005}O_{3.01}$. Then the powder was mixed with distilled water, dried and ground. The ground powder was calcined in air at 1150^oC for 2h. X-ray diffraction pattern (XRD) analysis was carried out on the calcined $BaTiO_3$ powder. In the calcined powder only the tetragonal $BaTiO_3$ phase was observed in XRD patterns. CuO-BaO mixture with the CuO/BaO ratio 2.5 (molar ratio) was prepared. 0.5wt%, 1wt%, 1.5wt%, and 2wt% CuO-BaO mixture were added to calcined $BaTiO_3$ powder by wetting mixing, respectively. The products were pressed into pellets using distilled water as binder. The pellets were sintered at temperature varying 1050^oC to 1250^oC, keeping the sintering duration fixed for 2h, to study the effect of sintering temperature on the morphology and densities of CuO-BaO fluxed $BaTiO_3$. Densities were calculated from the weights and the dimensions of the sintered ceramics bodies. Three sintering temperatures at equal spacings of $T(^oC)$ were investigated at 1150^oC, 1200^oC, and 1250^oC. Sintering was for five different times at each firing temperature, varying from 1 to 16h. The effects of duration on the grain growth were directly observed and measures from the sintered surfaces. The microstructural observations of the surfaces of sintered samples were directly observed from the SEM (scanning electronic micrograph). The grain size was directly measured from photomicrographs of the SEM pictures. The average grain size G is obtained as : [1]

$$G = 1.56 \, L \qquad\qquad (3)$$

where L is the average grain boundary intercept length of four random lines across the micrograph.

3. Results and Discussion

The liquid phase forming temperature of the CuO-BaO system could be obtained from the phase diagram of the Er-Cu-Ba-O system. The sintered morphology can prove that CuO-BaO mixture will act as a liquid phase promoter and improve the grain growth of $BaTiO_3$ ceramics. Sintering at 1100^oC and below for 2h, CuO-BaO mixture-doped $BaTiO_3$ ceramics reveal a porous structure. Sintering at 1150^oC for 2h, two different differently morphologies are revealed in the sintered ceramics. The bimodual non-uniform distribution of grain size which exhibits exaggerated discontinuous grain in a fine-grained matrix is observed in 0.5wt% CuO-BaO mixture-doped $BaTiO_3$ ceramics, as shown in Fig. 1(a). The abnormal grain growth (or called secondary recrystallization) is characterized by the rapid growth of only a small number of grains. This may result from the presence of small amount of the liquid phase flux or eutectic formed by the additive or certain impurities. In the $BaO-TiO_2$ system, this will cause the liquid phase to form is that performs with a small excess TiO_2 (Ti/Ba>1) for reacting with $BaTiO_3$ to form the other phases, and they may form eutectic with $BaTiO_3$. For example, $Ba_6Ti_{17}O_{40}$ would form eutectic with $BaTiO_3$ and melts at about 1312^oC. However, this is impossible because the sintering temperature is lower than 1300^oC. Therefore, the abnormal grain growth caused by the liquid-phase effect of CuO-BaO mixtures is readily.

As 1wt% or more CuO-BaO mixture content is added as liquid phase promoter, the $BaTiO_3$ ceramics will reveal the normal grain growth, as Fig. 1(b) shows. In this study, $BaTiO_3$ ceramics with 0.5wt%, 1wt%, 1.5wt%, and 2wt% CuO-BaO mixture added the temperatures to reveal the normal grain growth are 1200^oC, 1150^oC, 1150^oC, and 1150^oC. The microstructures of the 2wt% CuO-BaO mixture-doped $BaTiO_3$ ceramics and sintered at 1150^oC for 1, 2, 4, and 16h are shown in Fig. 2(a)-(d). It is obvious that the average grain size increases with the increase of sintering time.

The average grain size of $BaTiO_3$ ceramics as a function of CuO-BaO mixture content and sintered at different temperature for 2 h is depicted in Fig. 3, the average grain size increases with the increase of sintering temperatures. The average grain size increases initially as CuO-BaO mixture content increases up to 1~1.5wt%, however, then the average grain size decreases as the CuO-BaO mixture content is further increased. The results in Fig.3 confirm the increase in the grain size of $BaTiO_3$ system up to 1~1.5wt%, but the further addition only following a significant decrease in the grain size of $BaTiO_3$ ceramics.

The grain growth equation of the composition during sintering in this study is expressed by :

$$G^n/t = K_o \exp(-Q/RT) \qquad (4)$$

The slopes below 1100^oC for 1wt% and more CuO-BaO mixture added (1150^oC for 0.5wt%) $BaTiO_3$ ceramics are hard to list in Fig. 4 because of the no normal grain growth and bimodiual grain growth. However, the grain growth exponents at temperature equal to and above 1150^oC (1200^oC for 0.5wt%) could be calculated readily. The phenomenological kinetic grain growth equation can be readily plotted in the form:

$$\log(G) = (1/n) \log(t) + (1/n) [\, \log(K_o) - 0.434(Q/RT)] \quad (5)$$

From the slope of the log(grain size) versus log(time) line, which is $1/n$, the grain growth kinetic exponent is readily determined. The grain growth exponents obtained from Fig. 4 are summarized in Table I. There has not been a satisfactory explanation for any mechanism of grain-boundary migration with a grain growth exponent, even though similar behaviour has been observed. Large grain growth exponets are indicative of slowly coarsening microstructures, for the rate of grain growth (dG/dt or $d(\log G)/d(\log t)$) decreases with increasing n value, as can be readily seen by differentiating Eq. (3). In combination with the high exponents observed in this study, the results suggest that the apparent grain growth rate is lower during the initial stages of sintering and that this is characterized by a large apparent n value.

Figure 5 illustrates an Arrhenius plot constructed from the data of Fig. 4, in which $\log(G^n/t)$ is plotted versus the reciprocal of the absolute temperature (1/T). Rearranging Eg. (5) yields:

$$\log(G^n/t) = \log K_o - 0.434(Q/RT) \quad (6)$$

The slope of which yields the apparent activation energy for the grain growth process. There naturally exists some dispersion of the G^n/t values, especially for the temperature where the grain growth does not exactly ascribe to the n values as shown in Fig. 5. However, there generally exists a reasonably good linear relationship between $\log(G^n/t)$ and 1/T from 1150ºC. This implies that the mechanism of grain-boundary migration during grain growth of $BaTiO_3$ may be the same over this temperature range, even though the grain growth exhibits a slightly higher kinetic exponent at the higher temperatures. From Table I, the average n values are estimated. Using these average n values as a basis, numberous trial plots versus 1/T were constructed and an average n values presented in Table I are chosen on the basis of best fit for the plots presented in Fig. 5. These Arrhenius plots yield straight-line relationships in the range of $1150^oC \sim 1250^oC$. The apparent activation energy for grain growth of CuO-BaO mixture-doped $BaTiO_3$ ceramics are calculated from the slope of Fig. 5, and the measured results are also presented in Table I. Activation energies derived from the slopes of the Arrhenius plots are different as different amount of CuO-BaO mixture content is added into the $BaTiO_3$ ceramics. The activation energies for grain growth are 502±25 kJ/mol, 314±25 kJ/mol, 448±53 kJ/mol, and 392±48 kJ/mol as 0.5wt%, 1wt%, 1.5wt%, and 2wt% CuO-BaO mixture content is added into the $BaTiO_3$ ceramics, respectively.

4. Conclusion

In this study, the influence of CuO-BaO mixture (CuO/BaO=2.5) content on the grain growth of $BaTiO_3$ ceramics has been analyzed qualitatively. The average grain sizes of $BaTiO_3$ ceramics increase with the increase of sintering temperatures and sintering time. Form this study results, the CuO-BaO mixture content has large effect on the grain growth exponents, the average grain size, and the activation energies of $BaTiO_3$ ceramics.

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Table I. Summary of BaTiO$_3$ with CuO-BaO mixture grain growth parameter

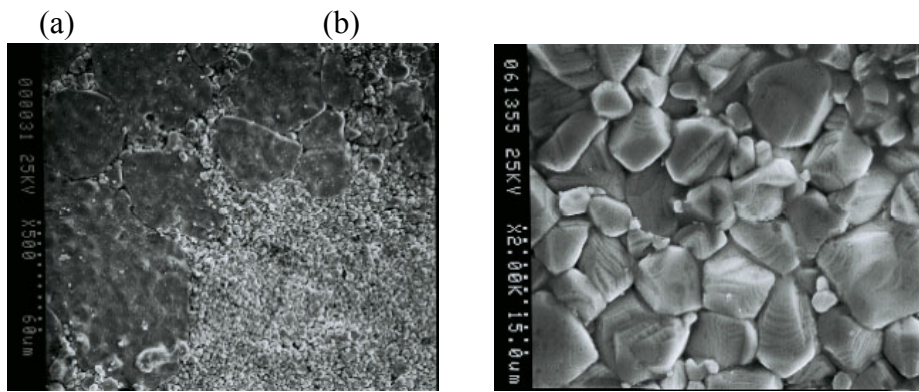| CuO-BaO mixture content	Sintering temperature (^{o}C)	Grain-growth exponent	Average grain-growth exponent	Activation Energy (kJ mol^{-1})
0.5wt%	1150 1200 1250	--- 5.318 5.068	5.193	502±25
1wt%	1150 1200 1250	4.960 4.180 3.781	4.307	314±25
1.5wt%	1150 1200 1250	6.479 5.482 5.089	5.773	448±53
2wt%	1150 1200 1250	10.539 8.821 8.186	9.182	392±48

Fig. 1 The micrographs of BaTiO$_3$ ceramics with x wt% CuO-BaO mixture added, sintered at 1150°C for (a) x=0.5, (b) x=1.
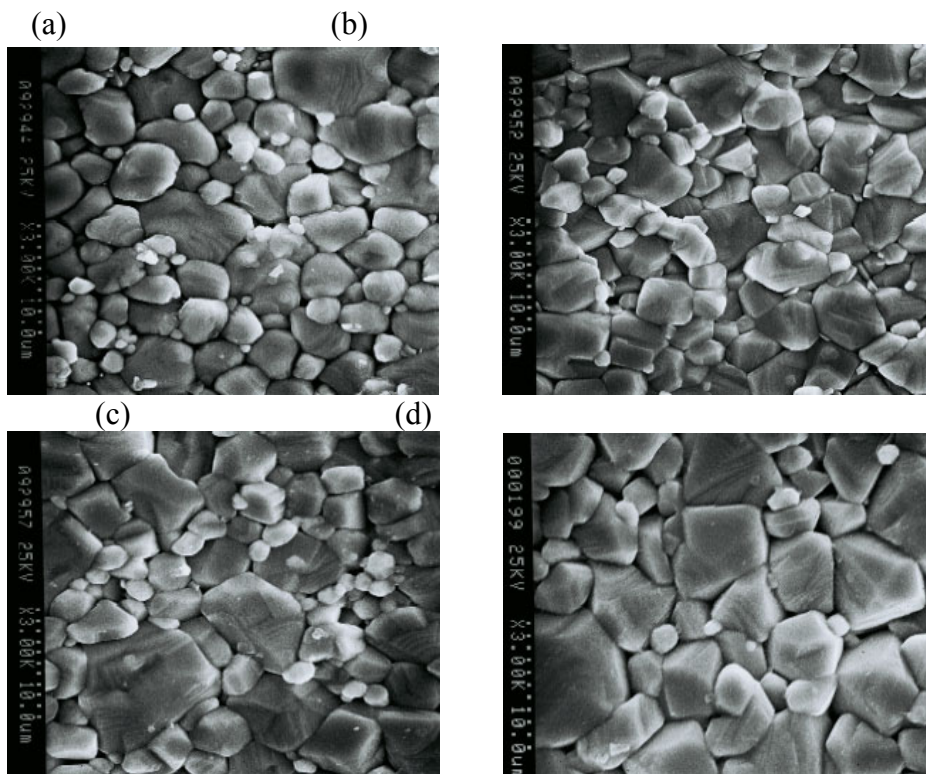

Fig. 2 The micrographs of 1wt% CuO-BaO mixture-doped BaTiO$_3$ ceramics, sintered at 1150°C for (a) 1 hr, (b) 2 hr, (c) 4 hr, and (d) 16 hr.
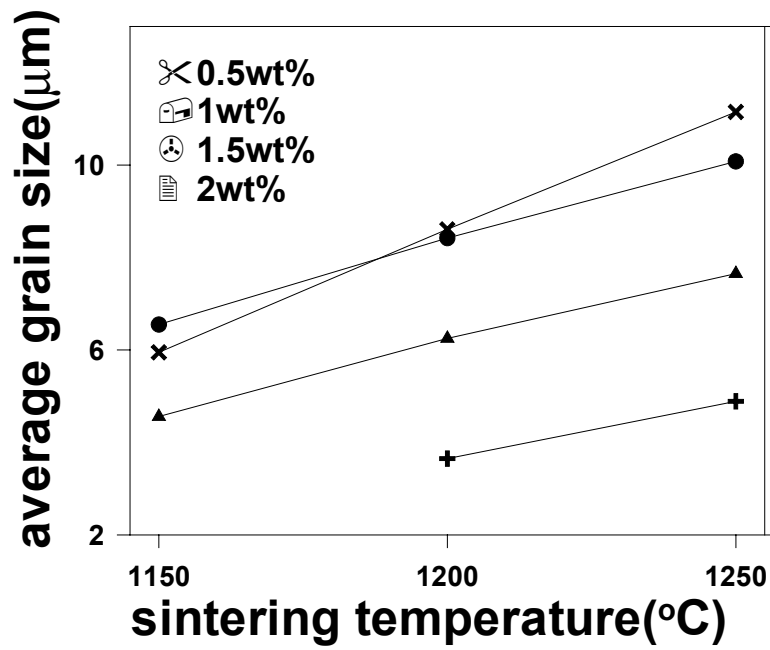
Fig. 3 The average grain sizes of BaTiO$_3$ ceramics, as a function of sintering temperature and CuO-BaO mixture content. The sintered time is 2h.
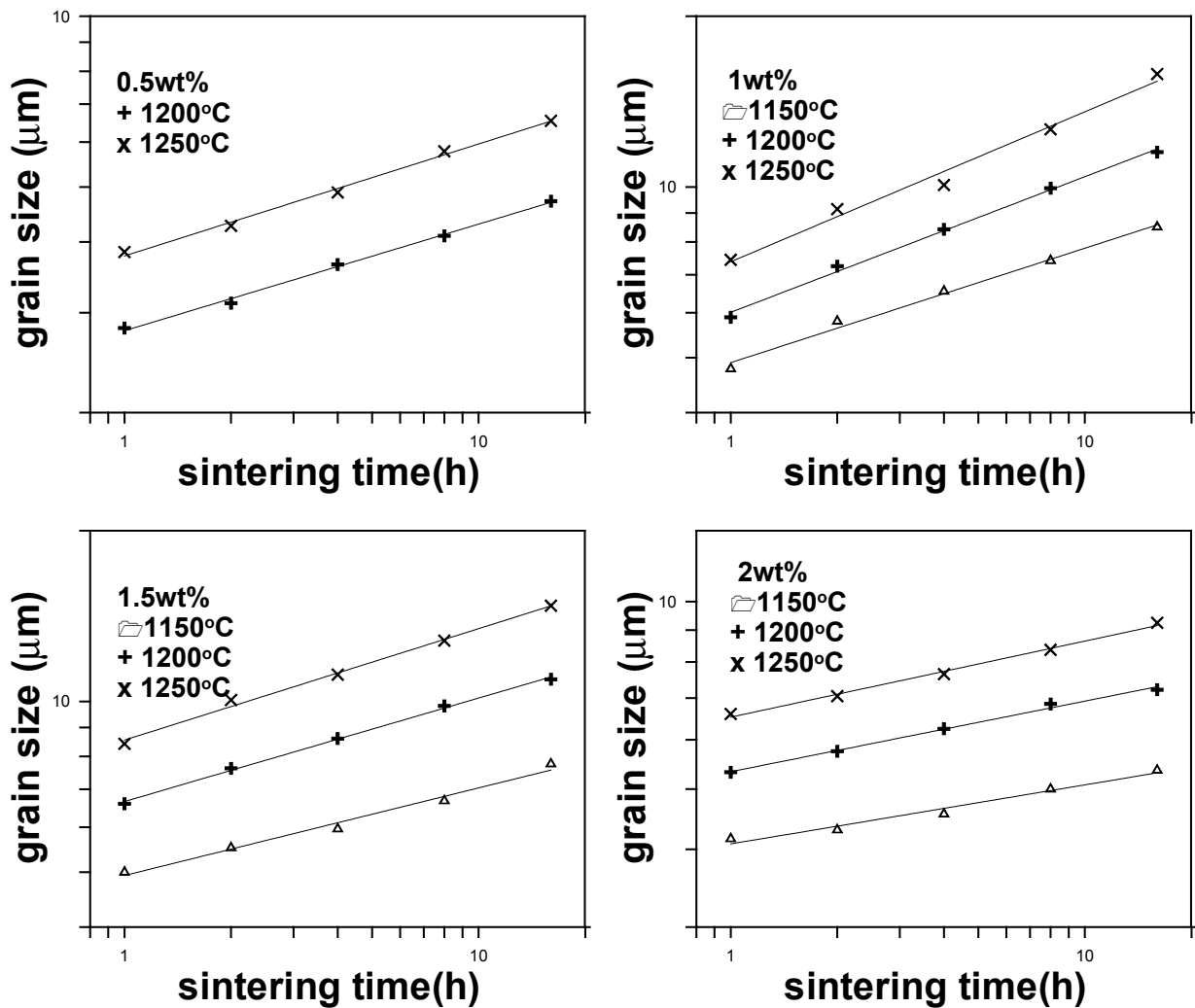

Fig. 4 The average grain sizes of BaTiO$_3$ ceramics, as a function of sintering temperature, sintering time, and CuO-BaO mixture content.
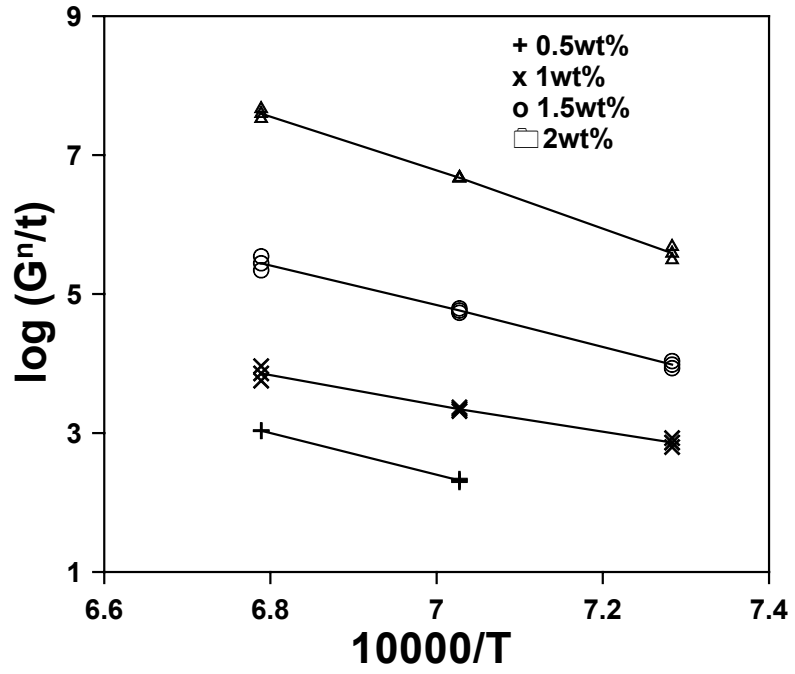
Fig. 5 log(G^n/t) vs 1/T Arrhenius plots for BaTiO3 with different CuO-BaO mixture content added.