Analysis of Crystallographic Orientation on Textured Ca-doped $(\text{ZnO})_m\text{In}_2\text{O}_3$ Ceramics by Electron Back Scattering Diffraction Pattern

Hisashi KAGA,* Toshihiko TANI, Hiroaki KADOURA, Juntaro SEKI and Ryoji ASAHII

Toyota Central Research and Development Laboratories Inc., 41-1, Yokomichi, Nagakute, Aichi 480-1192, Japan

*Present address: National Institute of Advanced Industrial Science and Technology (AIST),
2266-98, Anagahora, Shimo-shidami, Moriyama-ku, Nagoya-shi 463-8560, Japan

Crystallographic orientation and phase identification on textured Ca-doped $(\text{ZnO})_m\text{In}_2\text{O}_3$ ($m=3$ and 4, denoted as Z_mIO) ceramics were investigated for better understanding and further improvement of the high-efficiency n -type thermoelectric oxide materials. Textured ceramics were prepared by the reactive-templated grain growth (RTGG) method, in which plate-like reactive seeds were exploited. A combination of electron backscatter diffraction pattern (EBSP) and energy dispersive X-ray spectrometry (EDS) techniques was utilized for analyzing the textured specimen parallel and perpendicular to the original sheet plane in detail. We revealed that in the specimen plate-like grains were aligned parallel to the sheet plane with the thickness direction parallel to the c -axis of each grain. Parallel aligned trigonal Z_3IO domains with a 60° misorientation angle were observed in a single grain. Coexisting trigonal Z_3IO and hexagonal Z_4IO phases were also observed in a single grain. These axis-sharing crystallites must be formed by the in situ topotactic conversion from a common hexagonal template crystal.

[Received July 18, 2006; Accepted September 21, 2006]

Key-words: Textured ceramic, $(\text{ZnO})_m\text{In}_2\text{O}_3$, Reactive-templated grain growth, Electron back scattering diffraction pattern, Thermoelectric

1. Introduction

Thermoelectric power generation (TEG) has been paid much attention today because the TEG converts thermal energy into electric energy directly without using moving parts or producing CO_2 gas. Recovery of waste heat resources emitted by factories and automobiles is urgently needed from the viewpoint of the global environmental concerns. In particular, thermoelectric (TE) oxide materials have been investigated since they are composed of nontoxic elements and chemically stable in the high-temperature air atmosphere.^{1)–4)} The layer-structured CoO_2 -based oxides such as Na_xCoO_2 and $[\text{Ca}_2\text{CoO}_3]_{0.62}[\text{CoO}_2]$ (denoted as CCO), and a series of homologous compound $(\text{ZnO})_m\text{In}_2\text{O}_3$ (denoted as Z_mIO where m is an integer ≥ 3) have been extensively studied as candidates of a p -type and n -type TE oxide materials, respectively.^{2)–10)} These layer-structured TE oxides show higher electrical conductivities along the layers than in the other directions, which in turn, the thermoelectric properties of these materials have a strong anisotropy. Thus, highly textured bulk ceramics of these materials with the layers aligned parallel can exhibit higher TE properties than randomly oriented ceramics with the same composition if the temperature gradient is provided along the layer. In addition, the characteristics of the grain boundaries have a large influence on the TE properties of the polycrystalline materials. Therefore, it is essential to have a characterization technique that can readily provide information such as grain size, crystallographic phase and orientation.

The Lotgering's factor, a calculated value from X-ray diffraction (XRD) intensities in a given 2θ range, is usually used for evaluating the degree of orientation.¹¹⁾ However, it has been reported that the electrical conductivities of textured CCO ceramics were greatly varied depending on the microstructures for the specimens having similar Lotgering's degree of orientation.⁶⁾

A pole figure is a stereographic projection, with a specified orientation relative to the specimen that shows the variation of pole density with pole orientation for a selected set of crystal planes.¹²⁾ This method represents the statistical average distribution

of poles of a specific crystalline plane in polycrystalline materials. However, the pole figure cannot be used to evaluate local crystal orientations and misorientation angles between grains. It is well known that a polycrystalline oxide shows much smaller electrical conductivity than that of a single crystals because electrical conductivity is greatly influenced by the misorientation angles between the nearest neighboring grains.^{13),14)}

We used electron backscatter diffraction pattern (EBSP) with field emission scanning electron microscopy (FE-SEM) to collect the information on local grains. The EBSP technique involves an electron back scattering diffraction within a bulk specimen in an FE-SEM and it utilizes Kikuchi lines and bands for determining the crystallographic orientations.^{15),16)} This technique makes it possible to determine the phase, grain size, and individual crystal orientation. However, the study using EBSP has not been extended yet into the area of the TE oxide materials.

In this paper, we report the detailed results of microstructural characterization on highly textured Ca-doped Z_mIO ceramics fabricated by the reactive-templated grain growth (RTGG) method,¹⁷⁾ as compared with a randomly oriented specimen fabricated by the conventional solid-state reaction.

2. Experimental procedure

2.1 Preparation of specimens

Highly textured Ca-doped Z_mIO ceramics were fabricated by the RTGG method and the detailed procedure is available elsewhere.¹⁰⁾ Plate-like $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2$ particles (Hakusui Tech Co., Osaka, Japan) were used as reactive templates and mixed with In_2O_3 and CaCO_3 powders (Kojundo Chemical, Saitama, Japan) as complementary reactants for a composition of $(\text{ZnO})_3(\text{In}_{0.975}\text{Ca}_{0.025})_2\text{O}_3$. After a series of processing such as tape-casting, stacking, pressing, dewaxing, and cold isostatic pressing, the specimen was heat-treated for synthesis at 1150°C for 12 h and then sintered at 1300°C for 24 h. The sintered specimen showed mixed phases of Z_3IO (trigonal system) and Z_4IO (hexagonal system) with $\text{Z}_3\text{IO} > \text{Z}_4\text{IO}$ determined by a powder X-ray diffraction (XRD, RINT-TTR,

Fig. 1. Results of EBSD analysis for the (//) face of RTGG-processed $Z_m\text{IO}$ ceramic. (A) Phase identification map of $Z_3\text{IO}$ (red) and $Z_4\text{IO}$ (green). (B) Image quality map. (C) Inverse pole figure (crystal orientation) maps for ND, TD, and RD with color keys. Note that the inside of the square black in (A) was investigated by EDS.

Rigaku, Tokyo, Japan) analysis. The sintered specimen was confirmed to have a preferred $\{001\}$ orientation for both $Z_3\text{IO}$ and $Z_4\text{IO}$ parallel to the original sheet surface by a pole figure measurement.¹⁰⁾ A reference specimen with a random grain orientation whose composition is $(\text{ZnO})_{3.5}(\text{In}_{0.975}\text{Ca}_{0.025})_2\text{O}_3$ was also fabricated by a conventional solid-state reaction method for comparison.

2.2 EBSD analysis

Prior to the EBSD study, the sintered specimen was polished on the surfaces parallel (//) and perpendicular ($\perp$) to the original sheet surface with 15–1 μm diamond pastes and then finished with 0.05 μm alumina paste. The prepared specimen was mounted onto a holder and was inclined at an angle of 70° to the horizontal in the FE-SEM (JSM-7000F, JEOL, Tokyo, Japan). The FE-SEM with the orientation imaging microscopy (OIM) system (TexSEM Laboratories Inc., Draper, UT, USA) was used for the measurement. The EBSD analysis was made at a scan step of 0.4 μm over an area of 200 $\mu\text{m} \times 80 \mu\text{m}$. The lattice parameters ($a=0.336 \text{ nm}$ and $c=4.265 \text{ nm}$) of $Z_3\text{IO}$ used for this analysis were obtained from powder XRD analysis, while the lattice parameters ($a=0.334 \text{ nm}$ and $c=3.352 \text{ nm}$) of $Z_4\text{IO}$ were obtained from the JCPDS card data due to difficulty in the peak separation and identification from $Z_3\text{IO}$.¹⁸⁾ An energy dispersive X-ray spectroscopy (EDS) was also utilized for elemental analyses to support the results of EBSD with respect to the phase identification.

3. Results and discussions

3.1 Results of EBSD analysis for the (//) face

Figure 1(A) shows the phase identification map for $Z_3\text{IO}$ (red) and $Z_4\text{IO}$ (green) examined by EBSD for the textured specimen on a section parallel to the original sheet plane. The area ratio of $Z_3\text{IO}$, $Z_4\text{IO}$, and unidentified region (black) is 70 : 29 : 1. This result corresponds to the XRD analysis of the textured specimen where $Z_3\text{IO}$ is a main phase. However, it was very difficult to correctly distinguish between the trigonal $Z_3\text{IO}$ and hexagonal $Z_4\text{IO}$ phases since the EBSD technique is not sensitive to the lattice parameter but sensitive to the sym-

metry of a crystal structure. It should be noted that there are many parallel aligned grain boundaries within the $Z_3\text{IO}$ grain as well as between the $Z_3\text{IO}$ and $Z_4\text{IO}$ phases in Fig. 1(A).

Figure 1(B) shows an image quality (IQ) map. The EBSD data was numerically calculated at each point and plotted as a lighter colored point on the IQ map for a higher quality in determining the phase and orientation. In other words, grain boundaries, pores and amorphous phase are identified as in a lower quality; therefore they are expressed as in a darker color in the IQ map. The darker lines in Fig. 1(B) are thus considered as either grain or domain boundaries.

Figure 1(C) shows inverse pole figures (crystal orientation maps) in three directions (normal (ND), transverse (TD), and rolling (RD)) with color keys. Note that ND corresponds to the perpendicular to the original sheet plane. The crystal orientation map in ND shows that the $\{001\}$ planes of both $Z_3\text{IO}$ and $Z_4\text{IO}$ phases are preferentially aligned perpendicular to ND.

Figure 2 shows the $\{001\}$ pole figures of $Z_3\text{IO}$ and $Z_4\text{IO}$ obtained from the specimen parallel to the sheet plane. Large peak numbers at the center (ND) and radial symmetry for the contours in the pole figures indicate that the c -axes of the $Z_3\text{IO}$ and $Z_4\text{IO}$ phases are preferentially aligned along the ND and randomly oriented within the ab -plane. No difference was observed in the distribution of crystal orientation between the $Z_3\text{IO}$ and $Z_4\text{IO}$ phases because both phases were originated on the same plate-like $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2$ template material.

3.2 Results of EDS analysis for the (//) face

Figure 3 shows the results of EDS analysis for a selected area of the (//) face (square black in Fig. 1(A)). The Zn-poor and In-rich region corresponds to the $Z_3\text{IO}$ phase, while the Zn-rich and In-poor region corresponds to the $Z_4\text{IO}$ phase. The Zn-poor and Zn-rich regions found by EDS correspond to $Z_3\text{IO}$ and $Z_4\text{IO}$ phases identified by the EBSD, respectively. A part of the In-rich region was, however, determined as $Z_4\text{IO}$, which is accounted for by the misidentification of EBSD analysis. In particular, the $Z_3\text{IO}$ and $Z_4\text{IO}$ phases coexisted as a stripe pattern within a single grain (circles inset in Fig. 3) were confirmed as a single phase $Z_3\text{IO}$ by EDS. However, a stripe-

like color contrast was clearly observed in the Z_3IO grain by the SEM image. Similar characteristics were also found in some other grains. Hence, these grains are considered to have parallel domain boundaries such as twin boundaries or stacking faults originated from the layered structure of the Z_mIO .

3.3 Results of misorientation angle

Misorientation angles between nearest neighboring Z_3IO grains were analyzed for the surface parallel to the sheet plane.

Fig. 2. Results of the $\{001\}$ pole figures for Z_3IO and Z_4IO obtained from the $\langle 111 \rangle$ face of RTGG-processed Z_mIO ceramic.

The distribution of the misorientation angles is shown as a histogram in Fig. 4(A), where a sharp peak is found around 60° . Fig. 4(B) shows misorientation angle boundaries between 58° and 62° as red lines on the IQ map. Several parallel aligned boundaries with the misorientation angles near 60° are clearly observed in relatively round-shaped grains.

Figure 5 shows the phase identification image in Fig. 3, with the 60° misorientation angle boundaries colored in blue. These 60° misorientation angle boundaries in Z_3IO grains will correspond to the color contrast lines in the SEM image. On the other hand, these 60° misorientation angle boundaries in Z_3IO were partially misidentified as Z_4IO grains by EBSD. This is because the diffraction patterns of two neighboring grains of trigonal Z_3IO with a misorientation angle of 60° was duplicated and judged as the diffraction pattern of a hexagonal Z_4IO grain. There are several grains which are coexisting of Z_3IO and Z_4IO as shown in Fig. 5, and the grain bound-

Fig. 4. (A) Distribution of misorientation angles at the boundaries of Z_3IO crystallites for the $\langle 111 \rangle$ face of RTGG-processed Z_mIO ceramic. (B) 60° misorientation angle boundaries as red lines on the IQ map.

Fig. 3. Results of EDS analysis for the selected region in Fig. 1(A). The elements of Zn, In, O, and Ca correspond to green, yellow, red, and blue, respectively. The Z_3IO and Z_4IO phases correspond to red and green, respectively, in the phase identification map.

Fig. 5. Identification map of $Z_3\text{IO}$ (red) and $Z_4\text{IO}$ (green) phases by EBSD for the selected region of the (//) face of RTGG-processed $Z_m\text{IO}$ ceramic. 60° misorientation angle boundaries in the $Z_3\text{IO}$ are plotted as blue lines with the representative unit cell images of the crystallites at the side of the boundaries ($Z_3\text{IO}$: (a), (b), (c), and (e), $Z_4\text{IO}$: (d) and (f)).

daries between them are linearly aligned parallel to the 60° misorientation angle boundaries of $Z_3\text{IO}$ within the same grain.

The representative unit cell images are also shown as (a) to (f) in Fig. 5 for the phases at the sides of the examined unique boundaries. It is revealed that $Z_3\text{IO}$ phases at both sides of a 60° misorientation angle boundary have a common c -axis orientation as shown in Fig. 5(a) and (b). Furthermore, it is noted that the c -axis is perpendicular to the boundaries. Hence, 60° misorientation angle boundaries in a $Z_3\text{IO}$ grain are parallel to the ab -plane (basal plane) and perpendicular to the c -axis so that the $Z_3\text{IO}$ domains at both sides of the boundary are rotated by 60° around the c -axis. The observation of coexisting $Z_3\text{IO}$ and $Z_4\text{IO}$ phases within a grain has revealed that the trigonal $Z_3\text{IO}$ phase and the hexagonal $Z_4\text{IO}$ phase had a common c -axis orientation as clearly shown in (c) and (d), or (e) and (f) in Fig. 5. Moreover, the c -axis is perpendicular to the transgranular phase boundaries as in the case of the 60° misorientation angle boundaries in a $Z_3\text{IO}$ grain. These phase boundaries between $Z_3\text{IO}$ and $Z_4\text{IO}$ are also parallel to the ab -plane (basal plane).

Figure 6 shows schematic drawings for the formation mechanisms of a 60° misorientation angle boundary in a $Z_3\text{IO}$ grain and coexisting $Z_3\text{IO}$ and $Z_4\text{IO}$ phases in a single grain. The 60° misorientation angle boundary in a $Z_3\text{IO}$ grain is formed as follows. Wurtzite-type structured ZnO with the hexagonal system was formed by the thermal decomposition of a $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2$ reactive template.⁸⁾ Homologous compounds, $Z_m\text{IO}$, with large m values were then formed by the diffusion of In into ZnO.¹⁹⁾ These $Z_m\text{IO}$ crystallites act as oriented seeds for the *in situ* topotactic formation of $Z_3\text{IO}$ through the additional diffusion of In. The oriented $Z_3\text{IO}$ domains with 60° misorientation around the c -axis were concurrently generated due to the topotactic formation of trigonal nuclei at different sites on a hexagonal $Z_m\text{IO}$ or ZnO seed crystallites to form 60° misorientation angle boundaries schematically shown as a blue line in Fig. 6 below left. The coexistence of $Z_3\text{IO}$ and $Z_4\text{IO}$ phases sharing a common c -axis within a single grain was similarly originated from a common template shown in Fig. 6 below right. The topotactic conversion from ZnO into homologous compounds, $Z_m\text{IO}$, was ex-

Fig. 6. Schematic drawings for the formation mechanisms of a 60° misorientation angle boundaries in $Z_3\text{IO}$ grains and coexisting $Z_3\text{IO}$ and $Z_4\text{IO}$ phases in a single grain. The blue line shows a part of the 60° misorientation grain boundary in a $Z_3\text{IO}$ grain.

mined at an atomic level by high-resolution transmission electron microscopy (HRTEM) by Seo, et al.¹⁹⁾ They reported that the diffusion of In into ZnO and the formation of $Z_m\text{IO}$ occurred along the ab -plane.¹⁹⁾ Therefore, the transgranular phase boundaries between $Z_3\text{IO}$ and $Z_4\text{IO}$ parallel to the ab -plane are considered to be formed by the observed diffusion of In along the basal plane.

3.4 Results of EBSD analysis for the ($\perp$) face

Figure 7 shows the results of the EBSD analysis for the textured specimen on a section perpendicular to the original sheet plane. It is clearly observed in the TD figure that the c -axes of both $Z_3\text{IO}$ and $Z_4\text{IO}$ phases are preferentially aligned perpendicular to the surface of the specimen, which corresponds to the results for the (//) face. Two kinds of grains are observed in the ($\perp$) face. One is elongated along parallel to the tape-casting plane and the other is round. The former type of grains shows higher degrees of preferred orientation, i.e., darker red color in the TD figure, while the latter type of grains are with lower degrees of orientation. The elongated $Z_m\text{IO}$ grains are considered to be originated from large-sized plate-like templates which are easily aligned parallel to the sheet plane during tape casting. On the other hand, the equiaxed $Z_m\text{IO}$ grains were formed on templates with low aspect ratio or In_2O_3 particles. The parallel aligned domain boundaries within a grain are also observed frequently. According to the results of phase

Fig. 7. Results of the EBSD analysis for the ($\perp$) face of RTGG-processed $Z_m\text{IO}$ ceramic. (A) Phase identification map of $Z_3\text{IO}$ (red) and $Z_4\text{IO}$ (green). (B) Image quality map. (C) Inverse pole figure (crystal orientation) maps for ND, TD, and RD with color keys. Note that the inside of the square black in (A) was investigated by the EDS.

Fig. 8. Results of EDS analysis for the selected region in the Fig. 7(A). The elements of Zn, In, O, and Ca correspond to green, yellow, red, and blue, respectively. The $Z_3\text{IO}$ and $Z_4\text{IO}$ phases correspond to the red and green, respectively, in the phase identification map.

identification for the ($\perp$) face shown in Fig. 7(A), the area ratio of $Z_3\text{IO}$ (red), $Z_4\text{IO}$ (green), and unidentified region (black) is 32 : 66 : 2, which does not correspond to the results for the ($\parallel$) face. This discrepancy is attributable to the difficulty to distinguish between the trigonal (3-fold axis) and hexagonal (6-fold axis) systems by poor information on symmetry around c -axis for the ($\perp$) face.

3.5 Results of EDS analysis for the ($\perp$) face

Figure 8 shows the results of EDS analysis for the selected region of the ($\perp$) face (square black in Fig. 7(A)). Similarly to the results for the ($\parallel$) face, a part of the Zn-poor region, $Z_3\text{IO}$, was misidentified as $Z_4\text{IO}$. Parallel aligned $Z_3\text{IO}$ and $Z_4\text{IO}$ phases coexisting in a single grain were also observed in equiaxed grains as shown in the circles inset in Fig. 8. The representative unit cell images in (a) and (b), or (c) and (d) in Fig. 9 clearly shows that the coexisting $Z_3\text{IO}$ and $Z_4\text{IO}$

phases have a common c -axis orientation which is perpendicular to the transgranular phase boundaries. Therefore, this type of grain was also developed by in situ topotactic conversion and epitaxial grain growth with the preserved orientation of a common reactive template, plate-like $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2$ particle.

3.6 Results of EBSD analysis for a randomly oriented specimen

Figure 10 shows the results of EBSD analysis for a reference specimen of a $Z_m\text{IO}$ ceramic whose nominal composition was $m=3.5$. The area ratio of $Z_3\text{IO}$ (red), $Z_4\text{IO}$ (green), and unidentified region (black) is 13 : 86 : 1 for the phase identification of the reference specimen. The amount of $Z_4\text{IO}$ was overestimated mainly because most of the grains with large aspect ratios were determined as $Z_4\text{IO}$. This misidentification can be explained similarly to the misidentification of $Z_3\text{IO}$ for

$Z_4\text{IO}$ on the ($\perp$) face.

No specific differences were observed in terms of crystal orientation between ND, TD, and RD. Moreover, no particular relationship was found between crystal orientation and grain orientation of anisometric grains. As results, the obtained specimen was determined as a randomly oriented ceramic. In addition to this, parallel aligned boundaries observed in the textured specimens were not apparent in the randomly oriented specimen. The difference in the microstructures may result from the difference in the synthesis process. The parallel aligned boundaries in the series of homologous compound having the common c -axis may originate from the textured ceramics, which were formed on $\text{ZnSO}_4 \cdot 3\text{Zn}(\text{OH})_2$ particles as reactive templates.

4. Conclusions

The combination of the EBSD and EDS techniques made it

Fig. 9. SEM image for the selected region of the ($\perp$) face of RTGG-processed $Z_m\text{IO}$ ceramic with the representative unit cell images of the crystallites at the side of the transgranular phase boundaries ($Z_3\text{IO}$: (a) and (c), $Z_4\text{IO}$: (b) and (d)).

possible to reveal the relationship between the microtexture and crystallographic orientation of RTGG-processed $Z_m\text{IO}$ ceramics. The observation of the bulk ceramic surfaces parallel and perpendicular to the original sheet plane has revealed that the plate-like grains were preferentially aligned along the sheet plane and their thickness directions corresponded to their c -axis orientation. Parallel aligned boundaries were observed in $Z_3\text{IO}$ grains and between coexisting $Z_3\text{IO}$ and $Z_4\text{IO}$ phases within a single grain. The nearest neighboring crystallites sharing these boundaries had a common c -axis orientation and the boundaries were parallel to the ab -plane (basal plane). Two neighboring $Z_3\text{IO}$ crystallites sharing the unique boundary were confirmed to have a 60° misorientation angle around the c -axis to each other. The observation suggests that these axis-sharing crystallites were formed by the topotactic conversion and epitaxial grain growth from a common hexagonal template crystal.

This unique transgranular boundary in the homologous compounds might influence both electrical conductivity and thermal conductivity. The relationship between the microtexture and transport properties must be examined in further study.

Acknowledgements The work was partly carried out as a joint research and development project with the International Center for Environment Technology Transfer in 2003–2004, commissioned by the Ministry of Economy, Trade and Industry. The authors sincerely thank Dr. Yoshitake Masuda of National Institute of Advanced Industrial Science and Technology (AIST) for giving us structural information of $Z_m\text{IO}$.

References

- Ohtaki, M., Tsubota, T., Eguchi, K. and Arai, H., *J. Appl. Phys.*, Vol. 79, pp. 1816–1818 (1996).
- Ohta, H., Seo, W.-S. and Koumoto, K., *J. Am. Ceram. Soc.*, Vol. 79, pp. 2193–2196 (1996).
- Terasaki, I., Sasago, Y. and Uchinokura, K., *Phys. Rev. B*, Vol. 56, pp. R12685–R12687 (1997).
- Li, S., Funahashi, R., Mstsubara, I., Ueno, K. and Yamada, H., *J. Mater. Chem.*, Vol 9, pp. 1659–1660 (1999).
- Itahara, H., Seo, W.-S., Lee, S., Nozaki, H., Tani, T. and Koumoto, K., *J. Am. Chem. Soc.*, Vol. 127, pp. 6367–6373

Fig. 10. Results of EBSD analysis for the randomly oriented reference $Z_m\text{IO}$ ceramic. (A) Phase identification map of $Z_3\text{IO}$ (red) and $Z_4\text{IO}$ (green). (B) Image quality map. (C) Inverse pole figure (crystal orientation) maps for ND, TD, and RD with color keys.

- (2005).
- 6) Itahara, H., Sugiyama, J. and Tani, T., *Jpn. J. Appl. Phys.*, Vol. 43, pp. 5134–5139 (2004).
 - 7) Hiramatsu, H., Ohta, H., Seo, W.-S. and Koumoto, K., *J. Jpn. Soc. Power and Power Metallurgy*, Vol. 44, pp. 44–49 (1997).
 - 8) Tani, T., Isobe, S., Seo, W.-S. and Koumoto, K., *J. Mater. Chem.*, Vol. 11, pp. 2324–2328 (2001).
 - 9) Kaga, H., Asahi, R. and Tani, T., *Jpn. J. Appl. Phys.*, Vol. 43, pp. 3540–3543 (2004).
 - 10) Kaga, H., Asahi, R. and Tani, T., *Jpn. J. Appl. Phys.*, Vol. 43, pp. 7133–7136 (2004).
 - 11) Lotgering, F. K., *J. Inorg. Nucl. Chem.*, Vol. 9, pp. 113–123 (1959).
 - 12) Cullity, B. D., “Elements of X-ray diffraction,” Addison Wesley (1977) pp. 297–300.
 - 13) Itoh, H., Kajita, M., Fujitsu, S. and Yanagida, H., *J. Ceram. Soc. Japan*, Vol. 100, pp. 823–825 (1992).
 - 14) Nakamura, Y., Harada, T., Kuribara, H., Kishimoto, A., Motohira, N. and Yanagida, H., *J. Am. Ceram. Soc.*, Vol. 82, pp. 3069–3074 (1999).
 - 15) Dingley, D. J., “Electron Backscatter Diffraction in Materials Science,” Klumer Academic/Plenum Publishers (2000) pp. 6–6.
 - 16) Randle, V., “Microtexture Determination and its Application,” The Institute of Materials (1992) pp. 10–12.
 - 17) Tani, T., *J. Korean Phys. Soc.*, Vol. 32, pp. S1217–S1220 (1998).
 - 18) JCPDS card No. 20–1438.
 - 19) Seo, W.-S., Lee, Y. H., Lee, M. H., Tani, T. and Koumoto, K., Proc. of 15th Fall Meeting of the Ceram. Soc. of Japan (2001) pp. 21–21 [in Japanese].