Original Paper

Crystal Growth and Characterization of $Ca_{12}Al_{14}O_{33}$ (12CaO-7Al_2O_3) Doped with Transition-metal Elements (Mn, Fe, Co, Ni and Cu)

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Single crystals of calcium aluminate doped with transition-metal elements were grown by the floating zone method. The substitution sites of the transition-metal elements were determined by electron probe microanalysis of the grown crystals. The substitution sites were dependent on the transition-metal elements used. Fe and Ni were substituted at the Al sites. The concentrations of Fe and Ni in the grown crystals were close to those in the feeds. In contrast, Mn, Co and Cu were substituted at the Ca sites and the concentrations of Mn, Co and Cu in the grown crystals were much smaller than those in the feeds.

Key Words: *Doping*, *Floating Zone Technique*, *Growth from Melt*

1. Introduction

$Ca_{12}Al_{14}O_{33}$ (12CaO-7Al_2O_3: C12A7) is one of the raw materials of cement. C12A7 has a cubic crystal structure with a positively charged frame structure with formula $[Ca_{24}Al_{28}O_{64}]^{4+}$. Twelve cages of ~0.4 nm diameter are contained in a unit cell. To compensate for the positive charge of the frame structure as above, two O^{2-} anions occupy two of the 12 cages in the stoichiometric composition. Since the O^{2-} anions can easily move between cages, this material is known as an oxide ion conductor[1].

Recently, the following unique phenomena of C12A7 have been reported[2-4]. Oxygen molecules become trapped in unoccupied cages by thermal annealing in oxygen gas. The oxygen molecules in the cages are reduced by the O^{2-} anions in the other cages, and then active oxygen species of O_2^- and O^- are produced in the cages[2]. Furthermore, the O^{2-} anions in the cages are exchanged with hydride ions (H^-) and electrons (e^-) upon thermal annealing in hydrogen gas and in vacuum, respectively[3,4]. The H^--trapped C12A7 is conversed from an insulator to an electrical conductor by UV radiation[3]. The e^--trapped C12A7 has high electrical conductivity of about 1500 $S \cdot cm^{-1}$[4]. The above phenomena result from the properties of the anion or the electron in the cage. It is possible that the enhancement of these novel properties and also the discovery of new unique properties of C12A7 might be achieved by substitution at the cation sites. To perform such research, single crystals are desirable. In this paper, crystals of C12A7 doped with transition-metal elements were grown by the floating zone (FZ) method and the substitution sites in C12A7 were determined by electron probe microanalysis (EPMA).

From the viewpoint of crystal growth, C12A7 is known as a congruently melting compound with a melting temperature of 1415 °C in a wet air or oxygen atmosphere[5]. The FZ and Czochralski (CZ) growth of C12A7 single crystals have been reported[6-8]. C12A7 crystals grown by the CZ method were pale yellow due to contamination from the iridium crucible[6]. C12A7 crystals grown by the FZ method without a crucible were colorless. In our experiments, the FZ method was applied for the growth of C12A7 crystals doped with transition-metal elements to prevent contamination from a crucible, which might affect the substitution sites of the dopants.

2. Experimental

To synthesize the feeds, γ-Al_2O_3 (> 99.99 %), $CaCO_3$ (> 99.99 %), MnO_2 (> 99.5 %), Fe_2O_3 (> 99.0 %), CoO (> 99.9 %), Ni_2O_3 (> 99.99 %) and CuO (> 99.9 %) were used as raw materials. After the calcination of powder mixture with an appropriate composition in an oxygen flow at 1000 °C for 12 h, the well-pulverized reactant was reheated in an oxygen flow at 1200 °C for 12 h then quenched from 900 °C to room temperature. The reactant was formed into a rod shape and pressed at a hydrostatic pressure of 300 MPa. The pressed rods were used without sintering for the FZ growth. The above procedure was based on a recent report[8]. For crystal growth, a four-mirror image furnace (Crystal Systems Co., model FZ-T-10000-H-TY-1) was used. The doped elements, the feed composition and the growth conditions are summarized in Table 1. The grown crystals were characterized using a polarized optical microscope and an electron probe microanalyzer (JEOL Ltd., model JXA-8200). Quantitative analysis was done at the center region of the samples using standard samples. The substitution sites of the transition-metal elements are discussed on the basis of the analysis results.

3. Results and Discussions

Figure 1 shows photographs of C12A7 crystals grown using feeds in which the transition-metal elements are doped into Ca sites in the nominal composition. Some of the crystals exhibit many cracks, bubbles and inhomogeneous coloring along the growth direction. It is reported that the concave growth interface induces bubbles and cracks during the FZ growth of undoped C12A7 crystals[7]. So the cracks and bubbles in the transition element doped C12A7 crystals might also be caused by the concave shape. The colors of the grown crystals are reddish brown for Mn and Co, brown for Fe, green for Ni and yellow ocher for Cu. For Mn and Cu, cross-sectional photographs are also shown in Fig.1. The inhomogeneity of the color in the cross-sectional photographs can be clearly observed. The colors are darker at the center of the crystals. These results indicate that the concentrations of the doped elements are higher at the center of the crystals. If the solid-liquid interface is flat, both the periphery and the center of the crystal are solidified in the same time. In the concave interface, the center of

Table 1 Composition of $Ca_{12-x}M_xAl_{14-y}M_yO_{33}$ (M: Mn, Fe, Co, Ni, Cu) feeds and growth conditions.

Nominal composition of feeds Dopant (M)	Doping content x	y	Growth rate (mm/h)	Growth atmosphere
Mn	0.012	—	1.0	O_2
	0.12	—	1.0	O_2
Fe	0.12	—	0.2	Air
	—	0.14	1.0	O_2
	—	0.14	3.0	Air
Co	0.012	—	1.0	O_2
	0.12	—	1.0	O_2
Ni	0.12	—	1.0	Air
	—	0.14	1.0	O_2
	—	0.14	1.0	Air
Cu	0.012	—	1.0	O_2
	0.12	—	1.0	O_2

the crystal is solidified later than the periphery. So the concave interface can cause higher dopant concentration at the center of the crystal in the zone leveling process for the dopant with smaller segregation coefficient than the unity. This phenomenon might also be caused by the concave solid-liquid interface during growth.

In Table 2, the results of quantitative analysis by EPMA are summarized. The values of Ca and M obtained by EPMA are normalized by the stoichiometric value of Al of 14. These are the average values of 10 points at center region of the samples. The errors of the analyzed values for M are significantly dependent on the elements as summarized in Table 2. This shows the distribution of the dopant in the crystals. For Co and Cu, the values of M obtained by EPMA are much smaller than the nominal values of M in the feeds. This means that the segregation coefficients of Co and Cu in C12A7 are much smaller than unity. For the doping of Co,

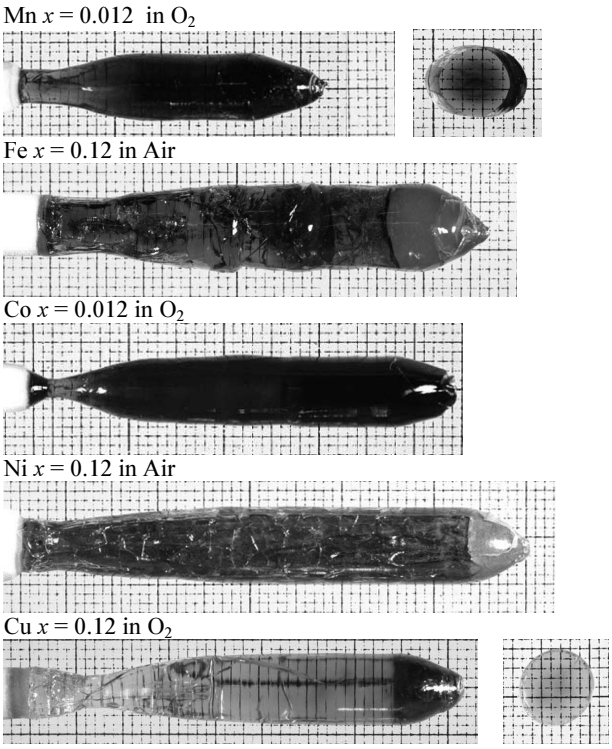


Fig.1 Photographs of crystals grown using feeds with $Ca_{12-x}M_xAl_{14}O_{33}$ (M: Mn, Fe, Co, Ni, Cu) composition.

Table 2 Results of analyzing crystals grown using feeds with $Ca_{12-x}M_xAl_{14}O_{33}$ composition.

Dopant (M)	x (feed)	Ca (analyzed)	M (analyzed)	Ca+M (analyzed)
Mn	0.012	11.97(4)	0.013(2)	11.98(4)
Fe	0.12	12.14(4)	0.14(5)	12.28(4)
Co	0.12	11.99(7)	0.07(2)	12.06(7)
Ni	0.12	12.15(4)	0.137(4)	12.29(4)
Cu	0.12	11.94(1)	0.037(1)	11.98(1)

Mn and Cu, the sum of the values of Ca and M (Ca+M) obtained by EPMA are consistent with the stoichiometric value of 12 within the measurement error. According to these results, Co, Mn and Cu are substituted at the Ca sites in C12A7. For the doping of Fe and Ni, however, the total values of Ca and M were 12.28 and 12.29, respectively, which are larger than the stoichiometric value of 12. When renormalized by the stoichiometric value of Ca of 12, the values of M and Al obtained by analysis were 0.14 and 13.83-13.84, respectively. The total of the values of M and Al (Al+M) was 13.97-13.98, which is close to the stoichiometric value of 14. These results suggested that Fe and Ni were substituted at the Al sites. Figure 2 shows the compositional image of the crystal grown using a feed of $Ca_{12-x}Fe_xAl_{14}O_{33}$ (x = 0.12) composition. The inclusions in Fig. 2 were identified to be $CaAl_2O_4$ by quantitative analysis using EPMA. The inclusions were segregated in the crystals grown at even 0.2 $mm \cdot h^{-1}$ of the low growth rate. According to the phase diagram of the $CaO\text{-}Al_2O_3$ system[5], $CaAl_2O_4$ phase coexists with C12A7 at a composition slight Al-richer than C12A7. The existence of a $CaAl_2O_4$ impurity phase means that the composition of the melt was Al-rich. This does not contradict the finding that Fe is substituted at the Al sites.

Using the feeds in which Fe or Ni was partly substituted at the Al sites in the nominal composition of C12A7, C12A7 crystals were grown in various atmospheres. Figure 3 shows photographs of the Fe- and Ni-doped crystals. No impurity phases were observed in the grown crystals by the compositional images by EPMA. Furthermore, the number of cracks was significantly reduced when the crystals were grown in a flow of oxygen. In oxygen flow condition, O^- ions and O_2^- ions are formed in a C12A7 crystal[2]. These anions are known to be strong oxidants. The doped Fe and Ni ions might be affected by these oxidants. The valence values of the doped element must be closely related with the formation of the cracks. In Table 3, the results of analysis are summarized. The obtained values of M and Al were normalized by the stoichiometric

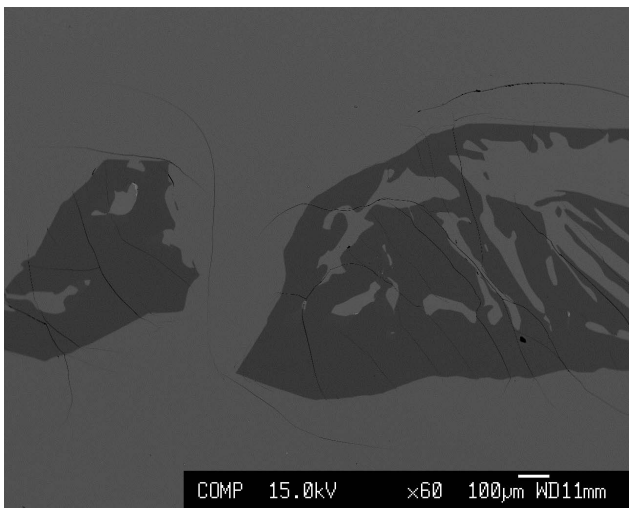
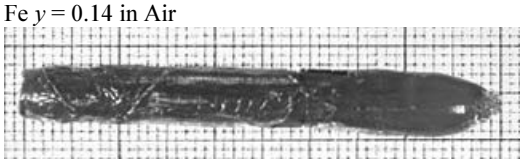


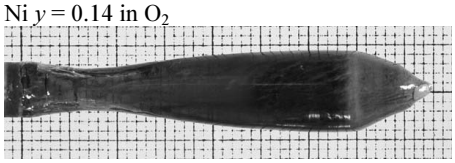
Fig.2 Compositional image of the crystal grown using a feed with $Ca_{12-x}Fe_xAl_{14}O_{33}$ (x = 0.12) composition obtained by EPMA.

Fe $y = 0.14$ in O_2

Fe $y = 0.14$ in Air



Ni $y = 0.14$ in O_2



Ni $y = 0.14$ in Air

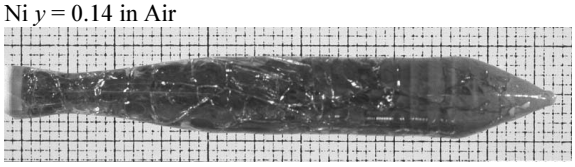


Fig.3 Photographs of crystals grown using feeds with $Ca_{12}Al_{14-y}M_yO_{33}$ (M: Fe, Ni) composition.

value of Ca of 12. The obtained values of Fe and Ni were relatively large compared with those of the other elements and were close to the feed compositions. This means that the segregation coefficients of Fe and Ni in C12A7 are close to unity. The total of the values of Al and M agreed with the stoichiometric value of 14 within the measurement error. These results also indicated that both Fe and Ni were substituted at the Al sites rather than at the Ca sites in C12A7 when the C12A7 crystals were grown in oxygen gas flow. As discussed in Table 1, the Al sites substitution of Fe and Ni were suggested when the C12A7 crystals were grown in Air. Therefore, the substation sites of Fe and Ni were not affected by the atmospheric gas condition during the FZ growth.

Table 3 Results of analyzing crystals grown using feeds with $Ca_{12}Al_{14-y}M_yO_{33}$ composition.

Dopant (M)	y (feed)	Al (analyzed)	M (analyzed)	Al+M (analyzed)
Fe	0.14	13.88(4)	0.14(5)	14.02(5)
Ni	0.14	13.867(5)	0.136(4)	14.003(5)

4. Summary

$Ca_{12}Al_{14}O_{33}$ crystals doped with transition-metal elements were grown by the floating zone method. The substitution sites were investigated by chemical analysis of the grown crystals. It was found that Mn, Co and Cu are substituted at the Ca sites. On the other hand, impurity phases were detected for Fe- and Ni-doped crystals and Fe and Ni are substituted at the Al sites in C12A7.

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