

THE EFFECT OF B₂O₃ AND TiCl₃ ADDITION ON THE TWIN FORMATION IN Sb₂O₃ DOPED Ti-EXCESS BaTiO₃

HILKAT ERKALFA, BERAT YUKSEL*, T. OSMAN OZKAN*

TÜBITAK Marmara Research Center, MCTRE, Gebze, Kocaeli, Turkey

*Istanbul University, Engineering Faculty, Avcilar, Istanbul, Turkey

E-mail: Hilkat.Erkalfa@mam.gov.tr

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The microstructure of B₂O₃ and TiCl₃ added Sb₂O₃ donor-doped Ti-excess BaTiO₃ compositions were investigated. Platelet type Ba₂Ti₃O₁₂ was detected as a secondary phase in the Ti excess undoped composition sintered at 1250°C for 10 hours. This phase decreased considerably in the Sb₂O₃ and B₂O₃ added samples. The Sb₂O₃ donor-doping was very effective for promoting the twin formation due to the increased concentration of the Ti³⁺ ions. The 0.5 mol% B₂O₃ addition to this composition gave rise to the polygonal type grains containing twin lamellae and Ti-rich rod-like grains. At 1 mol% the B₂O₃ addition level, the polygonal grains and twin lamellae grew to the order of 100 μm size in a fine grained matrix. A sudden grain growth occurred at 2 mol% the B₂O₃ addition level, with the loss of twin lamellae in the structure. The addition of 0.2 mol% excess TiO₂ as a liquid TiCl₃ form to the 0.5 mol% B₂O₃ containing sample, reduced the size and the number of polygonal grains and had a marked effect on the twin formation due to the homogeneous distribution of the excess Ti ions in the composition.

INTRODUCTION

BaTiO₃ (BT) is the best known ferroelectric material which is used in many applications and its electric properties are dependent on the microstructure, chemical composition and Ba/Ti stoichiometric ratio. Processing conditions influence the microstructure of BT ceramics in which normal and anomalous grain growth can occur [1]. In the normal grain growth case, during the sintering process grains grow uniformly. In anomalous or discontinuous grain growth some grains overgrow and a bimodal microstructure occurs at the intermediate stage of the sintering process. The abnormal grains contain (111) twin lamellae while the matrix grains do not. Several proposals have been made for the anomalous grain growth and for the origin of (111) twins in a fine-grained matrix.

Schemelz et al [1,2] proposed that this anomalous grain growth is initiated by the twinning process and takes place by solid state mechanism when sintering is carried out below the eutectic temperature on the TiO₂ rich side of the phase system. They also proposed that twinning is the decisive defect type for anomalous grain growth in BT because of the high growth rate obtained when the crystal exhibited certain lattice imperfections. Furthermore they pointed out that microregions having higher packing density than the matrix resulted in greater shrinkage and contained at least one twin. Kastner [3] supported the findings of Schemelz in that the mechanism of particle rearrangement during shrinking is able to form twins by mutual interactions of the neighbouring grains. The results of Detvel [4] contradict Schemelz's findings. He reported that twinning is not

the basic requirement for discontinuous grain growth. Eible et al [5] support the observations of Detvel that the existence of twins alone is not sufficient to trigger the anomalous grain growth. In his paper he also reported that twins were formed frequently during the calcinations process of BaCO₃-TiO₂ powder mixtures used in the production of BaTiO₃. Whereas, Krasevec [6] proposed that excess TiO₂ in the composition is an essential characteristic of the (111) twin. Juggle [7] also pointed out that in Ti excess BT, the twins appear during grain growth and the number of twins is proportional to the concentration of Ti³⁺ ions. However Lee and Kang [8] reported that the formation of (111) twins occurred only in the excess TiO₂ compositions in the presence of the Ba₆Ti₁₇O₄₀ phase in an oxidizing sintering atmosphere, which acted as nucleation sites for the (111) twins. They also observed that the (111) twin formation was affected by the particle size of the BaTiO₃ and the added excess TiO₂ powder. Furthermore they pointed out that the formation of (111) twins was reduced when the initial particle size of the BaTiO₃ increased and the particle size of the excess TiO₂ decreased.

In view of these reports on the formation of twins in BT, a Ti-excess and Sb₂O₃ donor-doped BT compositions were prepared in order to elucidate the effect of Sb₂O₃ donor-doping on the abnormal grain growth and on the twin formation in BT below the eutectic temperature. Also 0.5, 1.0 and 2.0 mol% of B₂O₃ were added to the composition in order to study the microstructure changes. Furthermore the 0.2 mol% excess part of the TiO₂ in the 0.5 mol% B₂O₃ - Sb₂O₃ containing composition was replaced with TiCl₃ in order to deduce the effect of chemical homogeneities on the twin formation.

EXPERIMENTAL

Commercial $BaCO_3$ (BDH-272885Y), TiO_2 (Fisher-780915), Sb_2O_3 (Merck-7836) and $TiCl_3$ (Merck-808307) were used in this study. $BaCO_3$ and TiO_2 contained major impurities Fe, Pb, K and Na, in totals of 760, 160 ppm respectively. The BT powders were prepared by conventional ceramic processing techniques. The prepared compositions are given below:

Code: Compositions:

- (A) Ba/Ti = 0.980
- (B) Ba/Ti = 0.980 + 0.25 mol% Sb_2O_3
- (C) Ba/Ti = 0.980 + 0.25 mol% Sb_2O_3 + 0.5 mol% B_2O_3
- (D) Ba/Ti = 1.0 + 0.2 mol% TiO_2 as $TiCl_3$ + 0.25 mol% Sb_2O_3 + 0.5 mol% B_2O_3
- (E) Ba/Ti = 0.980 + 0.25 mol% Sb_2O_3 + 1.0 mol% B_2O_3
- (F) Ba/Ti = 0.980 + 0.25 mol% Sb_2O_3 + 2.0 mol% B_2O_3

The powders were weighed according to their compositions and mixed for 10 hours using ZrO_2 balls and deionized water as a grinding media in an ashless rubber-lined jar. The ground mixture was then dried at $110^\circ C$ and cakes were prepared in a steel die of 50 mm diameter at 15 MPa without using any binder. The cakes were calcined at $1000^\circ C$ for 2 hours employing a $200^\circ C/h$ heating rate and then crushed to < 0.5 mm and reground for 10 hours in the stated conditions. The median diameter of the ground powder was found to be $1.2 \mu m$. After drying the ground material, granulation was done using distilled water as a binder. The 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 and $1300^\circ C$ for 10 hours employing $300^\circ C/hr$ heating rate and then cooled naturally in the furnace. The microstructure observations were carried out by a scanning electron microscope (Jeol 840 A) using the optically polished samples and etched in a $50H_2O/45HNO_3/5HF$ (vol%) solution for 15 to 30 seconds. The phases were identified by X-ray diffraction (XRD-6000 Shimadzu-Japan) using CuK radiation at 40 kV/30 mA.

RESULTS AND DISCUSSION

The un-doped Ti-excess code A, Sb_2O_3 doped Ti-excess code B and 0.5, 1.0, 2.0 mol% B_2O_3 doped Ti-excess Sb_2O_3 containing samples code C, E, F were sintered at $1250^\circ C$ for 10 hours. The XRD results of these samples are given in figure 1. The tetragonal and the cubic BT phases (PDF No: 050-626, PDF No: 31-0174) are marked on the diffraction patterns as T and C, respectively. The remaining peaks marked as X fit to the diffraction patterns of $Ba_2Ti_5O_{12}$ (PDF No: 17-0661) or $Ba_4Ti_{12}O_{27}$ (PDF No: 44-0013) phases which give similar diffraction peaks at Bragg angles close to each other and differing only in intensity. Since the investigated

composition is on the Ti-rich side on the BaO - TiO_2 phase diagram, this phase must be $Ba_2Ti_5O_{12}$. Diffraction patterns showed that the intensity of this phase decreased considerably in the Sb_2O_3 and B_2O_3 added samples. The XRD studies do not show any phases related to B_2O_3 which indicates either the loss of B_2O_3 by evaporation from the structure or to its presence as an amorphous phase. Rhim et al [9, 10] has also reported similar results in his work on the 0.5wt% B_2O_3 -added samples.

The microstructure of the samples sintered at $1250^\circ C$ for 10 hours is given in the micrographs shown in figure 2. The un-doped Ti-excess sample code A revealed polygonal grains $\sim 3-5 \mu m$ in size in a very fine-grained matrix (figure 2a). The twin lamellae were not observed in the microstructure as mentioned in the literature [1, 11]. This is probably due to the long sintering of the order of 100 hours employed in these studies. However, when sintering is carried out at $1300^\circ C$ for 10 hours the polygonal grains grew and the twins within become more pronounced (figure 2b). This shows that the twinning is markedly dependent on the sintering temperature and time which indicate a solid state reaction in their formation. The Sb_2O_3 added Ti-excess composition coded B revealed very long elongated plate-like grains contained twin lamellae within a porous matrix of fine grains as shown in figure 2c. The microstructure also contained some small dark-coloured rounded grains as a secondary phase. A careful EDX analysis carried out revealed them as a Ti-rich phase. Hence, Sb_2O_3 donor doping at 0.25 mol% level is very effective in the formation of twin lamellae. Although

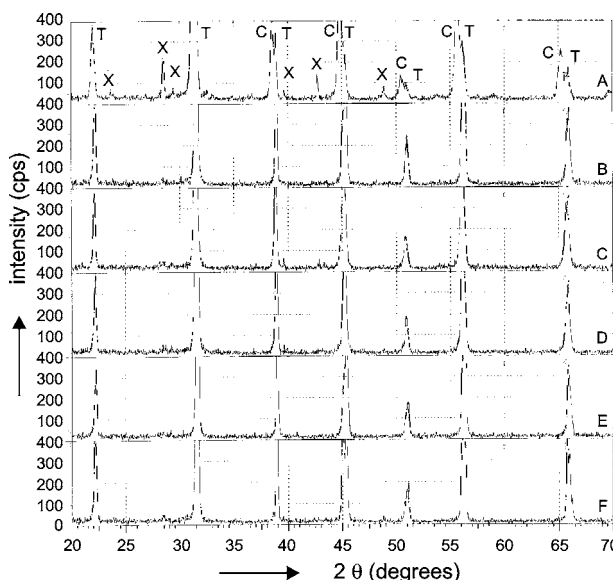
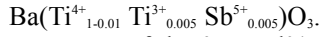


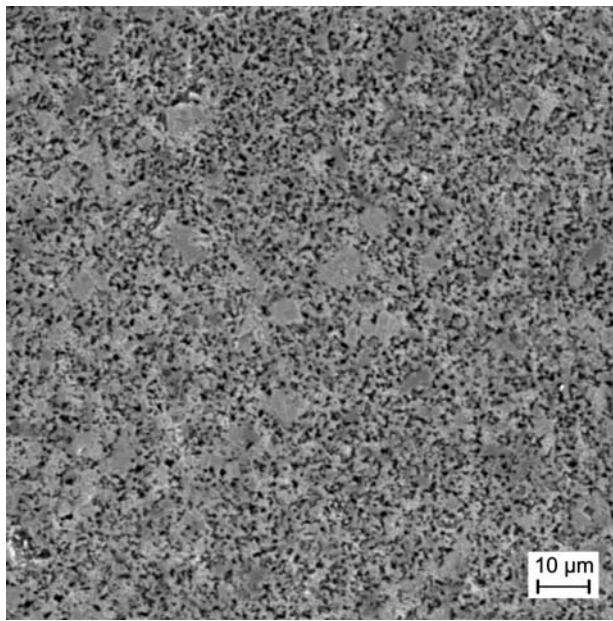
Figure 1. XRD patterns of $BaTiO_3$ sintered at $1250^\circ C/10$ hours (A) Ti-excess (Code A), (B) Ti-excess + Sb_2O_3 (Code B), (C) Ti-excess + Sb_2O_3 + 0.5 mol% B_2O_3 (Code C), (D) Code C prepared with $TiCl_3$ (Code D), (E) Ti-excess + Sb_2O_3 + 1.0 mol% B_2O_3 (Code E), (F) Ti-excess + Sb_2O_3 + 2.0 mol% B_2O_3 (Code F).

Lee and Kang [8] pointed that the presence of the $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ phase is essential for the twin formation, this phase was not detected in our XRD patterns (figure 1). Therefore, twin formation in the composition coded B can only be attributed to the solid state reaction by the diffusion of Sb^{5+} ions to Ti lattice sites giving rise to Ti^{3+} ions due to the charge compensation mechanism which can be represented by the formula of

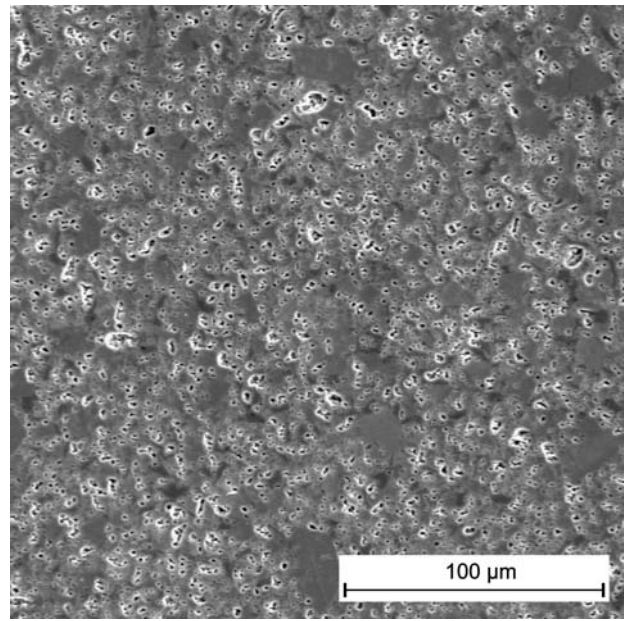


The microstructure of the 0.5 mol% B_2O_3 added to Sb_2O_3 doped Ti-excess sample coded C shown in figure

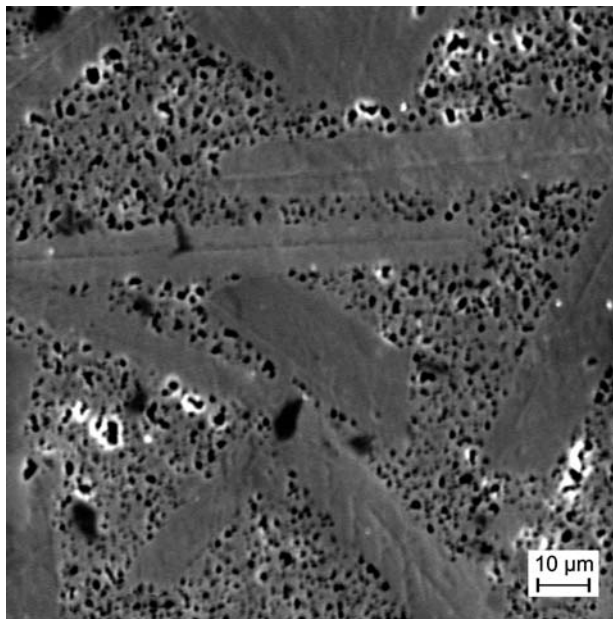
2d revealed a different structure than that of the Sb_2O_3 added Ti-excess sample. In this sample the microstructure showed polygonal grains containing the twin lamellae and Ti-rich rod-like grains dispersed in a fine-grained matrix. The possible source for this rod-like Ti-rich phase arises from the chemical inhomogeneities in processing the samples. In order to elucidate this the sample coded D was prepared by the same method but a 0.2 mol% excess TiO_2 was added in a liquid TiCl_3 form. The microstructure of this sample, given in figure 2e, showed that the thin bar-like grains in figure 2d



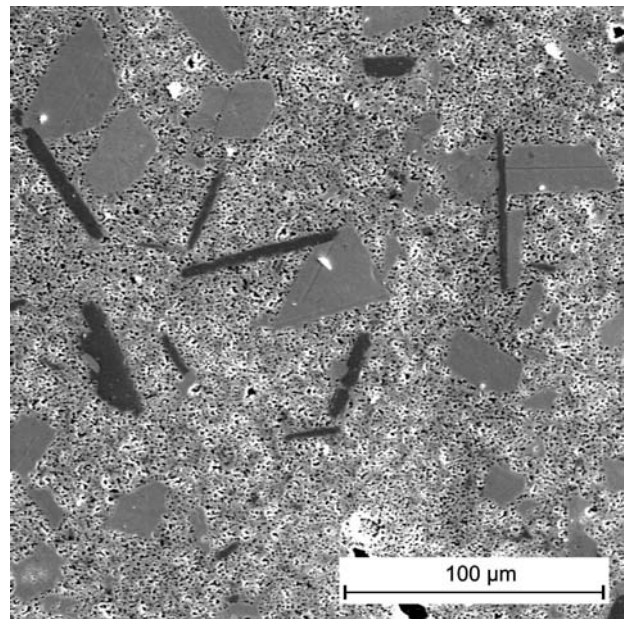
a)



b)



c)



d)

Figure 2. Microstructure of the BaTiO_3 sintered for 10 hours: a) Ti-excess (Code A), 1250°C; b) Ti-excess (Code A), 1300°C; c) Ti-excess + Sb_2O_3 (Code B), 1250°C; d) Ti-excess + Sb_2O_3 + 0.5 mol% B_2O_3 (Code C), 1250°C.

were replaced by very small size grains of Ti-rich phases. The size and the number of the twin containing polygonal grains also decreased when the excess Ti was added in a liquid $TiCl_3$ form. This shows that the microstructure is very susceptible to chemical inhomogeneities, which is also supported by Lee and Kang [8] findings. They pointed out that the number of the grains containing twins decrease with the decreasing size of the excess TiO_2 powder used in preparation of the sample. Furthermore, Schmelz and Mayer [2] also

reported that microregions contain at least one twin, where the shrinkage is more advanced. Therefore, the local variations in the rate of shrinkage caused by inhomogeneities is reduced with the addition of $TiCl_3$ in composition of coded C as shown in figure 2c.

The increment of the B_2O_3 addition to 1 mol% the sample coded E again caused a drastic effect in the microstructure when compared with the 0.5 mol% B_2O_3 added sample (figure 2d and f) In this case, the polygonal grains containing twin lamellae grew to the order of

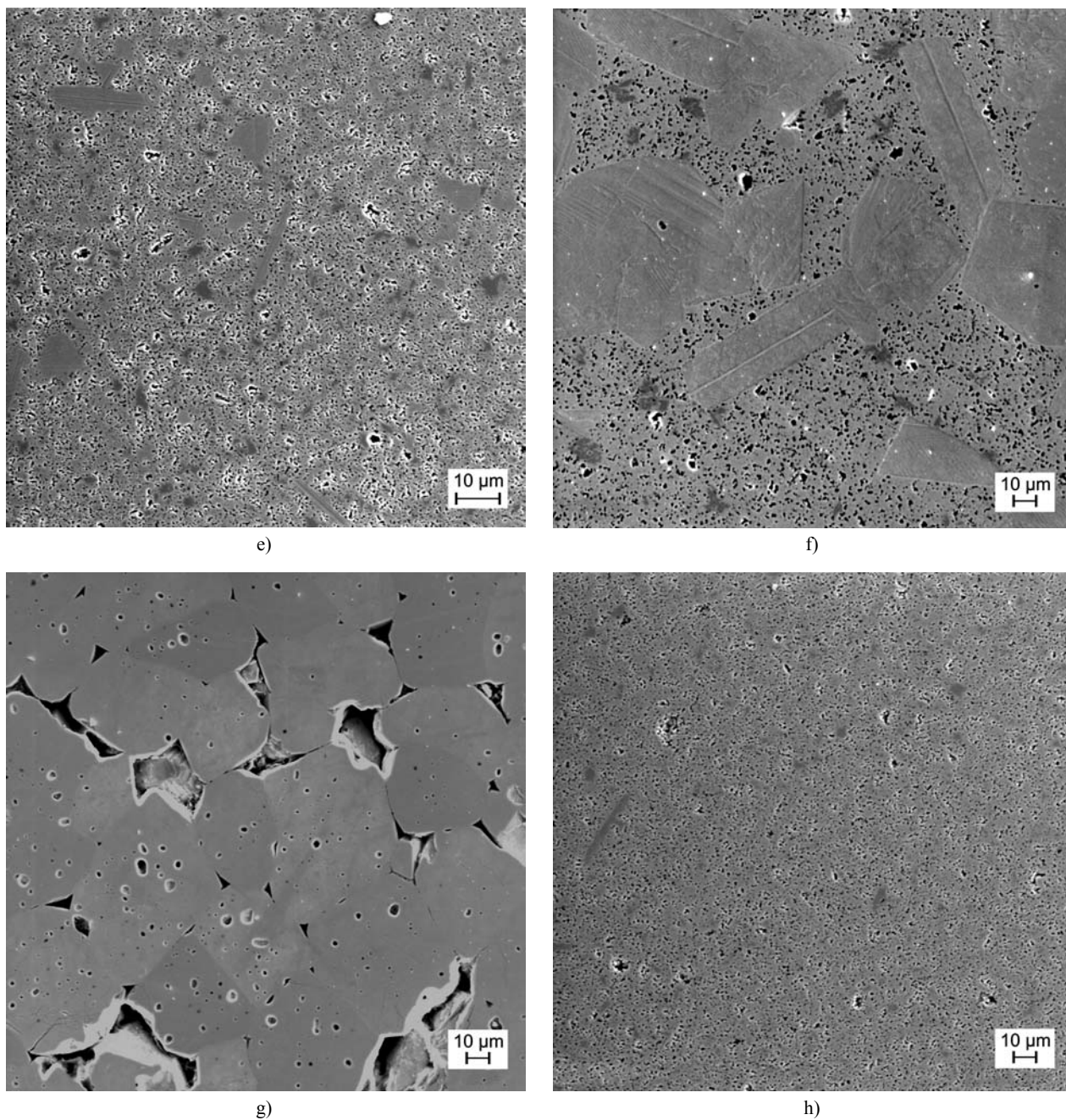


Figure 2. Microstructure of the $BaTiO_3$ sintered for 10 hours: e) Code C prepared with $TiCl_3$ (Code D), 1250°C; f) Ti-excess + Sb_2O_3 + 1.0 mol% B_2O_3 (Code E), 1250°C; g) Ti-excess + Sb_2O_3 + 2.0 mol% B_2O_3 (Code F), 1250°C; h) Ti-excess + Sb_2O_3 + 2.0 mol% B_2O_3 (Code F), 1225°C.

100 μm in size due to the liquid phase sintering. The increased liquid phase level by the 2 mol% B_2O_3 addition coded F resulted in a sudden uniform grain growth with pores trapped among the grains when sintered at 1250°C for 10 hours (figure 2g). The pronounced effect of the B_2O_3 addition on the microstructure was revealed when the sintering temperature was reduced to 1225°C for 10 hours. The decreasing of the sintering temperature by 25°C showed only a very fine-grained porous structure (figure 2h). Therefore the microstructure is very sensitive to the B_2O_3 addition level and the sintering temperature. The result indicates that the 2 mol% B_2O_3 doping suppressed the twin formation similar to that with the Na_2O doping in Lin et al studies[11].

CONCLUSIONS

The effect of 0.5, 1.0, 2.0 mol% B_2O_3 and the TiCl_3 addition on the microstructure and twin formation in Sb_2O_3 donor-doped Ti-excess BaTiO_3 compositions were investigated. Platelet type $\text{Ba}_2\text{Ti}_5\text{O}_{12}$ was detected as a secondary phase in the Ti excess undoped composition sintered at 1250°C for 10 hours. This phase decreased considerably in the Sb_2O_3 and B_2O_3 added samples. The XRD studies do not show any phases related to B_2O_3 which indicates either the loss of B_2O_3 by evaporation from the structure or to its presence as an amorphous phase. The undoped Ti-excess sample sintered at 1250°C for 10 hours revealed no twinning. However, the sample sintered at 1300°C for 10 hours revealed twins in the polygonal grains. The Sb_2O_3 -added Ti-excess composition revealed very long elongated plate-like grains containing twin lamellae within a porous matrix of fine grains. The Sb_2O_3 donor doping at the 0.25 mol% level was very effective for promoting the twin formation due to the increased concentration of the Ti^{3+} ion. The 0.5 mol% B_2O_3 addition to the Sb_2O_3 donor-doped Ti excess composition modified grain morphology from very long elongated platelike to a polygonal type grains containing twin lamellae and Ti-rich rod-like grains. At the 1 mol% B_2O_3 addition level the polygonal grains and twin lamellae grew in the order of 100 μm in size in the fine-grained matrix. At the 2 mol% B_2O_3 addition level sudden grain growth occurred with the loss of twin lamellae from the structure. However, this sample revealed an homogeneous fine-grained microstructure when sintered at 1225°C for 1 hour. This result indicated that the 2 mol% B_2O_3 doping suppressed the twin formation.

The addition of 0.2 mol % excess TiO_2 in a liquid TiCl_3 form to the 0.5 mol% B_2O_3 containing Sb_2O_3 donor-doped BT sample reduced the size and the number of polygonal grains which contained twins. The addition of excess TiO_2 in a liquid TiCl_3 form had a marked effect on the twin formation due to the homogeneous distribution of the excess Ti ions. This shows that the microstructure is very susceptible to chemical inhomogeneities.

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VLIV PŘÍDAVKU B_2O_3 A TiCl_3 NA DVOJČATĚNÍ BaTiO_3 DOPOVANÉHO Sb_2O_3 A S PŘEBYTKEM Ti

HILKAT ERKALFA, BERAT YUKSEL*, T. OSMAN OZKAN*

TÜBITAK Marmara Research Center, MCTRE, Gebze, Kocaeli-Turkey

**Istanbul University, Engineering Faculty, Avcilar, Istanbul-Turkey*

Byl zkoumán vliv přídatku B_2O_3 a TiCl_3 na BaTiO_3 dopovaného Sb_2O_3 donorem a s přebytkem Ti. V nedopovaném preparátu s přebytkem Ti vznikl jako sekundární fáze při desetihodinovém zahřívání na 1250°C destičkovitý $\text{Ba}_2\text{Ti}_5\text{O}_{12}$. Tato fáze byla významně potlačena ve vzorcích dopovaných Sb_2O_3 a B_2O_3 . Dopování Sb_2O_3 donorem se ukázalo velmi účinné pro vznik dvojčat při rostoucí koncentraci iontů Ti^{3+} . Přídavek 0.5 mol% B_2O_3 vedlo ke vzniku mnohostěnných krystalů s destičkovitými dvojčaty a tyčinkovitých krystalů bohatých Ti. Při úrovni dopování 1 mol% B_2O_3 narostly mnohostěnné krystaly a destičkovitá dvojčata na rozměr řádově 100 μm v jemně krystalické mase. Přídavek 2 mol% B_2O_3 vyvolal vzrůst částic a vedl k vymizení destičkovitých dvojčat. 0.2 mol % přbytek TiO_2 , dodaný ve formě roztoku TiCl_3 ke vzorkům s 0.5 mol% B_2O_3 , vedl ke zmenšení velikosti částic a počtu mnohostěnných krystalů a měl značný vliv na dvojčatění díky rovnoměrnější distribuci přebytku Ti iontů ve směsi.