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The effect of stoichiometry and the $TiCl_3$ addition on the microstructure of $BaTiO_3$

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Abstract

The effect of stoichiometry, i.e. Ba/Ti ratios (1.0025, 1.0 and 0.98) and the $TiCl_3$ addition on the microstructure and densification of $BaTiO_3$ were investigated. The $BaTiO_3$ powders were prepared by the conventional ceramic processing method. The samples were sintered at 1250, 1300, 1335 and 1360 °C for 1 h. The $Ba_4Ti_2O_{27}$ phase was found in the Ba excess $BaTiO_3$, the platelet type $Ba_2Ti_5O_{12}$ phase was detected in the Ba and Ti excess compositions which were sintered at 1250 and 1300 °C, but not in the stoichiometric composition. When the sintering temperature was increased to 1335 °C the platelet type grain growth disappeared in the Ba excess composition, but remained in the Ti excess composition. In the stoichiometric composition, the fine grained microstructure occurred at 1250 and at 1300 °C large polygonal grains of 20–30 μm in size were obtained within the fine grained matrix. The addition of 0.2 mol% TiO_2 as $TiCl_3$ to the stoichiometric composition revealed a similar structure at 1250 °C. Below the eutectic temperature, the densification rates of the Ti excess samples were lower than the Ba excess samples, but above this temperature they showed a higher densification.

Keywords: A. Grain growth; A. Sintering; B. Microstructure; Barium titanate

1. Introduction

The sintering of $BaTiO_3$ (BT) based materials is normally performed with a small excess of TiO_2 (Ba/Ti atomic ratio <1) as a sintering aid [1–3]. A TiO_2 excess gives a eutectic melt which is reported as 1312, 1320 or 1332 °C in the literature ([1,4,3], respectively). The presence of a eutectic liquid not only promotes densification but also gives rise to a pronounced discontinuous grain growth in BT. Below the eutectic temperature grain growth of BT is extremely slow. Discontinuous or abnormal grain growth, sometimes called secondary recrystallisation is characterised by the rapid growth of a small number of grains which consume the small matrix grains [1]. At sintering temperatures below the eutectic, nearly all large crystallites were found in the form of lamellae [5]. Earlier research revealed that a Ti-rich liquid phase is a necessary condition for anomalous grain growth via a dissolution and reprecipitation process. However it was recently shown that anomalous grain growth is also possible below the eutectic temperature via solid state diffusion [5]. This process is accompanied by the growth of double twinned crystallites. Twins are often observed in undoped and weakly donor doped BT ceramics.

Hence in this work, barium titanate compositions having Ba/Ti ratios of 1.0025, 1.0, 0.98 were prepared to elucidate the effect of stoichiometry on the grain growth and densification. Also part of TiO_2 in the stoichiometric composition was replaced with $TiCl_3$ in order to deduce its effect on similar properties.

2. Experimental procedure

The BT powders were prepared by conventional ceramic processing techniques. The compositions which were prepared are given below:

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Code:	Compositions:
(1)	$Ba/Ti = 1.0025$
(2)	$Ba/Ti = 1.0$
(3)	$Ba/Ti = 0.980$
(21)	$Ba/Ti = 1.0$ (0.2 mol TiO_2 as $TiCl_3$)

$BaCO_3$ (BDH-272885Y), TiO_2 (Fisher-780915), and the other additives were weighed according to their compositions and milled in an ashless rubber-lined jar for 10 h using ZrO_2 balls and deionized water as a grinding media. $BaCO_3$ and TiO_2 contained major impurities Fe, Pb, K and Na, in totals of 760, 160 ppm respectively. The ground mixture was then dried at 110 °C and cakes were prepared in a steel die of 50 mm diameter at 15 MPa without using any binder. The calcination of the cakes were carried out at 1000 °C for 2 h employing a 200 °C/h heating rate. The calcined material was then crushed to <0.5 mm and reground for 10 h in the stated conditions and the median diameter of the ground powder was found to be 1.2 μm. After drying the ground material, granulation was done using distilled water as binder. Granules were die pressed into discs of 17 mm in diameter and 4 mm in thickness under a pressure of 100 MPa. The samples were sintered in air at 1250, 1275, 1300, 1335 and 1360 °C for 1 h employing 300 °C/h heating rate and then cooled naturally in the furnace. The microstructure of the samples were studied using a scanning electron microscope (Jeol JSM 5600). The phases were identified by X-ray diffraction (XRD-6000 Shimadzu-Japan) using CuK_α radiation at 40 kV/30 mA.

3. Results and discussion

The microstructures of the Ba excess $BaTiO_3$ (BT) samples (Code1) sintered at 1250 and 1300 °C for 1 h are shown in Fig. 1. A platelet type grain growth within a fine grained BT matrix occurred in the Ba excess samples sintered at 1250 and 1300 °C for 1 h (Fig. 1a,b). This platelet type microstructure was observed by some researchers only in the TiO_2 excess BT composition [2,6,7], but not in the Ba excess composition. The platelet type grains disappeared when the Ba excess sample was sintered at 1335 °C which is above the eutectic temperature of 1332 °C.

The backscattered image of the Ba excess sample in Fig. 1a is given in Fig. 1c. The bright polygonal grains indicate a Ba rich phase and the dark platelet type structure indicates a Ti rich phase. This Ti rich phase consists of microcrystalline grains aligned in a line forming the platelet type structure which is clearly seen

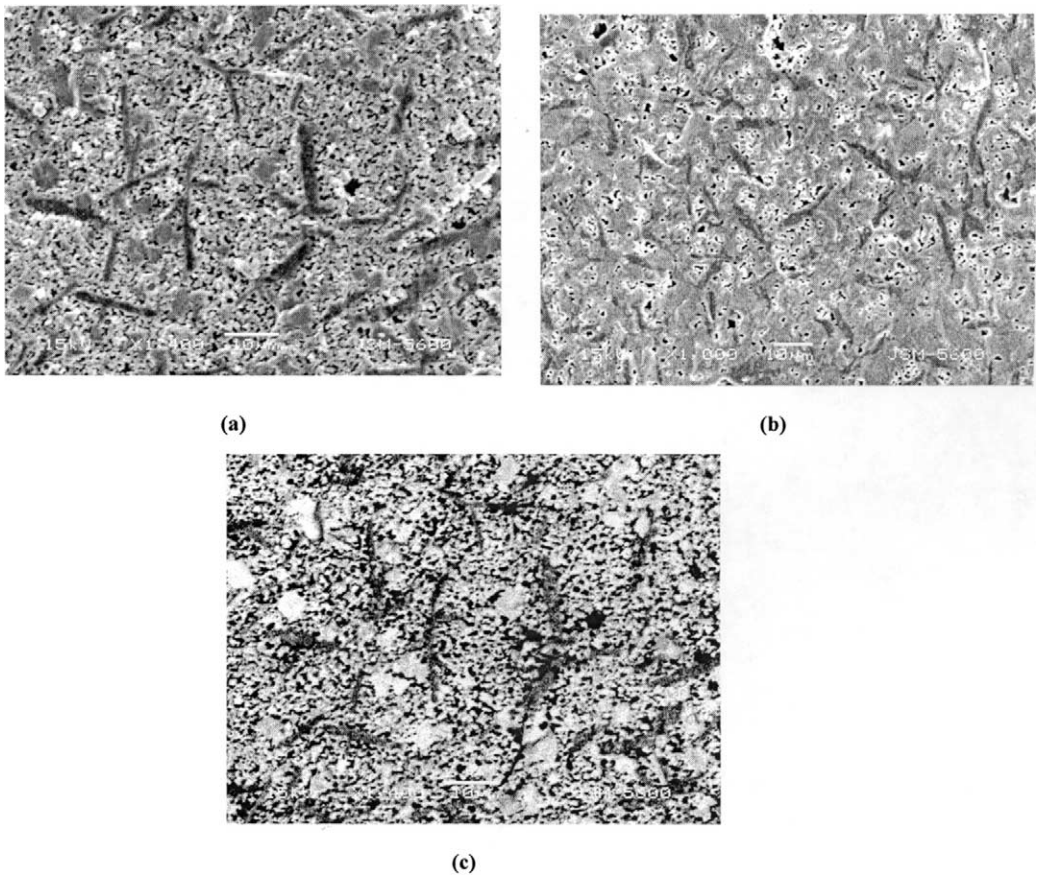


Fig. 1. Microstructure of Ba excess $BaTiO_3$ sintered at (a) 1250 °C/1 h, (b) 1300 °C/1 h, (c) backscattered image of (a).

in the backscattered image. The backscattered image of the Ti excess sample (Code3) sintered at 1250 °C could not be obtained due to the very small grained structure. The backscattered images of the Ti excess samples sintered at 1300 and 1335 °C given in Fig. 2a,b also showed a similar type of platelet structure again indicating Ti rich areas. Among the numerous investigations carried out on the identification of these phases, Oppelzer and Schmelz [5] determined these dark phases as $Ba_6Ti_{17}O_{40}$ by microprobe analysis. Hennings et al. [1] reported that in the TiO_2 rich section of the BaO-TiO_2 binary system, excess TiO_2 reacts with $BaTiO_3$ to form $Ba_6Ti_{17}O_{40}$ which gives a eutectic melt at 1312 °C. The XRD studies for the samples of the Ba excess, stoichiometric and Ti excess compositions sintered at 1250 °C for 1 h are given in Fig. 3. The peaks of tetragonal and cubic $BaTiO_3$ phases (PDF No:050626, PDF No:31–0174 respectively) are marked on the XRD patterns as T and C respectively. The stoichiometric composition yielded only the tetragonal BT phase. Cubic BT phase occurred in the Ba and Ti excess compositions. This indicates that Ba or Ti excess conditions stabilise the high temperature cubic form to room temperature. Especially the Ti excess is more effective in stabilising the cubic BT phase to room temperature than the Ba excess as seen from the diffraction patterns given in Fig. 3. The remaining peaks are marked as "x" on the XRD patterns. These peaks fit the diffraction patterns of $Ba_4Ti_2O_{27}$ (PDF No: 44–0013) or $Ba_2Ti_5O_{12}$ (PDF No: 17–0661) which show similar diffraction peaks at Bragg angles very close to each other but only differs in intensity. Hence, the bright polygonal phase in Fig. 1c

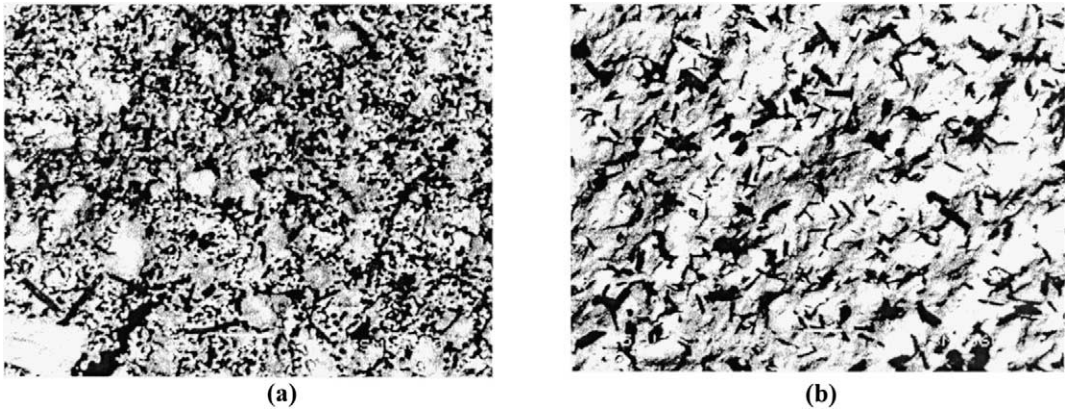


Fig. 2. Backscattered image of the Ti excess $BaTiO_3$ sintered at (a) 1300 °C/1 h, (b) 1335 °C/1 h.

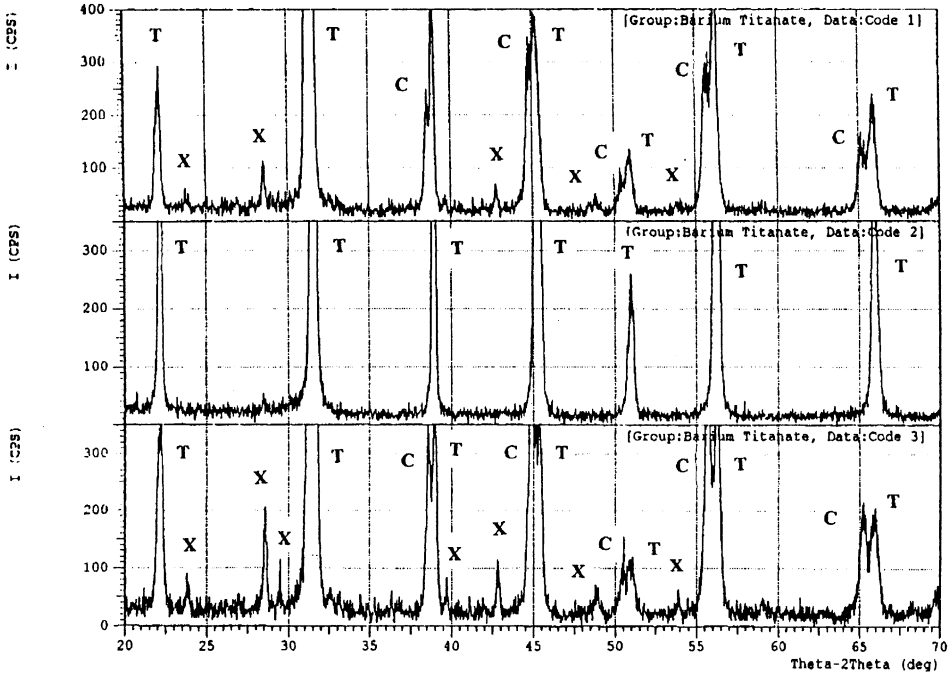


Fig. 3. XRD patterns of $BaTiO_3$ sintered at 1250 °C/1 h: (1) Ba excess, (2) stochiometric, (3) Ti excess. C: Cubic BT, T: Tetragonal BT, X: Ba or Ti excess phase.

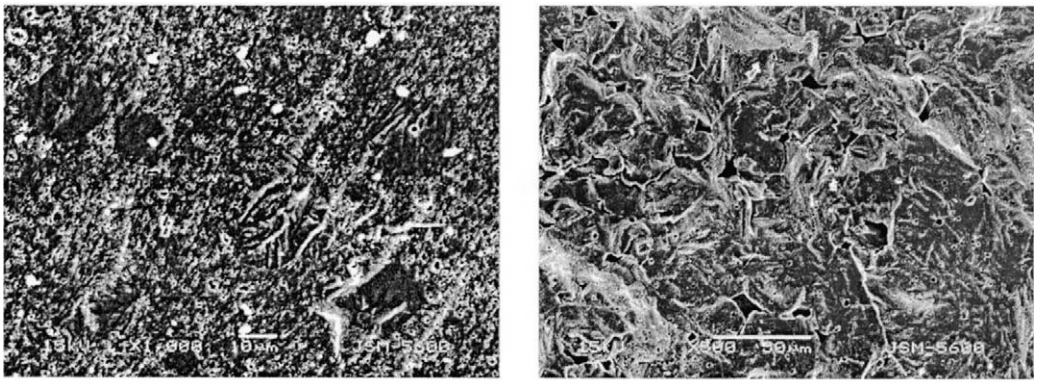


Fig. 4. Microstructure of the stochiometric $BaTiO_3$ 1 h sintered at (a) 1300 °C, (b) $TiCl_3$ added 1300 °C.

must be $Ba_4Ti_2O_{27}$ and the platelet type dark phase found in the Ba and Ti excess samples (Figs. 1c and 2a,b) must be $Ba_2Ti_5O_{12}$. O'Bryon and Thomson [8] reported that the structure of $Ba_6Ti_{17}O_{40}$ resembles that of the $Ba_2Ti_5O_{12}$ which was also observed by Jonker and Kwestroo [9]. He reported that $Ba_2Ti_5O_{12}$ compound forms near 1300 °C in the presence of slight impurities SnO_2 or ZrO_2 [9]. In this work, ZrO_2 impurities can arise from the ZrO_2 milling media used.

The stoichiometric BT composition was prepared by two different methods. The sample coded 2 was prepared from $BaCO_3$ and TiO_2 powders by conventional ceramic processing. The sample coded 21 was prepared by the same method but 0.2 mol% TiO_2 was added as a $TiCl_3$ form. The sample coded 2 sintered at 1250 °C for 1 h exhibited small grained porous structure. When the sintering temperature was increased to 1300 °C, polygonal grains occurred in the order of 25–30 μm in size within the fine grained structure (Fig. 4a). The samples prepared with $TiCl_3$ showed a similar structure when sintered at 1250 °C. However, when the sintering temperature was increased to 1300 °C, rapid growth occurred with a large amount of pores trapped within the grains (Fig. 4b). This showed that the $TiCl_3$ addition enhanced the densification. The densification rate of the sample coded 1,2,3 and 21 at different sintering temperatures are shown in Fig. 5. Below the eutectic temperature of 1332 °C, the densification of the Ba and the Ti excess samples were lower than that of the stoichiometric composition. The addition of $TiCl_3$ to the stoichiometric composition had a marked effect on the densification. At 1335 °C, which is slightly above the eutectic temperature, the Ti excess, stoichiometric and $TiCl_3$ added stoichiometric compositions showed 97% densification of the theoretical value of 6.02 g/cm^3 [10]. However, above 1335 °C the Ti excess and the Ba excess samples showed dedensification due to the pores trapped within the grains and at the grain boundaries as shown in Fig. 6a,b, but, the stoichiometric composition

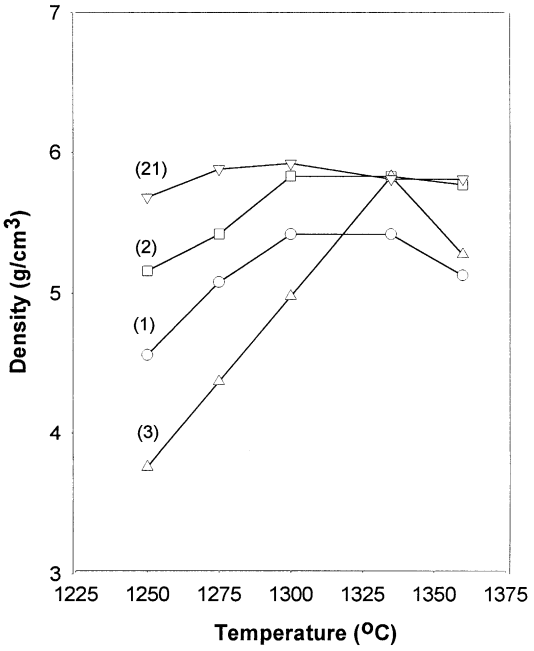
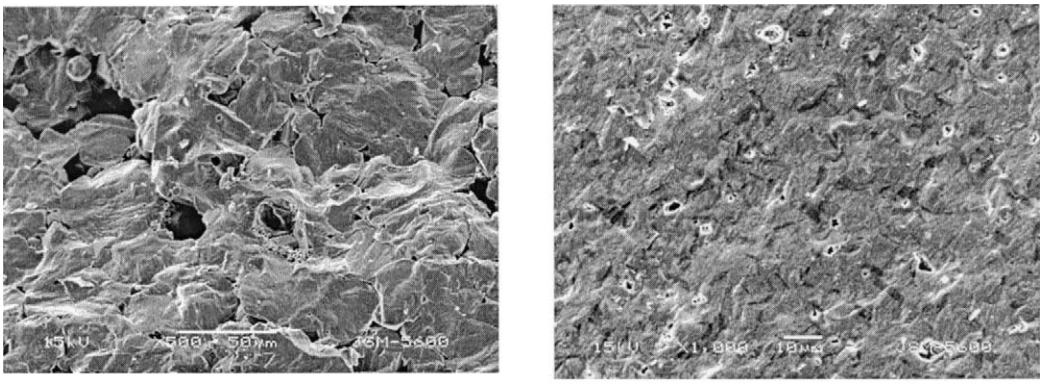


Fig. 5. Densification of the $BaTiO_3$: (1) Ba excess, (2) stoichiometric, (3) Ti excess, (21) $TiCl_3$ added stoichiometric.

did not show this effect. Demartin et al. [10] reported that dedensification was due to the simultaneous effect of different processes, namely abnormal grain growth, pore coalescence and closure of porosity. These effect are interrelated in a complex manner and are also influenced by the impurity content. And also Choi and Kim [11] observed that the eutectic melt inhibited rather than promoted further densification above 1320 °C. Many pores were trapped in grains and large pores were formed at the grain boundary due to the fast growth above 1320 °C. However, the densification of the Ba excess and stoichiometric samples were promoted at a lower temperature than the eutectic temperature. These results are contradictory to the results of Choi and Kim



(a) (b)

Fig. 6. Microstructure of the $BaTiO_3$ sintered at 1335 °C/1 h: (a) Ba excess, (b) Ti excess.

[11] and agree with the results of Lin et al. [6,12] because, different impurities and differences in the quantity of these impurities found in the raw materials affect the densification rate. $BaTiO_3$ is very sensitive to the processing conditions and to the impurities in the raw materials used. Therefore such contradictions found in the literature can be attributed to these impurities.

4. Conclusions

In the Ba excess samples sintered below the eutectic temperature, Ba rich and Ti rich phases were found. The Ti rich phase is in a microcrystalline chain formation. This structure disappeared when the sample sintered at above the eutectic temperature of 1332 °C. Ba and Ti rich phases were identified as $Ba_4Ti_2O_{27}$ and $Ba_2Ti_5O_{12}$ respectively.

The stoichiometric composition yielded only the tetragonal BT phase. The cubic BT phase occurred in Ba and Ti excess compositions. The Ba or Ti excess condition stabilise the high temperature cubic form to the room temperature. The Ti excess is especially more effective in stabilising the cubic BT phase at room temperature than the Ba excess.

In the stoichiometric composition the fine grained microstructure was obtained at 1250 °C. When sintered at 1300 °C rapid large polygonal grains of 20–3 0 μm in size are obtained within the fine grain matrix. The addition of $TiCl_3$ as part of TiO_2 to this stoichiometric composition reveals the same structure at a lower sintering temperature of 1250 °C. The backscattered image of the Ti excess BT composition shows platelet type grains when sintered at 1300 and 1335 °C. These platelet grains are the $Ba_2Ti_5O_{12}$ phase. The densification rate of the Ba excess composition below the eutectic temperature, is higher than the Ti excess composition. Above the eutectic temperature the densification rate of the Ti excess samples becomes higher.

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