

EELS Analysis for Grain Boundaries in Ti-excess BaTiO₃

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Grain boundary structure in Ti-excess BaTiO₃ was examined by high-resolution transmission electron microscopy (HREM) and electron energy-loss spectroscopy (EELS). It was found that grain boundaries were faceted with {210} habits. HREM study has revealed that an extra ordered structure was formed along the habit. Oxygen K-edge ELNES (electron energy-loss near edge structure) clearly showed the difference in the chemical bonding state between at the faceted grain boundary and grain interior. Comparing with molecular orbital calculation, TiO₆ octahedral linkage changed from corner-sharing at grain interior to edge-sharing at faceted grain boundaries.

Key words : BaTiO₃, HREM, EELS, abnormal grain growth, molecular orbital method (DV-X α)

1. INTRODUCTION

BaTiO₃, a perovskite structure ABO₃, is often used for electroceramic materials. In order to obtain good electroceramic components, it is necessary to control microstructure of sinters and to fabricate uniform-grained sinters. In particular, the suppression of abnormal grain growth during sintering is important from the view point of practical use. It is well known that the grain growth behavior in BaTiO₃ is affected with type and amount of various dopants. Yamamoto et al. reported that the grain growth behavior in BaTiO₃ can be controlled by an extremely small amount of dopants [1]. In addition, the grain growth behavior is very sensitive to the substitute site of dopant, i.e., abnormal grain growth takes place in the compounds doped with B-site type dopant and normal grain growth with A-site type dopant.

Meanwhile, the microstructure in BaTiO₃ doped with B-site type dopant in as-sintered state exhibits bimodal grain structure consisting of abnormally coarse grains with a size of about 100 μ m scattered in fine-grained matrix of about 2 μ m. Detail investigation of the abnormal grain growth behavior in such compounds showed the distinct feature, namely, grained structure in the matrix is very stable even after annealed at about 0.8T_m (T_m is melting point of BaTiO₃, 1620°C) [2]. This fact suggests that the abnormal grain growth results from the strong suppression of normal grain growth. Our kinetic model also describes the mechanism of the abnormal grain growth in terms of grain growth suppression [3]. However, it is not clear what stops the normal grain growth even at high temperature.

In this study, grain boundary structure was examined with a special interest in the chemical bonding state by HREM and EELS analysis.

2. EXPERIMENTAL PROCEDURE

Commercial BaTiO₃ powder was used as raw material. Nominal grain size, purity and Ba/Ti ratio of the raw powder was 0.1 μ m, 99.98% and 1.000, respectively. Ti, Zr, Nb and Ba, Ca, Y were chosen for B-site and A-site type dopants in a perovskite structure

ABO₃. The amount of dopants was fixed to be 0.1mol%. They were added to the raw powder with dilute solutions including each cation. Details for sample preparation method is described in Ref. [1]. Hereafter, each compound will be noted as Ti-excess compound, Zr-excess compound, and so on. Microstructure was examined by an optical microscope for chemically or thermally etched sections or by a conventional transmission electron microscope (CTEM, HITACHI H-800) or a high-resolution (HRTEM, TOPCON EM-002B) operated at 200kV using ion-thinned foils. In order to obtain chemical bonding state, electron energy-loss spectroscopy (EELS) was carried out with EELS spectrometer (GATAN Model 666) attached to HRTEM with a field emission type gun (TOPCON EM-002BF).

3. RESULTS & DISCUSSION

Fig. 1 shows optical micrographs of (a) Ba-

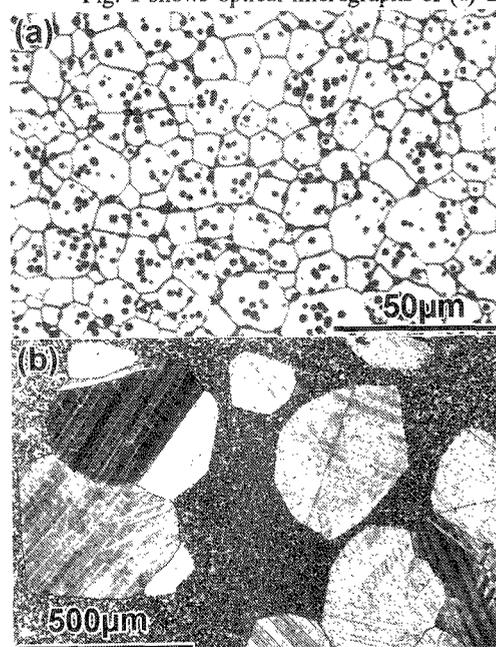


Fig. 1 Optical micrographs in (a) 0.03mol%Ba-excess, and (b) 0.03mol%Ti-excess BaTiO₃.

excess and (b) Ti-excess compounds in as-sintered state. Uniform-grained structure of about 10 μ m is obtained in Ba-excess compound. On the contrary, coarse grains of about 100 μ m are generated in fine-grained matrix of about 2 μ m in Ti-excess compound. The grain growth behavior in Ti-excess compound is typical one of abnormal grain growth. It is noted that this change in the microstructure between the two compounds is caused by a small difference in the Ba/Ti ratio of 0.06mol%. The microstructure as presented in Fig. 1 clearly indicates the sensitivity of the microstructure to a dopant effect.

Transmission electron microscopy study has revealed that grain boundaries in the B-site dopant excess compounds are faceted with {210} type habits [4]. Typical example is presented in Fig. 2. Fig. 2(a) is a micrograph in the vicinity of grain boundary in Ti-excess compound taken by a CTEM. The habits are indexed as (210) and (120) from the grain B, and (1342) and (121310) from the grain A from TEM-trace analysis. Other facet planes such as {310} are sometimes observed instead of {210} type, however, most of faceted boundaries investigated in this study are found

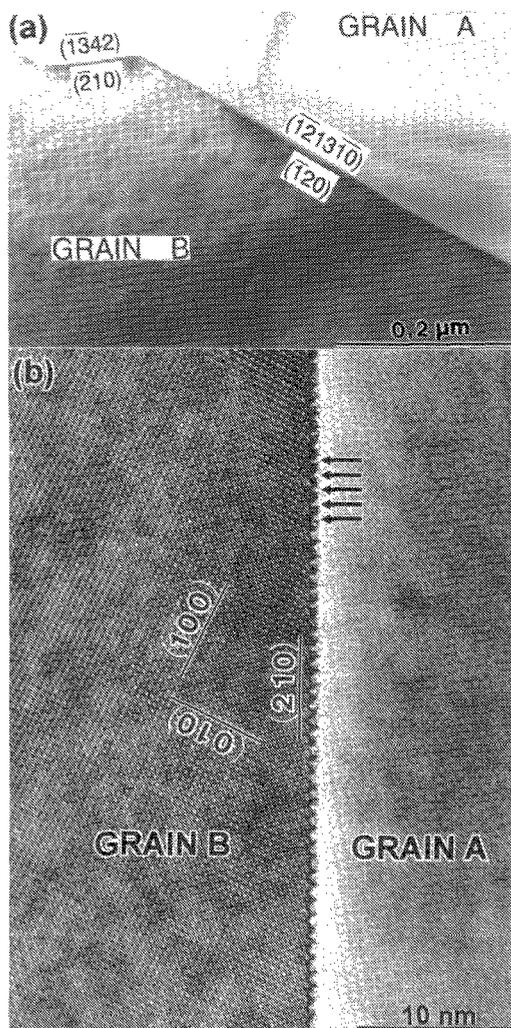


Fig. 2 Microstructure in the vicinity of the grain boundary in 0.1mol%Ti-excess BaTiO₃, (a) CTEM image, and (b) HRTEM image. Note that the grain boundary is faceted with {210} habit.

to have {210} type habits in one side of grain and high indexed planes from the other side. Fig. 2(b) shows a HRTEM image of a faceted grain boundary. In this image, the habit of (210) is set at edge-on and the grain B with a (210) facet is oriented to the [001] beam direction. The adjacent grain A is slightly inclined from the [110] direction. It is noted that the array of white dots appears periodically along the faceted grain boundary as indicated by the arrows. This fact suggests the existence of an extra ordered structure along the faceted grain boundary. The faceted grain boundary is a distinct feature observed in the B-site dopant excess compounds.

Fig. 3 shows EELS spectra obtained from grain boundaries in B-site type dopant excess compound (B-site excess compounds) (a) Ti, (b) Zr, and (c) Nb, and in A-site type dopant excess compounds (A-site excess compounds) (d) Ba, (e) Ca, and (f) Y, respectively. In the figure, oxygen K-edge ELNES (electron energy-loss near edge structure) is shown. It is noted that the shape of the spectra is clearly different between the B-site excess and the A-site excess compounds. In the case of ELNES in the A-site excess compounds, which exhibit normal grain growth, the spectra are clearly split as indicated by the arrows in the figure. On the contrary, the spectra in the B-site excess compounds, which exhibits abnormal grain growth, show plateau-like features. The difference in the ELNES must be caused

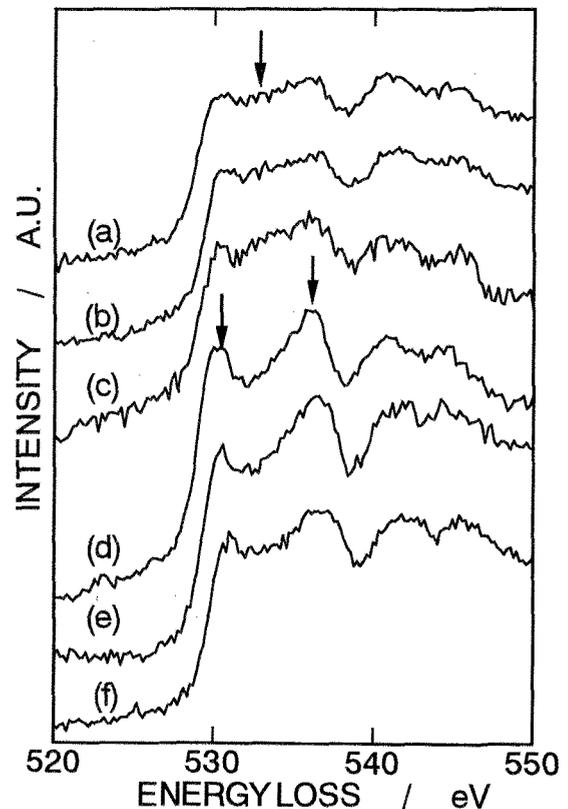


Fig. 3 Experimental oxygen K-edge ELNES in the B-excess compounds (a) Ti, (b) Zr, (c) Nb-doped, and the A-excess compounds (d) Ba, (e) Ca, and (f) Y-doped.

by the change in the chemical bonding state, i.e., the atomic structure of grain boundaries in the B-site excess compounds may be different from that in the A-site excess ones.

It has been demonstrated that a first principle molecular orbital calculation using DV-X α cluster method is useful for interpretation of experimental ELNES [5]. Fig. 4 shows clusters used for the DV-X α calculation in (a) $(\text{Ba}_8\text{TiO}_8)^{8+}$ for BaTiO_3 and (b) $(\text{TiO}_6)^{18-}$ for rutile type TiO_2 . The calculation of TiO_2 was carried out as a reference. Both structures have TiO_6 octahedrons in the structure but their linkage manner is different between the two structures. In a perovskite structure of BaTiO_3 , TiO_6 octahedrons are linked at corners of the octahedrons while at edges in rutile structure of TiO_2 . The each cluster as shown in Fig. 4 includes the difference in such linkage manner.

Fig. 5 is the theoretical oxygen K-edge ELNES calculated for (a) BaTiO_3 and (b) TiO_2 using clusters as shown in Fig. 4(a) and (b), respectively. The oxygen K-edge ELNES corresponds to the partial density of the states (PDOS) of O-2p. The main peaks in the theoretical ELNES are alphabetically indexed in Fig. 5. There are three peaks of A, B, and C in BaTiO_3 , and two peaks of D and E in TiO_2 in the energy-loss range from 534eV to 543eV. According to the analysis by Tanaka et al., the peaks of D and E are identified as t_{2g}

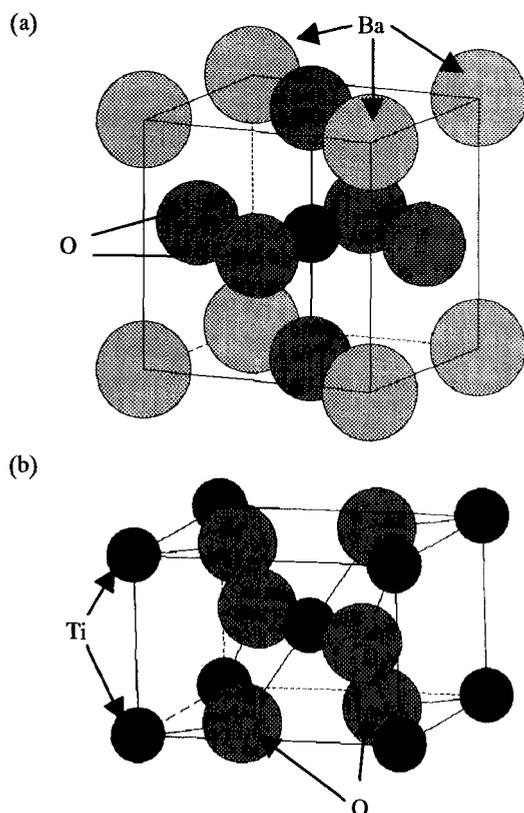


Fig. 4 Clusters used for the DV-X α calculation in (a) $(\text{Ba}_8\text{TiO}_8)^{8+}$ for BaTiO_3 and (b) $(\text{TiO}_6)^{18-}$ for rutile type TiO_2 . As for $(\text{TiO}_6)^{18-}$ cluster, Ti ions at the vertex position of a rutile unit cell are also indicated. and e_g bands in rutile structure which results from O-2p

orbital antibonding with Ti-3d orbital. In addition, the peaks D and E are explained to be closely related to the linkage manner of TiO_6 octahedrons. Tanaka et al. insisted that the height ratio of peaks A and B or D and E strongly depend on the bonding angle of Ti-O-Ti in each structure [6]. The bonding angle is different between a perovskite and a rutile structures because the perovskite structure has corner-shared TiO_6 octahedrons while rutile has edge-shared TiO_6 ones. As a result, a shoulder emerges at the peak B in BaTiO_3 so that the intensity of the peak A is higher than that of the peak B in the perovskite structure (Fig. 5(a)) while the peak D is lower than the peak E in the rutile structure (Fig. 5(b)).

The experimental ELNES from the faceted grain boundary shows the plateau-like feature. This fact suggests that the intensity of the peak as indicated by the arrow in Fig. 4(a-c) increases. This can be interpreted in terms of the overlapping of the two ELNES of BaTiO_3 (Fig. 5(a)) and TiO_2 (Fig. 5(b)). Namely, the TiO_6 octahedral linkage changes from corner-sharing in the grain interior to edge-sharing at the grain boundary in the B-site excess compounds.

The abnormal grain growth in Ti-excess BaTiO_3 is often discussed in terms of the eutectic liquid formed between BaTiO_3 and $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ at 1332°C [7]. In contrast, there are several reports that abnormal grain growth takes place even in solid state [8-9]. One of the present authors showed that the initial grain growth is strongly suppressed in Ti-excess compounds below the eutectic temperature and the suppression may result in abnormal grain growth [1-2]. As mentioned above, the

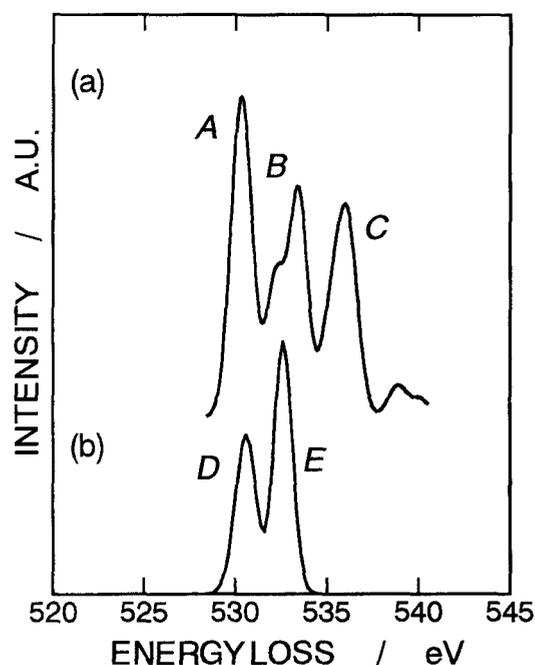


Fig. 5 Theoretical ELNES calculated from DV-X α cluster method for (a) BaTiO_3 and (b) TiO_2 .

distinct feature in the abnormal grain growth in the B-site excess compounds is the strong suppression of normal grain growth. The suppression mechanism can be concluded to be the formation of extra Ti-O₂ bonding at the grain boundaries in the B-site excess compounds.

4. CONCLUSION

The grain boundary structure of BaTiO₃ doped with a small amount of dopants was examined by high-resolution transmission electron microscopy and electron energy-loss spectroscopy, and the following conclusion could be obtained.

1. Grain boundaries in the B-site excess compounds are faceted with {210} habits. An ordered structure exists along the habits from HRTEM observation.
2. EELS analysis clearly showed the difference in the chemical bonding state between grain interiors and faceted grain boundaries in the B-site excess compounds.
3. Comparing with the theoretical ELNES obtained from molecular orbital method, an ordered structure along the faceted grain boundaries results from the change in the TiO₆ octahedral linkage, i.e., from corner-sharing in grain interiors to edge-sharing in grain boundaries.
4. The suppression of the normal grain growth observed in the B-site excess compounds is due to the formation of the extra ordered structure along the grain boundaries.

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