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Investigations on the liquid phase in barium titanate ceramics with silica additives

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Abstract

Additives of SiO_2 lower the sintering temperature of $BaTiO_3$ ceramics and promote anomalous grain growth. However, the nature of the working liquid phase is not clear. A binary eutectic is out of the question because the system $BaTiO_3$–SiO_2 is not a binary one, as shown by Robbins [Robbins, C. R., Synthesis and growth of fresnoite ($Ba_2TiSi_2O_8$) from a TiO_2 flux and its relation to the system $BaTiO_3$–SiO_2. *Journal of Research of the National Buereau of Standards — A. Physics and Chemistry*, 1970, **74A,** 229–232]. Guha and Kolar [Guha, J. P. and Kolar, D., Phase equilibria, sintering characteristics and dielectric properties in the $BaTiO_3$-rich portion of the system BaO–TiO_2–SiO_2. In *5th Conference on Ceramics for Electronics*, Liblice, 1974, pp. 1–9] found a ternary eutectic with a composition of 33 mol% BaO, 54 mol% TiO_2 and 13 mol% SiO_2. We examined powder tips of this composition and ones of pure SiO_2 in contact with $BaTiO_3$ green bodies by heating microscopy. The results suggest that the ternary eutectic develops in sintering bodies with SiO_2 addition. During further sintering the composition of the liquid phase is changed and this modified melt is able to trigger anomalous grain growth.

Keywords: $BaTiO_3$ and titanates; Sintering; SiO_2

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1. Introduction

The positive temperature coefficient of resistance (PTCR) effect in $BaTiO_3$ ceramics is the basis of numerous technical applications. Usually, the microstructure of such ceramics is a result of liquid phase sintering. The required liquid phase is formed by a reaction between a suitable additive and the $BaTiO_3$ matrix powder. An easy example for an additive is a small titania excess from 1–4 mol%. This excess forms the well-known eutectic[3] $BaTiO_3$–$Ba_6Ti_{17}O_{40}$ at 1332°C and promotes anomalous grain growth, which is controlled by a solution–diffusion–reprecipitation process. Also, additives of SiO_2 can promote anomalous grain growth and they lower the sintering temperature of $BaTiO_3$ ceramics. However, the nature of the working liquid phase is not clear.

Unfortunately, the much-cited phase diagram of the system $BaTiO_3$–SiO_2 by Rase and Roy[4] is not correct because this system is not binary, as shown by Robbins.[1] Especially, the compound $BaTiSiO_5$ does not exist. Actually, the compound is $Ba_2TiSi_2O_8$ (fresnoite), as confirmed by Belous et al.[5] as well as Köppen and Dietzel.[6] On the other hand, fresnoite was detected[7] in sintering bodies with additives of SiO_2 at temperatures from about 700 °C. Senz et al.[8] and Hesse et al.[9] studied the reactions between $BaTiO_3$ and SiO_2 by model experiments. Annealing the amorphous SiO_2 films on $BaTiO_3$ single-crystal substrates at temperatures >700°C resulted in the formation of the crystalline phases fresnoite and $Ba_6Ti_{17}O_{40}$. These results suggest the presence of the three phases fresnoite, $Ba_6Ti_{17}O_{40}$ and $BaTiO_3$ in sintering bodies with SiO_2 additives already at temperatures below the melting point of the liquid phase. A ternary eutectic is located exactly inside a triangle constructed from these compounds (in the system BaO–TiO_2–SiO_2), as found by Guha and Kolar.[2]

The aim of this investigation was to test the effect of this eutectic on anomalous grain growth.

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2. Experimental

2.1. Materials

The starting materials were reagent grade $BaCO_3$, TiO_2 and SiO_2. The powders were dried at 160°C for 24 h and stored in a desiccator until used. The source substances for making stoichiometric $BaTiO_3$ substrates were mixed in a molar proportion of 1:1 in destilled water with zirconia balls in rolling polyethylene bottles for 24 h. The powder was calcined at 1100°C for 2 h and fine-milled. After addition of 5% polyvinylalkohol as a binder, discs (diameter 6 mm, height 1.5 mm) were pressed uniaxially with a green density of 3.1 g cm^{-3}. The starting powders for making the ternary eutectic were mixed in appropriate molar proportions in distilled water with agate balls in rolling polyethylene 24 h. The substance was calcined at 1100°C for 2 h and then crushed with an agate pestle. This procedure was repeated twice at 1150°C to achieve a homogeneous material. Then the powder was heated in a platinium crucible at 1400°C for 10 min with a heating rate of 10 K min^{-1}. Finally the quenched material was ground with a pestle.

2.2. Heating microscopy

The melting behaviour of the ternary eutectic and of the pure SiO_2 was investigated using a heating microscope. For this purpose a small quantity of a powder with the appropriate composition was tipped onto a green compact of stoichiometric $BaTiO_3$. This arrangement was sintered with different heating regimes. The melting process was detected by measuring the height of the tip in dependence on the temperature (for details see elsewhere).[10] The contact region between the former tip and the substrate was inspected by optical microscopy and by environment scanning electron microscopy (ESEM) to evaluate the progress of the sintering process in the $BaTiO_3$ substrate. The experiments were carried out on a Carl Zeiss, Jena model MHO 2 heating microscope.

3. Results and discussion

Guha and Kolar[2] found a ternary eutectic with a composition of 33 mol% BaO, 54 mol% TiO_2 and 13 mol% SiO_2 and a melting point of 1195 ± 5°C. This composition corresponds to a molar ratio for $BaTiO_3$:$Ba_6Ti_{17}O_{40}$:fresnoite of 2:1:2.6. An arrangement of a tip of the ternary eutectic was heated up to 1280°C and held for 1 h. As a result of this treatment the developing liquid phase was completely sunk into the substrate. Besides, the melt was evenly distributed in the sintering body. Surprisingly, the microstructure shows not any sign of anomalous grain growth, as seen in Fig. 1. In contrast, similar arrangements with pure silica tips reveal the beginning of anomalous grain growth, as shown by the large grains in the region near the former tip (bright) in Fig. 2. This sample was heated up to 1282°C at 1 K min^{-1} and then cooled down at 10 K min^{-1}.

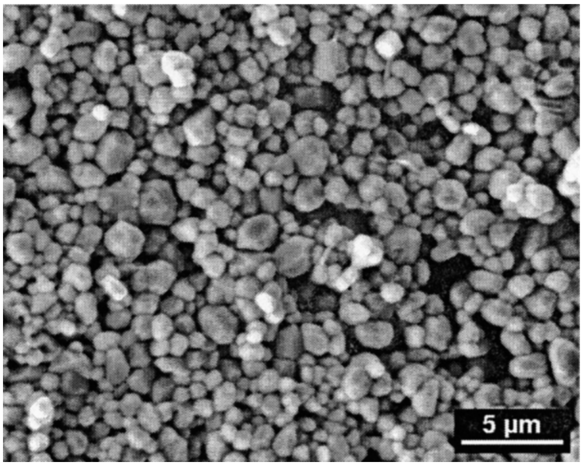


Fig. 1. Surface (ESEM) of the $BaTiO_3$ substrate near the former tip, sintered for 1 h at 1280°C.

These findings seem to indicate that the ternary eutectic cannot promote anomalous grain growth. Nevertheless, we assume that this eutectic is formed inside the sintering bodies with additives of silica, as discussed in the following.

The solid phase reaction between $BaTiO_3$ and SiO_2 (see Hesse et al.)[9] can be written as $28BaTiO_3+22SiO_2\rightarrow11Ba_2TiSi_2O_8+Ba_6Ti_{17}O_{40}$. If this reaction runs also in the sintering body, the three phases $BaTiO_3$, $Ba_2TiSi_2O_8$ and $Ba_6Ti_{17}O_{40}$ should be already present at temperatures below the eutectic temperature. Consequently, the ternary eutectic should be developed from these compounds at the eutectic temperature in regions where these phases are in contact. On the other hand, from the molar ratio of the eutectic for $BaTiO_3$:$Ba_6Ti_{17}O_{40}$: fresnoite of 2:1:2.6 follows that the

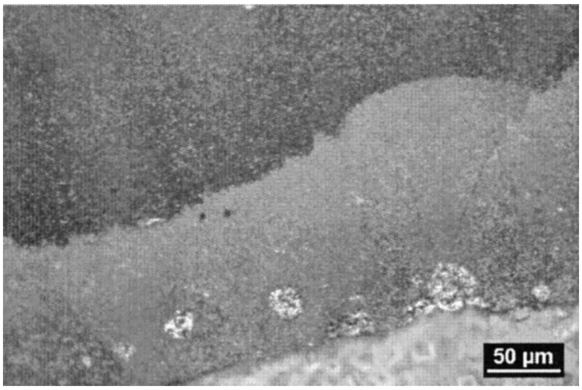
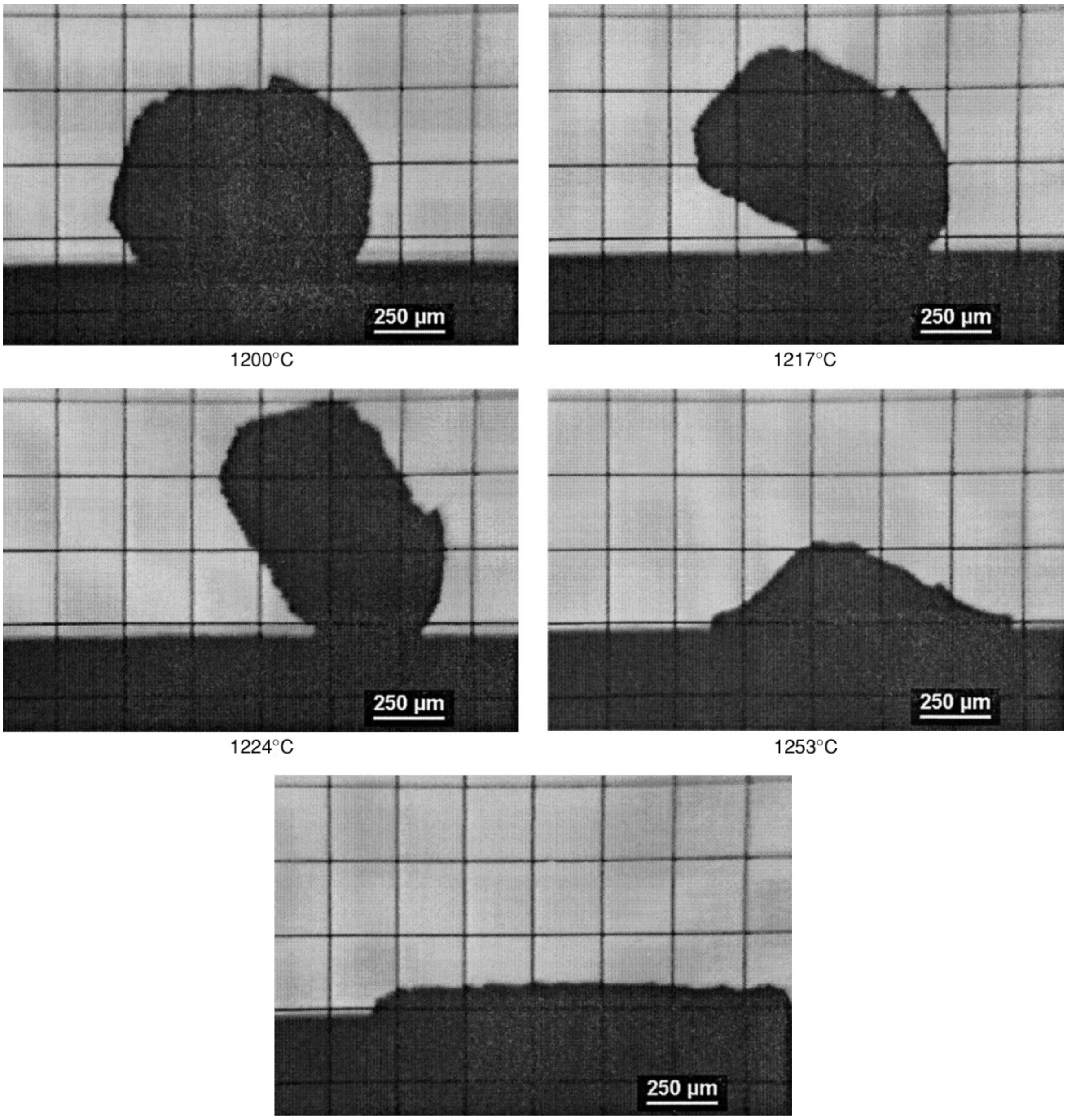


Fig. 2. Large grains near the SiO_2 tip, grown by anomalous grain growth.



1200°C 1217°C 1224°C 1253°C 1260°C

Fig. 3. Contours of a SiO_2 tip on a $BaTiO_3$ single crystal at different temperatures.

amount of developing liquid phase is limited by the phase $Ba_6Ti_{17}O_{40}$ and only about 24% of fresnoite is consumed in the formation of the ternary eutectic. Thus, $BaTiO_3$ and fresnoite are available in a sintering body with silica additives after creation of the eutectic. During further heating the liquid phase can dissolve $BaTiO_3$ and fresnoite and the composition of the liquid phase will be changed in this way. In contrast the 'pure' eutectic melt (as result of the melting tip) can only dissolve $BaTiO_3$. Consequently, the compositions of the two liquid phases are quite different at higher temperatures. Obviously, a liquid phase formed from the ternary eutectic melt by solution of fresnoite and barium titanate makes possible anomalous grain growth. However, the ternary eutectic melt modified only by barium titanate is not able to trigger this process.

Indeed, experiments with silica tips and substrates of $BaTiO_3$ single crystals reveal the formation of a liquid phase in the contact region between $BaTiO_3$ and SiO_2 at temperatures near the eutectic temperature, as seen in Fig. 3.

4. Conclusions

In barium titanate ceramics with silica additions, SiO_2 reacts with $BaTiO_3$ and forms fresnoite and $Ba_6Ti_{17}O_{40}$. The first developing liquid phase is a ternary eutectic found by Guha and Kolar.[2] This melt does not trigger anomalous grain growth. During further sintering the liquid phase dissolves $BaTiO_3$ and fresnoite. The modified liquid phase allows anomalous grain growth.

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