Exploration of novel inorganic compounds using diffractometry and microscopy toward innovative functions

Koichiro FUKUDA[†]

Department of Materials Science and Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

The author will briefly review the recent progress and future perspective on the research topics of (i) highly *c*-axis-oriented polycrystals of lanthanum silicate oxyapatite in the pseudo-binary system $\text{La}_2\text{SiO}_5\text{--La}_2\text{Si}_2\text{O}_7$, (ii) homologous layered carbides in the system Zr--Y--Si--Al--C , (iii) layered oxycarbonitrides in the system Al--Si--O--C--N , (iv) crystal structures and ordered atom arrangements in SiAlON polytypoids, and (v) disordered crystal structure of $\text{Al}_3\text{O}_{3.5}\text{C}_{0.5}$. The crystal structures were necessarily expressed by the split-atom models for the layered oxycarbonitrides and SiAlON polytypoids, indicating that each of these compounds was composed of domains related by merohedral twinning. With $\text{Al}_3\text{O}_{3.5}\text{C}_{0.5}$ the antiphase domains (APDs) were observed, which were formed by the high-low phase transition involving loss of translational symmetry elements. The formation mechanisms of merohedral and pseudo-merohedral twin domains as well as APDs will be discussed in detail.

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1. Introduction

The demand for the development of new innovative materials is ever increasing. The syntheses of new materials and subsequent characterization of their crystal structures and microtextures are indispensable for the advancement in the field of materials science and engineering. Under the circumstances the author's recent research has mainly focused on the oxide-ion conductors as electrolytes and the thermoelectric conversion materials. The electrolytes for solid oxide fuel cells (SOFCs) working at intermediate temperatures (873–973 K) are advantageous than the widely used yttria stabilized zirconia which operates as electrolyte at the relatively high temperatures (1023–1073 K). Thus, lanthanum silicate oxyapatite (LSO) is among the most promising oxide-ion conductors because it exhibits relatively high ionic conductivity at around 873 K.^{1,2)} Thermoelectric materials with high efficiency of energy conversion are of interest for applications as heat pumps and power generators. Low-dimensional materials consisting of, for example, conducting two-dimensional (2D) layers are adequate to thermoelectric energy conversion.^{3–8)} The homologous layered carbides in the system Zr--Y--Si--Al--C can be regarded as the natural superlattice quantum-well materials. Hence, they are one of the promising materials with *n*-type thermoelectricity.

Phase transitions of inorganic compounds often induce intra-crystalline microstructures.⁹⁾ When the low-symmetry phase is a subgroup of the high-symmetry phase, two basically different types of microstructures result (Fig. 1). They are twin domains and antiphase domains (APDs). The twin domains arise from the loss of a point symmetry element. When the high- and low-symmetry phases have the same Bravais lattices, the resulting twinning is by merohedry. On the other hand, the pseudo-merohedral twins will be formed by the change in the Bravais

Fig. 1. Three types of intra-crystalline microstructures of merohedral twins, pseudo-merohedral twins and antiphase domains induced by high-low phase transition. Modified from Fig. 12-1 by Nord, Jr. (1992).⁹⁾

lattice. The latter twinning is rather easily detectable because the adjacent twin domains produce slightly split diffraction spots. The APDs are formed by the transitions in which the point group remains the same but the number of lattice points per unit volume is reduced and/or the translational symmetry elements are lost. The displacement vectors relating the domains are the vectors from the origin to the lost lattice points. The APD boundaries are made visible in transmission electron microscopy (TEM) because of a change in the phase of the electron beam as it crosses the boundary. The formation of APDs is usually accompanied by the appearance of extra reflections in the electron diffraction pattern.

In the present paper, the author reviewed the recent progress and future perspective on the research topics of (i) highly *c*-axis-oriented polycrystalline LSO, (ii) homologous carbides in the system Zr--Y--Si--Al--C , (iii) layered oxycarbonitrides in the system Al--Si--O--C--N , (iv) crystal structures of SiAlON poly-

[†] Corresponding author: K. Fukuda; E-mail: fukuda.koichiro@nitech.ac.jp

typoids, and (v) materials in the system $\text{Al}_2\text{O}_3\text{--Al}_4\text{C}_3$. The typical experimental procedures used in the relevant studies consist of syntheses of new inorganic materials, characterization of crystal structures and microtextures, and characteristics evaluation of the compounds.

2. Methodology

2.1 Diffractometry

The single-crystal X-ray diffraction (XRD) is definitely one of the most powerful methods to determine the crystal structures of inorganic compounds. However, the relatively large single crystals with sufficiently high crystallinity are required, which sometimes makes it unable to apply this method for the precise structural characterization. Cases where single-crystal specimens are not available, we have an alternative technique of powder diffractometry. The X-ray powder diffraction (XRPD) method has made remarkable progress in recent years. The advances in the field of crystal-structure analysis from XRPD data have enabled us to investigate the structural details that had not been introduced into the structural models. In order to disclose the structural details, combined use of a maximum-entropy method (MEM)⁽¹⁰⁾ and a MEM-based pattern fitting (MPF) method⁽¹¹⁾ is employed. The Rietveld⁽¹²⁾ and MEM analyses are insufficient to readily determine charge densities because the observed structure factors, F_o (Rietveld), are biased toward the structural models assuming intensity partitioning of the overlapped reflections. The subsequent MPF method reduces the bias as much as possible, giving it advantages over the classical Fourier method. Thus, the MEM and MPF analyses are alternately repeated until the reliability indices no longer decrease.⁽¹³⁾ Crystal structures are represented not by structural parameters but by three-dimensional electron-density distributions (EDDs) in MPF. The sophisticated computer programs are available for Rietveld refinement (RIETA-FP),⁽¹⁴⁾ MEM analysis (Dysnomia),⁽¹⁵⁾ and visualization of structural models and corresponding EDDs (VESTA).⁽¹⁶⁾

2.2 Microscopy

Optical methods of examining transparent inorganic compounds with the polarizing microscope have an overriding importance not only in mineralogy and petrology but also in materials science and engineering.⁽¹⁷⁾ Even today the relevant method retains its unique position as the most useful characterization technique. The microscopic examination is essential for the preliminary identification of constituent phases and for the determination of optical properties, including the deduction of optical axis orientation. The crystals with hexagonal symmetry, such as LSO with the space group $P6_3/m$, are optically uniaxial. Hence, the optical axis of LSO exactly coincides with the crystallographic c -axis. When we observe the extinction behavior of the highly c -axis oriented LSO polycrystal, each of the constituent crystal grains will come to the extinction position at the same time.

TEM is normally used as a determinative tool in the identification of fine-scale materials. The microscopists are, as the high level of expertise, required to be familiar with diffraction theory as well as the origin of contrast effect since the microscopy and diffractometry are complementary methods. It is sometimes difficult for XRPD solely to determine the unit cells of unknown structures. Under the circumstances, the selected-area diffraction patterns obtainable by TEM can be essential to the solution strategy. The lattice images, the light and dark fringe patterns of which are consistent with the atom arrangements, are also helpful for the crystal-structure determination.

3. Discussion

3.1 Syntheses and oxide-ion conductivity of highly c -axis-oriented polycrystals of lanthanum silicate oxyapatite

Nakayama et al. have paid much attention to LSO as a promising electrolyte of SOFCs because of the relatively high oxide-ion conductivity at moderate temperatures as well as at low oxygen partial pressures.^(1),2) The general formula of LSO is expressed by $\text{La}_{9.33+2x}\text{Si}_{6-y}\text{O}_{26+3x-2y}$, where x and y represent, respectively, the amounts of excess La_2O_3 component and Si deficiency.⁽¹⁸⁾ The oxide-ion conductivity is much higher along the c -axis than perpendicular to this direction, hence we prepared the c -axis-aligned polycrystalline LSO using a reactive diffusion technique.^(18)–20) This technique is epochal in that it is unnecessary for the complicate procedures nor special equipments, both of which are normally required to produce ceramics with grain-oriented microtextures; the popular texturing methods include the templated grain growth process, pressing at high temperatures (hot pressing), applying magnetic field and utilizing centrifugal force.^(21)–23) These fabrication processes are rather complex, and also, the orientation degrees of the textured ceramics are not always satisfactory.

We successfully prepared the grain-aligned polycrystalline LSO by isothermal heating of the diffusion couples consisting of La_2SiO_5 and $\text{La}_2\text{Si}_2\text{O}_7$ at 1873 K for 50–100 h. The Si-deficient LSO has been for the first time discovered in the annealed sandwich-type diffusion couple of $\text{La}_2\text{SiO}_5/\text{La}_2\text{Si}_2\text{O}_7/\text{La}_2\text{SiO}_5$ [Fig. 2(a)].⁽²⁰⁾ The annealed couple was mechanically processed, and the thin-plate electrolyte consisting of the grain-aligned polycrystal was obtained, the chemical formula of which was expressed by $\text{La}_{9.50}\text{Si}_{5.87}\text{O}_{26}$ ($x = 0.087$ and $y = 0.130$). The highly c -axis-oriented polycrystal of oxygen stoichiometric LSO with $x = y = 0$ ($\text{La}_{9.33}\text{Si}_6\text{O}_{26}$) was prepared by the heat treatment of the reverse sandwich-type diffusion couple of $\text{La}_2\text{Si}_2\text{O}_7/\text{La}_2\text{SiO}_5/\text{La}_2\text{Si}_2\text{O}_7$ [Fig. 2(b)].⁽¹⁹⁾ The oxide-ion conductivity at 873 K along the c -axis was 4.2×10^{-2} S/cm for the Si-deficient LSO, which was ~ 2.5 times higher than that of the oxygen

Fig. 2. Syntheses of highly c -axis-oriented lanthanum silicate oxyapatite polycrystals by isothermal heating of diffusion couples of (a) $\text{La}_2\text{SiO}_5/\text{La}_2\text{Si}_2\text{O}_7/\text{La}_2\text{SiO}_5$ and (b) $\text{La}_2\text{Si}_2\text{O}_7/\text{La}_2\text{SiO}_5/\text{La}_2\text{Si}_2\text{O}_7$ at 1873 K for 100 h.

Fig. 3. Atomic configurations in $(MC)_lAl_3C_2$ ($M = Zr$ or Y) with $l = 1$ (YAl_3C_3), 2 ($Zr_2Al_3C_4$) and 3 ($Zr_3Al_3C_5$).

Fig. 4. Atomic configurations in $(MC)_l(T_4C_3)_m$ ($M = Zr, Y$ and/or Hf , $T = Al, Si$ and/or Ge) with $1 \leq l \leq 3$ and $1 \leq m \leq 2$.

stoichiometric LSO. For further detailed information on the texturing method of reactive diffusion and the oxide-ion conductivity of the c -axis-oriented polycrystalline LSO, the readers can refer to the author's recent review paper.²⁴⁾

3.2 Syntheses and advanced features of new homologous layered carbides in the system Zr–Y–Si–Al–C

In the ternary system M –Al–C ($M = Zr, Y, Sr$ or U), the three types of homologous layered carbides, the general formula of which is $(MC)_lAl_3C_2$ with $l = 1, 2$ and 3 , were reported before 2007.^{25)–31)} The crystal structure of YAl_3C_3 ($l = 1$), for example, is hexagonal with space group $P6_3mc$ ($Z = 2$) and the unit-cell dimensions are $a = 0.34216$ nm and $c = 1.7282$ nm. The other two types of compounds, $Zr_2Al_3C_4$ ($a = 0.33468$ nm and $c = 2.2239$ nm) and $Zr_3Al_3C_5$ ($a = 0.3346$ nm and $c = 2.7649$ nm), also belong to the same space group.^{25),26),30)} These compounds show intergrowth structures with the $[MC_2]$ thin slabs separated by the Al_4C_3 -type $[AlC]$ layers (Fig. 3).³¹⁾

In 2007, we have discovered a new quaternary layered carbide $Zr_2(Al,Si)_4C_5$, which is trigonal (space group $R\bar{3}m$ and $Z = 3$) with the unit-cell dimensions of $a = 0.33106$ nm and $c = 4.0945$ nm.³²⁾ Since then we successively reported the five types of new homologous compounds in total, the general formula of which is expressed by $(MC)_l(T_4C_3)_m$ ($M = Zr, Y$ and/or Hf , $T = Al, Si$ and/or Ge) with $1 \leq l \leq 3$ and $1 \leq m \leq 2$ (Fig. 4).^{32)–38)} The crystal structures were determined by the combined use of XRPD and TEM. These compounds show a close relationship in crystal structure and chemical composition; the formula requires two integers l and m that can be changed independently, and hence

Fig. 5. A part of the layered structure of $(ZrC)(Al_4C_3)_m$ with $l = 3$ and $m = 1$, demonstrating the two-dimensional networks of C atoms at the boundary between NaCl-type $[Zr_3C_4]$ layer and Al_4C_3 -type $[Al_4C_4]$ layer.

causes evolution of the structure in two different dimensions. The atom arrangements are regarded as intergrowth structures consisting of the NaCl-type $[MC_{l+1}]$ layers separated by the Al_4C_3 -type $[T_{4m}C_{3m+1}]$ layers. These two types of structural elements share the two-dimensional networks of carbon atoms at their boundaries; the C–C distances are about 0.333 nm (Fig. 5). The C–C distance of ZrC is 0.330 nm $[=a(ZrC)/\sqrt{2}]$ and that of Al_4C_3 is 0.334 nm $[=a(Al_4C_3)]$, where $a(ZrC)$ and $a(Al_4C_3)$ are the a -axis lengths of ZrC and Al_4C_3 crystals, respectively. These distances are close to each other, and also to those of the carbon-atom networks in $(MC)_lAl_3C_2$ and $(MC)_l(T_4C_3)_m$. Thus, the closeness of the C–C distances between the ZrC and Al_4C_3 crystals, being expressed by the equation $a(ZrC)/\sqrt{2} \approx a(Al_4C_3)$, would be the principal reason for the formation of these layered carbides.^{26),31)–38)}

The layered carbides aforementioned can be regarded as the natural superlattice quantum-well materials since all of these crystal structures are characterized by the alternative stacking of the electric conductive $[MC_{l+1}]$ layers and rather insulative $[T_{4m}C_{3m+1}]$ layers.³⁹⁾ The advantage of the low dimensionality can be interpreted in terms of the carrier confinement effect in the 2D layers, which leads to an enlarged absolute value of the Seebeck coefficient (S) compared to the materials with three dimensional conducting paths.^{3)–8)} In addition, the 2D layered materials are expected to have relatively low thermal conductivity (κ) due to phonon scattering at layer interfaces. Hence, the materials with layered nanostructures could show high performance of thermoelectricity, which is quantified by a figure of merit $S^2\sigma/\kappa$, where σ is electrical conductivity. Thus, the layered carbides have prospects for application of thermoelectric power generators. Actually, we determined the temperature dependence of thermoelectric power factor ($S^2\sigma$) from the σ - and S -values for $Zr_2(Al,Si)_4C_5$, $Zr_3(Al,Si)_4C_6$, $Zr_2Al_3C_4$, $Zr_3Al_3C_5$ and YAl_3C_3 (Fig. 6).^{31)–33)} The signs of S were necessarily negative for these compounds irrespective of temperature, suggesting the predominant negative mobile charge carriers. The absolute value of S was the largest for YAl_3C_3 among the five types of layered carbides, which steadily increased to 112 $\mu V/K$ with increasing temperature up to 1073 K [Fig. 6(b)].³²⁾ Accordingly, the intergrowth structure with the thinner electroconductive layer would be more favorable for thermoelectric power generation. The sintered specimens examined were necessarily composed of randomly grain-oriented polycrystals. The grain alignment could further increase the σ -values and consequently improve the $S^2\sigma$ -values.

Fig. 6. Temperature dependences of (a) electrical conductivity σ , (b) Seebeck coefficient S and (c) thermoelectric power factor $S^2\sigma$ for $Zr_2(Al,Si)_4C_5$, $Zr_3(Al,Si)_4C_6$, $Zr_2Al_3C_4$, $Zr_3Al_3C_5$ and YAl_3C_3 .

3.3 Discovery and characterization of five types of new layered oxycarbonitrides in the system Al–Si–O–C–N

In the system Al_4C_3 –SiC, the five types of aluminosilicon carbides, Al_4SiC_4 , $Al_4Si_2C_5$, $Al_4Si_3C_6$, $Al_4Si_4C_7$ and Al_8SiC_7 , were reported during 1961–1989.^{40)–44)} In 1966, the structural models, being isomorphous with those of aluminosilicon carbides, were

Fig. 7. Atomic configurations in $(Al,Si)_{4m+n}(O,C,N)_{3m+n}$ with $1 \leq m \leq 2$ and $1 \leq n \leq 4$.

presented for a series of aluminum carbonitrides of Al_5C_3N , $Al_6C_3N_2$, $Al_7C_3N_3$ and $Al_8C_3N_4$.⁴⁵⁾ All of these carbides and carbonitrides are characterized by the layered structures made up of two types of layers. One is an $[(Al,Si)_4(C,N)_4]$ unit layer (denoted by A), consisting of an $[(Al,Si)_2(C,N)_2]$ double layer of $(Al,Si)(C,N)_4$ tetrahedra surrounded by two $[(Al,Si)(C,N)_2]$ single layers of $(Al,Si)(C,N)_4$ tetrahedra. The other is an $[(Al,Si)(C,N)_2]$ single layer (denoted by B) of $(Al,Si)(C,N)_4$ tetrahedra. The crystal structures of $Al_4Si_3C_6$ and $Al_7C_3N_3$ are built up of alternately stacking two types of layers with the sequence of $\langle BBABBBAB \rangle$ (space group $P6_3mc$ and $Z = 2$). With the rhombohedral structures of $Al_4Si_4C_7$ and $Al_8C_3N_4$, the common stacking sequence is $\langle BBABBBBABBBBAB \rangle$ (space group $R3m$ and $Z = 3$). The crystal structures of the other aluminosilicon carbides and aluminum carbonitrides are also made up of the combinations of A and B layers with the stacking sequences of $\langle BABA \rangle$ (space group $P6_3mc$ and $Z = 2$) for Al_4SiC_4 and Al_5C_3N , and $\langle BABBBABAB \rangle$ (space group $R3m$ and $Z = 3$) for $Al_4Si_2C_5$ and $Al_6C_3N_2$. The crystal structure of Al_8SiC_7 is still uncertain.

In the system Al–Si–O–C–N, we have discovered and structurally characterized the five types of new aluminosilicon oxycarbonitrides (Fig. 7), the general formula of which is expressed by $(Al,Si)_{4m+n}(O,C,N)_{3m+n}$ ($1 \leq m \leq 2$, $1 \leq n \leq 4$).^{46)–50)} These oxycarbonitrides are made up of merohedral twin domains consisting of A -type $[(Al,Si)_4(O,C,N)_4]$ unit layer and B -type $[(Al,Si)(O,C,N)_2]$ single layer. With $(Al,Si)_5(O,C,N)_4$ (space group $P6_3/mmc$ and $Z = 2$), the stacking sequences within individual domains are $\langle ABAB \rangle$ and/or $\langle BABA \rangle$, indicating that the atom arrangements of these domains are very similar to those of Al_5C_3N (Fig. 8).^{47),49)} Thus, this compound can be regarded as being homeotypic to Al_5C_3N . The layer stacking sequences are $\langle BABBBABAB \rangle$, $\langle BBABBBABBA \rangle$ and/or $\langle ABBABBBAB \rangle$ for the three types of domains of $(Al,Si)_6(O,C,N)_5$ (space group $R\bar{3}m$ and $Z = 3$), which is homeotypic to $Al_6C_3N_2$.⁴⁸⁾ In a similar manner, the layered oxycarbonitrides with the chemical formulas $(Al,Si)_7(O,C,N)_6$ and $(Al,Si)_8(O,C,N)_7$ are also homeotypic to, respectively, $Al_7C_3N_3$ and $Al_8C_3N_4$.⁵⁰⁾ The stacking sequence within the unit cell of $(Al,Si)_7(O,C,N)_6$ was $\langle BABBBABBB \rangle$, $\langle BBABBBAB \rangle$, $\langle BBBABBBBA \rangle$ and/or $\langle ABBABBBB \rangle$. The detailed atom arrangement in $(Al,Si)_8(O,C,N)_7$ is still uncertain.⁵⁰⁾ The dimensions of the domains would be within the coherence range of X-rays, hence the crystal structures were successfully represented by the split-atom models.

Fig. 8. Crystal structures of the two orientation states of $(\text{Al,Si})_5-(\text{O,C,N})_4$ viewed along $[110]$, showing the crystal structures being made up of two types of layers A and B . The two structural configurations (a) and (b) are related by the pseudo-symmetry inversion.

3.4 Determination of disordered atom arrangements in five types of SiAlON polytypoids

The SiAlON polytypoids have been well recognized from about 40 years ago since Jack (1976) has published a review paper on the phase stability in the quaternary system $\text{Si}_3\text{N}_4\text{--SiO}_2\text{--Al}_2\text{O}_3\text{--AlN}$.⁵¹⁾ The polytypoids have the general formula $(\text{Si,Al})_m(\text{O,N})_{m+1}$ ($m = 4, 5, 6, 7$ and 9) and are, in the notation of Ramsdell,⁵²⁾ denoted as $2mH$ (m even, space group $P6_3/mmc$ and $Z = 2$) and $3mR$ (m odd, space group $R\bar{3}m$ and $Z = 3$). We determined the crystal structures of $8H$ ($m = 4$), $15R$ ($m = 5$), $12H$ ($m = 6$), $21R$ ($m = 7$) and $27R$ ($m = 9$) to clarify the disordered atom arrangements of all these polytypoids (Fig. 9).^{53–58)} We adopted the recent XRPD techniques such as MEM and MPF methods to disclose the structural details by the three-dimensional EDDs. The crystal structures of the SiAlON polytypoids necessarily showed the disordering of (Si,Al) sites. Hence, we constructed the split-atom models that are consistent with the three-dimensional EDDs. In our previous studies on the oxycarbonitrides in the Al--Si--O--C--N system, these compounds were found to be composed of several domains that are related by pseudo-symmetry inversion.^{46)–50)} In a similar manner, we interpreted each of the disordered crystal structures of SiAlON polytypoids to be a statistical average of several structural configurations related by merohedral twinning.

The crystal structure of $15R\text{-SiAlON}$, for example, is trigonal with the unit-cell dimensions of $a = 0.30133$ nm and $c = 4.1862$ nm.⁵⁵⁾ The structural model shows seven independent sites in the unit cell. They are four (Si,Al) sites at Wyckoff positions $3a$ ($(\text{Si,Al})1$) and $6c$ ($(\text{Si,Al})2A$, $(\text{Si,Al})2B$ and $(\text{Si,Al})3$), and three (O,N) sites at $6c$ [Fig. 10(a)]. Since the distance of $(\text{Si,Al})2A\text{--}(\text{Si,Al})2B$ (≈ 0.085 nm) is unusually short, these $6c$ sites are regarded as the split sites of the same symmetry site of $6c$. We successfully extracted three types of ordered atom arrangements, termed I, II and III [Figs. 10(b)–10(d)], from the parent disordered structural model. In the ordered structural configurations, there are vacant sites between the two oxygen layers, which correspond to the vacant cation sheet of the ordered models. The atom-arrangement models of not only $15R\text{-SiAlON}$ but also $8H$ -, $12H$ -, $21R$ - and $27R\text{-SiAlON}$ are probably for the

Fig. 9. Atomic configurations in SiAlON polytypoids of $(\text{Si,Al})_m(\text{O,N})_{m+1}$ with $m = 4$ ($8H$), 5 ($15R$), 6 ($12H$), 7 ($21R$) and 9 ($27R$).

Fig. 10. Parts of the (a) disordered and (b)–(d) ordered atom arrangements of $15R\text{-SiAlON}$ viewed along $[110]$. Atomic configurational model I in (b) with the space group $R\bar{3}m$. The two models II in (c) and III in (d) with the space group $R\bar{3}m$. The two atomic configurations of II and III are related by the pseudo-symmetry inversion.

domains with the size distribution ranging from the unit-cell size to the coherence range of X-rays. These domains with ordered structures would be combined randomly and construct the whole disordered structure.

With $15R\text{-SiAlON}$, the neighboring $(\text{Si,Al})2B$ atoms are absent in the ordered models because the $(\text{Si,Al})2B\text{--}(\text{Si,Al})2B$ distance ($= 0.2415$ nm) is unusually short as compared with the $(\text{Si,Al})2A\text{--}(\text{Si,Al})2B$ ($= 0.3070$ nm) and $(\text{Si,Al})2A\text{--}(\text{Si,Al})2A$ ($= 0.3806$ nm) distances [Figs. 10(b)–10(d)].⁵⁵⁾ The atom arrangement of model I is centrosymmetric (space group $R\bar{3}m$), and those of the other two models (II and III) are noncentrosymmetric (space group $R\bar{3}m$). The latter two structural configurations are thus related by merohedral twinning. The g -values of the disordered structural model are characterized by $[g((\text{Si,Al})2A):g((\text{Si,Al})2B)] = [5:2]$. From these values we estimated the abundance (A) of each domain with the ordered structure by the following procedure. We defined the numbers of cation site M in

the unit cell of each domain d_m ($m = \text{I, II and III}$) as $N(M)_m$. The total number of M site in the unit cell of the disordered structural model is determined by $\Sigma\{A(d_m) \times N(M)_m\}$. Hence, we obtain $[g((\text{Si,Al})2\text{A}):g((\text{Si,Al})2\text{B})] = [\Sigma\{A(d_m) \times N((\text{Si,Al})2\text{A})_m\} : \Sigma\{A(d_m) \times N((\text{Si,Al})2\text{B})_m\}]$. The simplest and most plausible $A(d_m)$ -values satisfying the equation of $[\Sigma\{A(d_m) \times N((\text{Si,Al})2\text{A})_m\} : \Sigma\{A(d_m) \times N((\text{Si,Al})2\text{B})_m\}] = [5:2]$ are $[A(d_{\text{I}}):A(d_{\text{II}}):A(d_{\text{III}})] = [3:2:2]$. This implies that the formation abundance of domain I is 1.5 times larger than that of the other domains. The unequal abundance between the centrosymmetric and noncentrosymmetric domains still remains enigmatic. The more detailed investigation is necessary to clarify the formation mechanism of the disordered structures of the polytypoids.

3.5 Synthesis and disordered crystal structure of $\text{Al}_3\text{O}_{3.5}\text{C}_{0.5}$

In the system $\text{Al}_2\text{O}_3\text{--Al}_4\text{C}_3$, there are three intermediate compounds established; they are $\text{Al}_3\text{O}_{3.5}\text{C}_{0.5}$, $\text{Al}_4\text{O}_4\text{C}$ and Al_2OC .^{59,60} We have determined the crystal structure of $\text{Al}_3\text{O}_{3.5}\text{C}_{0.5}$ (space group $R\bar{3}m$ and $Z = 3$), which was satisfactorily represented by the split-atom model. The crystal structure can be regarded as the layered structure, consisting of the $\alpha\text{-Al}_2\text{O}_3$ -type $[\text{AlO}_2]$ single layers (denoted by C) separated by the $[\text{Al}_2(\text{O,C})_4]$ unit layers (denoted by D). The atom arrangement of the latter layer is described in terms of a three dimensional network of $[\text{Al}(\text{O,C})_4]$ tetrahedra which are associated by sharing corners. These two types of layers are alternately stacked in the c -axis direction with a sequence $\langle \text{CDCDCD} \rangle$ in the unit cell to form the three dimensional structure.

The dark-field TEM showed the crystal to be composed of several APDs that are related by the unit-lattice translation (refer to Fig. 6 in the original manuscript).⁶⁰ The most plausible explanation for the formation of APD structure is that the phase transition from the high-symmetry (H) phase to the low-symmetry (L) phase occurred on cooling. The H-to-L phase transition should be accompanied by the loss of translational symmetry. The size of the unit cell is increased by 4 during transition since the unit-cell dimensions of the H-phase (cell dimensions of a_{H} and c_{H}) and those of the L-phase (cell dimensions of a_{L} and c_{L}) are related by $a_{\text{L}} \approx 2 \times a_{\text{H}}$ and $c_{\text{L}} \approx c_{\text{H}}$.⁶⁰ Thus, the number of variants possible to produce during the phase transition is 4. These four variants (I, II, III and IV) are related across the APD boundaries by the displacement vectors $1/2[100]_{\text{L}}$ for variants I and II, $1/2[010]_{\text{L}}$ for variants I and III and $1/2[110]_{\text{L}}$ for variants I and IV as schematically illustrated in Fig. 11. We actually observed the APDs that are related by the displacement vector $1/2[010]_{\text{L}}$.⁶⁰ The structural model determined by XRD is probably of the average crystal structure of the L-phase.

4. Conclusion

We succeeded in the syntheses of new inorganic materials and subsequent determination of their crystal structures and intracrystalline microtextures using the complementary methods of diffractometry and microscopy. We discovered the Si-deficient LSO and successfully prepared its highly c -axis-oriented polycrystal by the reactive diffusion technique, which showed the significantly increased oxide-ion conductivity along the common c -axis. We demonstrated, for the first time, the thermoelectric conversion property of the layered carbides in the system Zr--Y--Si--Al--C , and revealed the design guidelines to achieve the high performance as n -type thermoelectric conversion materials. We expect in the future the realization of as-yet-unrecognized innovative functions for the other layered compounds in the systems

Fig. 11. Schematic illustration of antiphase domain structure in $\text{Al}_3\text{O}_{3.5}\text{C}_{0.5}$. The variants I and II are related by $1/2[100]_{\text{L}}$, those of I and III by $1/2[010]_{\text{L}}$ and those of I and IV by $1/2[110]_{\text{L}}$.

Al--Si--O--C--N , Si--Al--O--N and Al--O--C by focusing on their characteristic crystal structures.

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Koichiro Fukuda received his BS (1984), MS (1986), and Dr. Sci. (1992) degrees in Mineralogy from the University of Tokyo, Japan. In 1986, he became a research associate at Nagoya Institute of Technology. From 1997 to 1998, he was a research fellow in Department of Chemistry at the University of Aberdeen, UK. He has been a Professor of Materials Science and Engineering at Nagoya Institute of Technology since 2008.