PIV: Supplementary Subjects

Defect Chemistry and Sintering

- Formation of point defects by additives
- Diffusion (ambipolar) in ionic compounds
- Boundary segregation in pure and impure compound

Electrostatic potential effect

Diffusion Induced Interface Migration

- Effect of chemical instability on boundary migration
- Control of boundary migration and physical properties

Discussion on Potential Strategies for Full Densification

Kang, *Materials,* **13**, 3578 (2020).

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Chap. Defect Chemistry & Sintering

Point Defects in Ceramics

Expression of Point Defects: Kroeger – Vink Notation

Subtraction/addition of neutral atoms and subtraction/addition of electrons, separately

A_B^C A: species; B: site; C: effective charge

Table I2.I. Various types of point defects in a compound MX

Defect type	Symbols
Vacancies	$V_M, V_X, V_M, V_X^{\bullet}, V_M'', V_X^{\bullet\bullet}, \ldots$
Interstitials	$M_i, X_i, M_i^{\bullet\bullet}, X_i'', \ldots$
Misplaced atoms	$X_M, M_X, \ldots$
Associated centres	$(V_M\ V_X), (X_i\ X_M), \ldots$
Foreign atoms	$L_M, L_i^{\bullet\bullet}, F_M^{\bullet}, \ldots$
Free electrons and holes	$e', h^{\bullet}$

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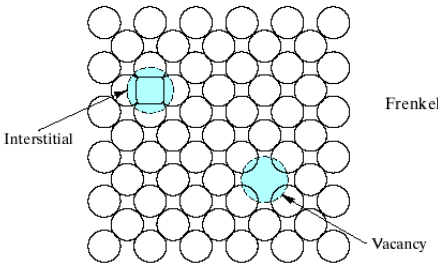
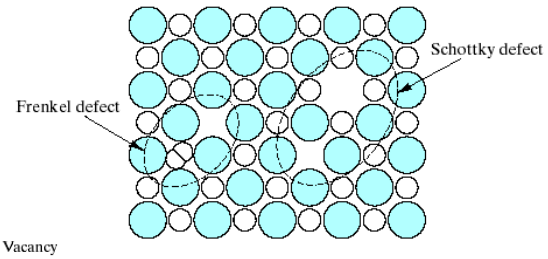
Types of Point Defects





Vacancy : unoccupied atom site
Interstitial : an atom occupying an interstitial site

Schottky defect : a pair of oppositely charged ion vacancies
Frenkel defect : a vacancy-interstitialcy combination

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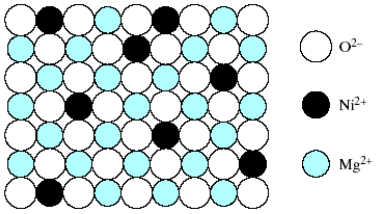
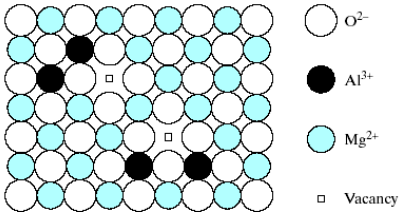
Substitutional solid solution in compounds

In addition to atomic (ionic) size, the charge balance is necessary in ionic solids.

MgO + NiO isovalent (homovalent)

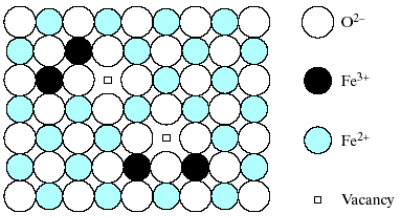


$MgO + Al_2O_3$ aliovalent (heterovalent)



$2\ Al^{3+}$ generate one Mg^{2+} vacant site due to charge balance.

FeO→Fe1-xO (x≈0.5)



$2\ Fe^{3+}$ generate one Fe^{2+} vacant site.
→ An example of nonstoichiometric compound

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Formulation of Reaction Eqns.

Defect Chemistry

(i) Defects are treated as legitimate chemical species
(ii) Reactions btw. Defects are written as conventional reactions
- Site relation: the ratio of the number of sites is maintained
- Site creation: the total # of regular sites may change
- Mass action law (mass balance)
- Electrical neutrality

Formation of Point Defects

Frenkel Defect $M_M^X \rightleftarrows M_i^{\bullet\bullet} + V_M''$

$$[M_i^{\bullet\bullet}][V_M''] = \exp\left(-\frac{\Delta g_F}{kT}\right) = K_F$$

Schottky Defect $M_M + O_O \rightleftarrows V_M'' + V_O^{\bullet\bullet} + M_B + O_B$ *or* $null \rightleftarrows V_M'' + V_O^{\bullet\bullet}$

$$[V_M''][V_O^{\bullet\bullet}] = \exp\left(-\frac{\Delta g_S}{kT}\right) = K_S$$

Electronic Defect *For low concentration,* $n = [e'] = \frac{n_e}{N_c} \cong \exp\left[-\frac{(E_c - E_F)}{kT}\right]$

$$np = [e'][h^\bullet] = \left[\exp\left(-\frac{E_g}{kT}\right)\right] = K_i \qquad p = [h^\bullet] = \frac{n_h}{N_v} \cong \exp\left[-\frac{(E_F - E_v)}{kT}\right]$$

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Formation of Point Defects by Additives

The rxs. that have to be considered (mass action expressions)

(a) the eqs. for the formation of the ionic defects
(b) the eq. for the formation of electronic defects
(c) a rx. eq. covering the interaction btw. material and atmosphere

At equilibrium, the expressions (a)-(c) are always true.

(d) a mass conservation eq. of the dopant
(e) an electrical neutrality eq. of the total defects

4(5) unknowns and 4(5) eqs.
3(4) eqs. in the form of product, 1 eq. in the form of addition

Brouwer approximation

First, assume the defect type of the dopant in the material and the charge neutrality btw. the major defects
(for (d) and (e), true only under particular conditions of T, oxygen partial pressure, and dopant concentration)

Plot the variation of defects concentrations as a function of dopant concentration in a *log-log* scale, the **Brouwer diagram**

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An Example of Brouwer diagram

Addition of L_2O_3 to MO

(a) $[V_M''][V_O^{\bullet\bullet}] = \exp\left(-\frac{\Delta g_S}{kT}\right) = K_S$

$[M_i^{\bullet\bullet}][V_M''] = \exp\left(-\frac{\Delta g_F}{kT}\right) = K_F$

(b) $np = [e'][h^{\bullet}] = \left[\exp\left(-\frac{E_g}{kT}\right)\right] = K_i$

(c) $\frac{[O_O^x][V_M'']p^2}{p_{O_2}^{1/2}} \approx \frac{[V_M'']p^2}{p_{O_2}^{1/2}} = K_g$

$\frac{1}{2}O_2 \rightarrow O_O^x + V_M'' + 2h^{\bullet}$

(d) $[L]_{total} = [L_M^{\bullet}]$

$L_2O_3 \xrightarrow{\text{MO}} 2L_M^{\bullet} + V_M'' + 3O_O^x$

(e) $[V_O^{\bullet\bullet}] \approx [V_M'']$

$[L_M^{\bullet}] + p + 2[V_O^{\bullet\bullet}] + 2[M_i^{\bullet\bullet}] = 2[V_M''] + n$

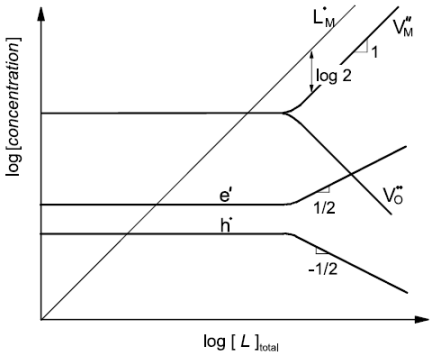

Figure I2.1. Effect of the concentration of foreign atom *L* on the defect situation in a compound MO; $p_{O_2} = \text{const.}$, $[V_O^{\bullet\bullet}] \geq [V_M'']$ and $n \geq p$.

- Addition of a dopant increases [ ] of defects with opposite charges decreases [ ] of those with similar charges. (Le Chatelier principle)
- The effects of a dopant on vacancies and interstitials are opposite.

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Diffusion & Boundary Segregation

Ambipolar Diffusion

In densification, the separate anions and cations move according to a chemical potential gradient and electrical potential gradient.

The diffusion of both ions occur in the same direction (ambipolar diffusion)

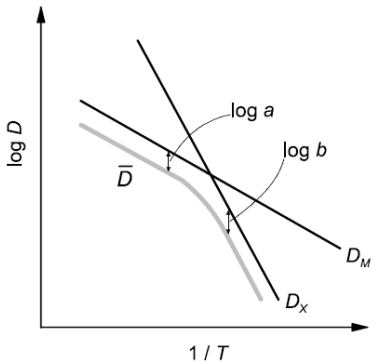
$$J_i = C_i v_i = -C_i B_i \nabla \eta_i = -C_i B_i [\nabla \mu_i + Z_i F \nabla \varphi]$$

$$J_M = -\frac{C_M D_M}{RT}[\nabla \mu_M + bF\nabla\varphi]$$

$$J_X = -\frac{C_X D_X}{RT}[\nabla \mu_X - aF\nabla\varphi]$$

$$J_{M_aX_b} = -\frac{C_{M_aX_b}}{RT}\left(\frac{D_M D_X}{bD_M + aD_X}\right)\nabla \mu_{M_aX_b} \equiv -\frac{C_{M_aX_b}}{RT}\overline{D}\nabla\mu_{M_aX_b}$$

$$J_{M_aX_b} = -\left(\frac{D_M D_X}{bD_M + aD_X}\right)\nabla C_{M_aX_b} \equiv -\overline{D}\nabla C_{M_aX_b}$$



The transport of free electrons and holes is assumed to be negligible.

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Effective Diffusivity: effect of multiple paths

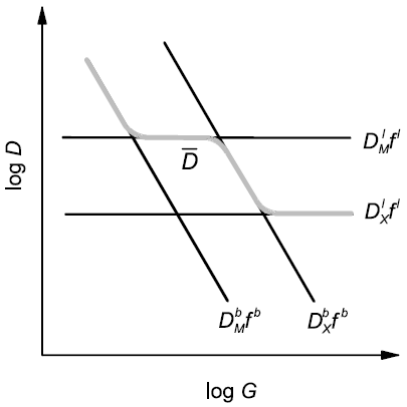
$$\overline{D}_i = \sum_p (D_i f)^p$$

$$\overline{D}_i = (D_i f)^l + (D_i f)^b$$

$$\overline{D} = \frac{(D_M^b f^b + D_M^l f^l)(D_X^b f^b + D_X^l f^l)}{\mathrm{b}(D_M^b f^b + D_M^l f^l) + \mathrm{a}(D_X^b f^b + D_X^l f^l)}$$

Effect of grain size:

$$f^b \propto 1/G$$



$$D_X^b > D_M^b \text{ and } D_X^l < D_M^l$$

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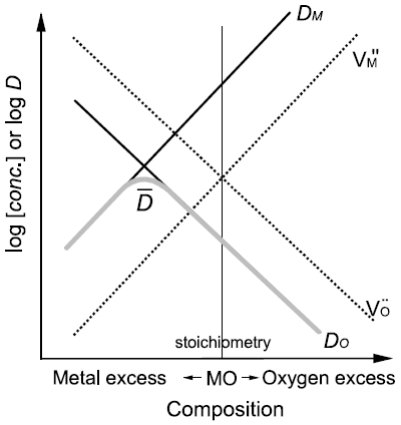
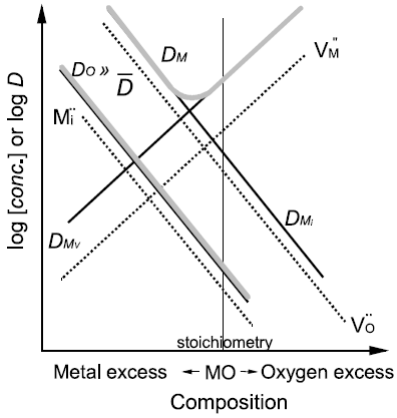
Effective Diffusivity: effect of nonstoichiometry





$$(Q_{M_i} < Q_{V_M} < Q_{V_X})$$

Limitation of defect chemistry for predicting effective diffusivity and sintering kinetics due to secondary effects, such as, grain boundary diffusivity, boundary and surface energy, boundary and surface energy anisotropy, and boundary mobility

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Boundary Segregation: electrostatic potential effect

Pure Material w/o dopant

$$M_M \rightleftarrows M_b^{\bullet} + V'_M$$

$$X_X \rightleftarrows X'_b + V_X^{\bullet}$$

$$[V'_M] = \exp\left(-\frac{g_{V'_M} - Ze\varphi(d)}{kT}\right)$$

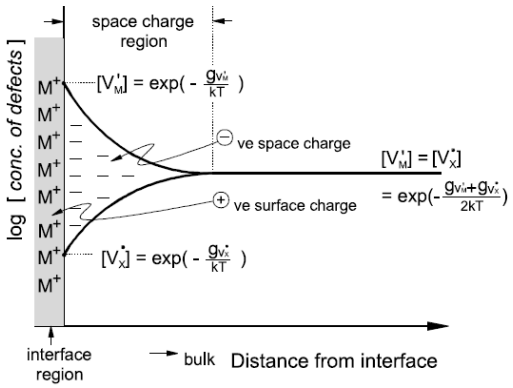
$$[V_X^{\bullet}] = \exp\left(-\frac{g_{V_X^{\bullet}} + Ze\varphi(d)}{kT}\right)$$

$$[V'_M] = \exp\left(-\frac{g_{V'_M}}{kT}\right)$$

$$[V_X^{\bullet}] = \exp\left(-\frac{g_{V_X^{\bullet}}}{kT}\right)$$

$$[V'_M]_{\infty} = [V_X^{\bullet}]_{\infty} = \exp\left(-\frac{1}{2}\frac{(g_{V'_M} + g_{V_X^{\bullet}})}{kT}\right)$$

$$e\varphi_{\infty} = \frac{1}{2}(g_{V'_M} - g_{V_X^{\bullet}})$$



MX compound with $g_{V'_M} < g_{V_X^{\bullet}}$

Boundary Segregation: electrostatic potential effect

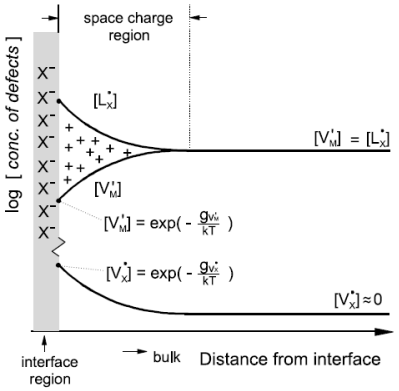
Impure Material with dopant

eg) Addition of $CaCl_2$ to NaCl

$$CaCl_2 \xrightarrow{2NaCl} Ca_{Na}^{\bullet} + V'_{Na} + 2Cl_{Cl}^{X}$$

When the concentration of vacancies generated by the addition of aliovalent solute Is higher than the intrinsic thermal vacancy concentration,

$$C_L \approx [V'_M]_{\infty} = \exp\left(-\frac{g_{V'_M} - e\varphi_{\infty}}{kT}\right)$$



isovalent (homovalent) or aliovalent (heterovalent)

Boundary Segregation: all effects

Table 13.I. Approximate ranges of contribution to the heat of segregation of solutes in metal oxides (kJ/mol)[28]

Interfacial energy (ΔH_γ)	Binary interaction (ΔH_m)	Strain energy (ΔH_e)	Electrostatic interaction (ΔH_e)
$0 \sim \pm 20^{(a)}$	$0 \sim \pm 60^{(b)}$	$0 \sim -140^{(c)}$	$0 \sim \pm 100^{(d)}$

(a) Assuming a maximum interface energy difference of 0.5 J/m^2.
(b) Based on heats of formation of various spinels.
(c) Computed from Eq. (7.4) with reasonable limiting values of the parameters.
(d) For $\varphi_\infty \approx 0.5V$ (corresponding to low temperatures) and an electronic charge difference of 2.

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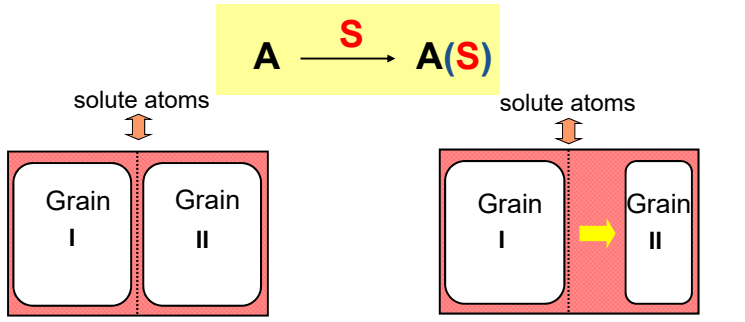
Chap. Diffusion Induced Interface Migration

DIIM (CIIM), DIGM (CIGM)

Qn: Possible processes of alloying?

DIGM



Characteristics
- **grain shape change**
- **increase in interface area**
- **fast alloying and grain growth**

change in material Properties

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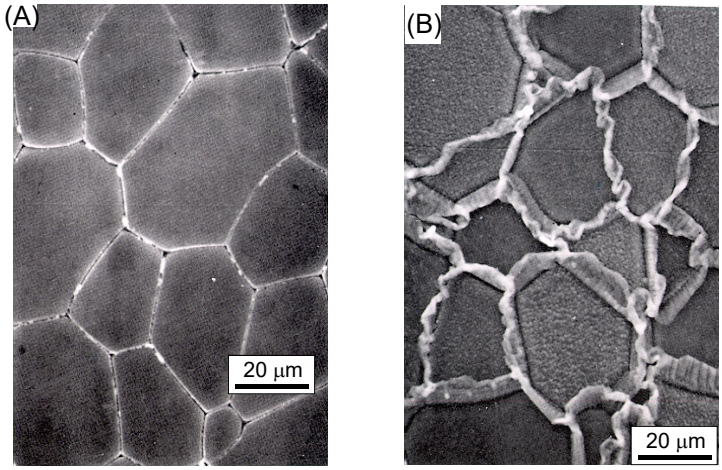
Microstructural Characteristics

Al_2O_3



Alumina samples (A) sintered (Lucalux) and (B) heat-treated at 1500°C for 6 h with a $75Al_2O_3$-$25Cr_2O_3$ powder mixture

Lee and Kang, *Acta Metall. Mater.*, **38**, 1307 (1990)

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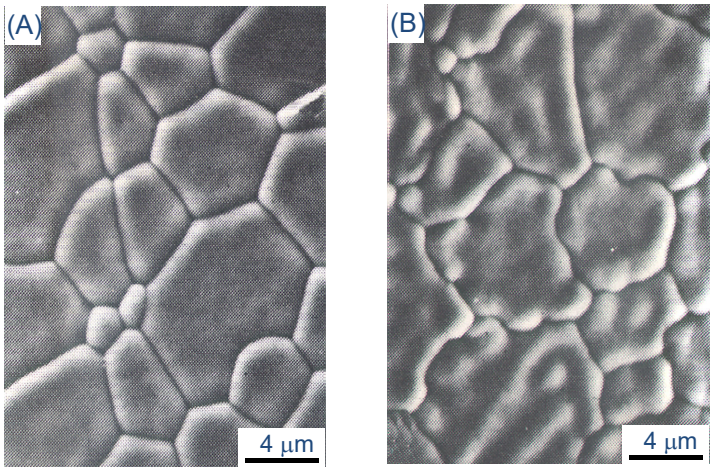
Microstructural Characteristics

PLZT



PLZT (A) hot pressed at 1200°C for 16 h and (B) heat-treated at 900°C for 16 h in air.

Kim, et al., *Ceram. Bull.*, **65,** 1390 (1986)

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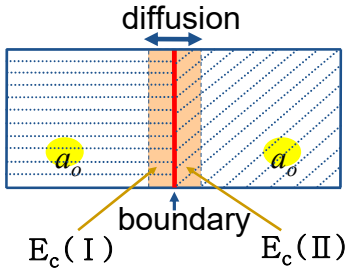
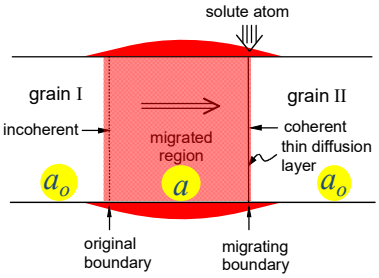
Driving Force of DIGM

Initiation of DIGM





Coherency Strain Energy

$$E_c = Y\delta^2 = Y(\eta\Delta C)^2$$

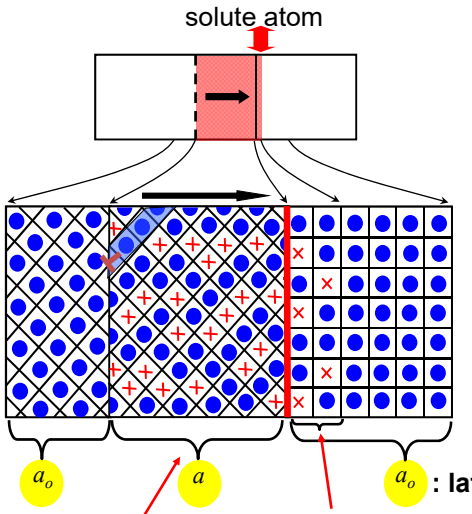
$Y = f$ (crystallographic plane)

$E_c(Ⅰ) \neq E_c(Ⅱ)$

Coherency strain energy map

a_o: lattice parameter of parent phase
a : lattice parameter of new solid solution

Driving Force of DIGM



Coherency Strain Energy

$$E_c = Y\delta^2 = Y(\eta\Delta C)^2$$

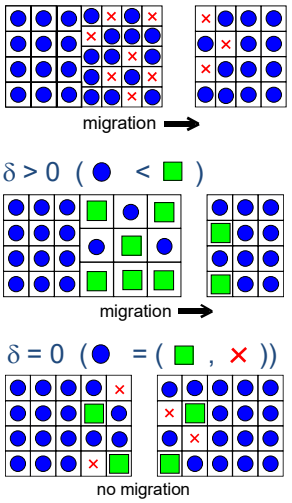
$$\left(\delta = \frac{a - a_o}{a_o} = \eta\Delta C\right)$$

a_o a a_o : **lattice parameter**

Scheme of Migration Control

●: Solvent ■ and ✕: Solutes

	Coherency Strain	Coherency Energy
i) $\delta < 0$ (● > ✕)	$\delta = \eta_1 \Delta C_1 < 0$,	$E_C \left(= Y\delta^2\right) > 0$
ii) $\delta > 0$ (● < ■)	$\delta = \eta_2 \Delta C_2 > 0$,	$E_C \left(= Y\delta^2\right) > 0$
iii) $\delta = 0$ (● = (■ , ✕))	$\delta = \eta_1 \Delta C_1 + \eta_2 \Delta C_2 = 0$, (lattice matching)	$E_C \left(= Y\delta^2\right) = 0$



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Some Questions and Considerations

Qn: Process of dissolution of W in Ni?

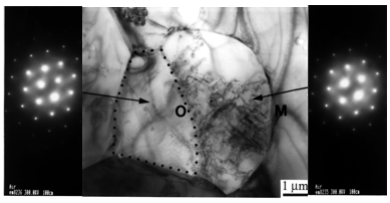
Qn: Can DIGM stop?

(i) Coherency breaking

(ii) Curvature effect

Qn: Microstructural change after coherency breaking?

Formation of many misfit dislocations



$99\bar{A}l_2O_3$-$1Fe_2O_3$(wt%)
Sintered at 1600 ºC in $95N_2$-$5H_2$
Annealed at 1500 ºC in air

Rhee, et al., *J. Eu. Ceram.* Soc. **23**, 1667 (2003)

Qn: Diffusion induced recrystallization? (Paek, et al., *J. Eu. Ceram. Soc.*, **24**, 613 (2004))

Qn: Grain growth promotion by DIGM? (Lee, et al., *Inter. Sci.*, **8**, 223 (2000))

Qn: Discontinuous precipitation and dissolution?

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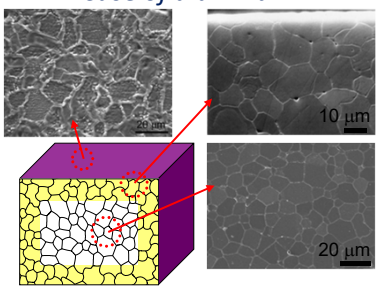
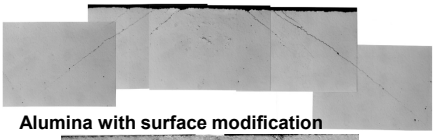
Application of DIGM in Materials Processing

Mechanical property enhancement

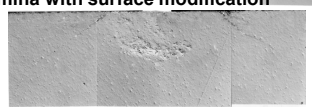
Case of alumina



Alumina without surface modification



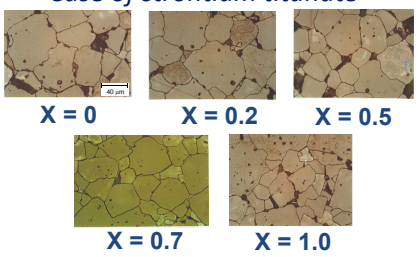
Alumina with surface modification



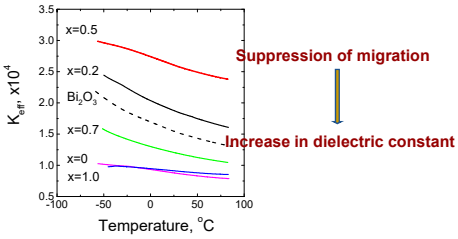
Rhee, et al., *J. Eu. Ceram*. Soc. **23**, 1667 (2003)

Electrical property enhancement

Case of strontium titanate



Microstructures of $SrTiO_3$ samples infiltrated with $80Bi_2O_3$-20[XCaO-(1-X)BaO] at 1300°C for 4h in Air.



Koo, et al., *J. Am. Ceram. Soc.* **87**, 1483 (2004)

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Qn: Full Densification?

S.-J. L. Kang, *Materials*, 13, 3578 (2020)

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