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Growth of Chlorapatite Crystals from a Sodium Chloride Flux

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Well-formed crystals of chlorapatite [$Ca_5Cl(PO_4)_3$] were first grown from a sodium chloride flux. The solubility of $Ca_5Cl(PO_4)_3$ in NaCl increased with increasing temperature. At 1100 °C, $Ca_5Cl(PO_4)_3$ had a solubility of about 0.15 mol%. The crystal growth of $Ca_5Cl(PO_4)_3$ was conducted by heating a mixture of solute and flux at 1100 °C for 10 h, followed by cooling to 500 °C at a rate of 5 $^\circ C\,h^{-1}$. Colorless and transparent crystals having lengths up to 4.0 mm and widths of 1.2 mm were grown from high-temperature solutions containing small amounts of solute (0.05—0.5 mol%). The obtained crystals were divided into two distinct morphological types: prisms and needles. The most suitable solute contents for the growth of prismatic and needle crystals were 0.15 and 0.1 mol%, respectively. The crystal forms were also dependent on the solute content. The prismatic crystals were bounded by the $\{10\bar{1}0\}$ and $\{10\bar{1}1\}$ faces. The needle crystals elongated in the $\langle 0001 \rangle$ directions. Calcium, chlorine, phosphorus, and oxygen were almost homogeneously distributed in the crystals.

Natural apatites, $Ca_5(Cl,F,OH)(PO_4)_3$, exhibit large variations in Cl, F, and OH contents.[1] The forms of apatites are prismatic and tabular. Pure end members are uncommon in nature.[1] Antimony and manganese-activated $Ca_5(Cl,F)(PO_4)_3$ powder has been synthesized and used in fluorescent lamps.[2] The chlorapatite has the formula $Ca_5Cl(PO_4)_3$ [pentacalcium chloride tris(phosphate)]. The crystals of $Ca_5Cl(PO_4)_3$ belong to the hexagonal system ($P6_3/m$)[1—4] or the pseudohexagonal system with the monoclinic space group $P2_1/b$ at room temperature.[5,6]

Crystalline powder of $Ca_5Cl(PO_4)_3$ was synthesized by the solid state reaction method.[4,7] Crystals of $Ca_5Cl(PO_4)_3$ were pulled from the melt using the Kyropoulos method, but vaporization of $CaCl_2$ at the melting point severely limited the size of the crystals.[8] Crystals of $Ca_5Cl(PO_4)_3$ have been grown by the $CaCl_2$ flux method.[6,9] In the system CaO–$CaCl_2$–P_2O_5 there is one ternary compound, chlorspodiosite (Ca_2ClPO_4), that melts incongruently at about 1040 °C into another solid [$Ca_5Cl(PO_4)_3$] and liquid.[6,9,10] In growing $Ca_5Cl(PO_4)_3$ crystals from a $CaCl_2$ flux, therefore, growth must take place above 1040 °C. We have grown $Ca_5Cl(PO_4)_3$ crystals from a $CaCl_2$ flux by heating a mixture containing 15 mol% Ca_2ClPO_4 at 1200 °C for 10 h, followed by cooling to 1050 °C at a rate of 5 $^\circ C\,h^{-1}$ and quenching from 1050 °C to room temperature.[9] The form of the grown crystals was a hexagonal prism with pyramidal end faces.[9] No report on the growth of $Ca_5Cl(PO_4)_3$ crystals from an NaCl flux has been published. The solubility of $Ca_5Cl(PO_4)_3$ in NaCl has not yet been reported.

The choice of flux is difficult because very little work has been done to date concerning the solubility of the solute in flux at high-temperatures. From a solubility point of view, a good flux should be chemically similar concerning the type of bonding to the solute. On the other hand, crystal-chemical differences should exist in order to prevent solid solubility between the solute and the flux. In this work, NaCl was chosen as a flux to grow crystals of $Ca_5Cl(PO_4)_3$. Sodium chloride has a common anion (Cl^-) with the solute. Another similarity is established by no large difference in the cationic radii between the flux (Na^+) and the solute (Ca^{2+}). The cationic valency (1+) of the flux is different from that (2+) of the solute. In this way, there are a similarity and a difference between NaCl and $Ca_5Cl(PO_4)_3$. Sodium chloride was expected to be a good flux.

The present paper describes the growth of $Ca_5Cl(PO_4)_3$ crystals from an NaCl flux. The effect of the solute content on the crystal growth was studied. The morphology, density, and imperfections of the resulting crystals were examined. The solubility of $Ca_5Cl(PO_4)_3$ in NaCl was also measured.

Experimental

Solubility. The solubility of $Ca_5Cl(PO_4)_3$ in NaCl was determined by measuring the mass loss of $Ca_5Cl(PO_4)_3$ in NaCl melts at temperatures of between 700 and 1100 °C. Mixtures of excess crystals (1—2 mm in size, about 0.5 g) of $Ca_5Cl(PO_4)_3$ and NaCl powder (about 5 g) were put into platinum vessels. After dissolution had proceeded for 1 h at a controlled temperature, the undissolved crystals were present upon quenching. The undissolved crystals were separated from the solidified saturated solution in warm water and reweighed. The loss in mass due to dissolution represents the solubility at that temperature. The eutectic temperature of the $Ca_5Cl(PO_4)_3$–NaCl system was determined on the basis of the measured differential thermal analysis (DTA) curves.

Flux Growth. Reagent-grade $CaHPO_4\cdot 2H_2O$, $CaCO_3$, $CaCl_2$, and NaCl were used for the flux growth of $Ca_5Cl(PO_4)_3$ crystals. A mixture of $6CaHPO_4\cdot 2H_2O+3CaCO_3+CaCl_2$ powders was used as a solute. Sodium chloride powder was used as a flux. Mixtures containing solutes of 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, and 0.5 mol% were prepared. The masses of the mixtures were about

30 g. The mixtures were put into platinum crucibles of 30 cm^3 capacity. The lids were fitted and the crucibles were placed in an electric furnace with silicon carbide heating elements. The furnace was heated at a rate of about 45 °C h^{-1} to 1100 °C, held at this temperature for 10 h, and then cooled at a rate of 5 °C h^{-1} to 500 °C. When the cooling program was completed, the furnace was allowed to cool down to room temperature. The crystalline products were then separated by dissolving the flux in warm water.

Characteristics. The obtained crystals were examined using an optical microscope and a scanning electron microscope (SEM). The crystal phases were identified by X-ray diffraction (XRD). The length, L (parallel to the $\langle 0001 \rangle$ directions), and width, W (perpendicular to the $\langle 0001 \rangle$ directions), of the $\mathrm{Ca_5Cl(PO_4)_3}$ crystals grown were measured. Concerning the dependence on the aspect ratio (L/W) of the grown crystals, they were divided into two morphological types: prism ($L/W \leqq 15$) and needle ($L/W > 15$). During respective growth runs, the average length (L_{av}) and width (W_{av}) of the first 50 largest crystals having the forms of a prism and a needle were calculated. The XRD data of the orientated crystals grown were obtained. The interfacial angles of the crystals were also measured. The density of the crystals was determined pycnometrically. An electron probe microanalyzer (EPMA) was used to study variations in the concentration of the major constituents in the grown crystals. The presence of impurities from the NaCl flux and Pt crucible was also checked.

Results and Discussion

Solubility of $\mathrm{Ca_5Cl(PO_4)_3}$ in NaCl. The dependence of the solubility on the temperature is shown in Fig. 1. A mixture of $\mathrm{Ca_5Cl(PO_4)_3}$–NaCl did not melt at 700 °C. At 800 °C, $\mathrm{Ca_5Cl(PO_4)_3}$ was dissolved in NaCl at a concentration of about 0.03 mol% (about 0.27 g in 100 g NaCl). The solubility gradually increased with increasing temperature. At 1100 °C, $\mathrm{Ca_5Cl(PO_4)_3}$ had a solubility of about 0.15 mol% (about 1.34 g in 100 g NaCl). The solubility of $\mathrm{Ca_5Cl(PO_4)_3}$ in NaCl was very low. However, the obtained solubility curve had an appreciable temperature coefficient of solubility. Therefore, $\mathrm{Ca_5Cl(PO_4)_3}$ could be crystallized by slowly cooling the solutions. Thus, NaCl is expected to be a suitable flux for the growth of $\mathrm{Ca_5Cl(PO_4)_3}$ crystals.

The obtained DTA data showed that the $\mathrm{Ca_5Cl(PO_4)_3}$–NaCl system had a eutectic temperature of 795±5 °C. Judging from the solubility curve and DTA data, the eutectic composition was considered to be about $\mathrm{Ca_5Cl(PO_4)_3}$ (0.03 mol%)–NaCl (99.97 mol%).

Figure 1 shows that mixtures containing between 0.05—0.15 mol% solute are unsaturated at a soak temperature of 1100 °C of the flux growth runs. Based on the solubility curve, the saturation temperatures of mixtures containing 0.05, 0.1, and 0.15 mol% solute are about 900, 1035, and 1100 °C, respectively. The solubility at the soak temperature corresponds to a starting composition of $\mathrm{Ca_5Cl(PO_4)_3}$ (0.15 mol%)–NaCl (99.85 mol%). In the case of mixtures containing 0.2—0.5 mol% solute, the solution is incomplete at the soak temperature.

It was confirmed in preliminary experiments that maintaining a given temperature for 1 h was a sufficient time for equilibration. The evaporation of NaCl was less than 5 mass% during solubility experiments. The evaporation had little influence on the solubility.

Flux Growth of $\mathrm{Ca_5Cl(PO_4)_3}$ Crystals. Well-formed prism- and needle-shaped $\mathrm{Ca_5Cl(PO_4)_3}$ crystals of lengths up to 4.0 mm and widths of 1.2 mm were grown from the NaCl flux. The crystals were mainly grown at the bottom of the crucible due to the difference between the densities of the solute and the flux. The obtained crystals were colorless and transparent. Prismatic and needle crystals were grown from mixtures containing 0.05—0.3 mol% solute. When the mixtures containing 0.4 and 0.5 mol% solute were used, only prismatic crystals were grown. Typical prismatic and needle crystals of $\mathrm{Ca_5Cl(PO_4)_3}$ are shown in Figs. 2 and 3, respectively.

Prismatic crystals up to $L = 4.0$ mm and $W = 1.2$ mm were grown from mixtures containing 0.05—0.5 mol% solute. The L_{av} and W_{av} of the prismatic crystals are plotted against the solute content in Fig. 4. Large crystals of $L_{\mathrm{av}} = 2.4$ mm

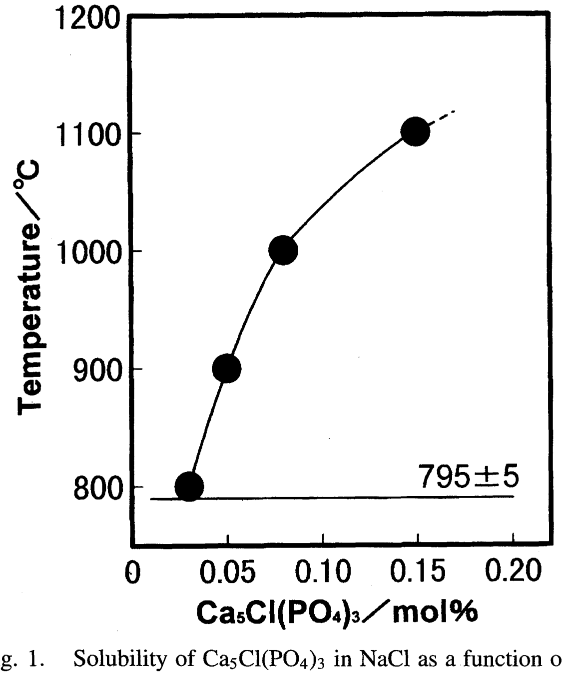

Fig. 1. Solubility of $\mathrm{Ca_5Cl(PO_4)_3}$ in NaCl as a function of temperature.

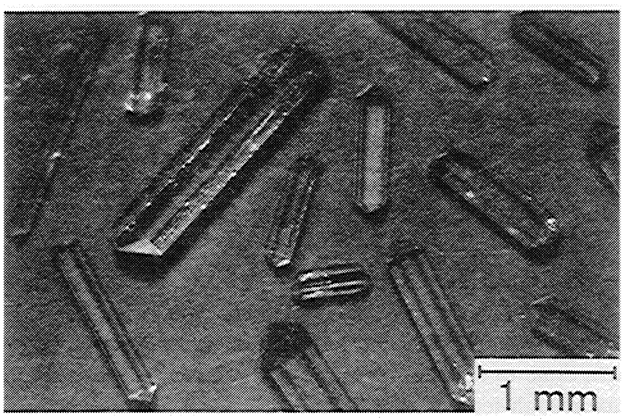

Fig. 2. Optical micrograph showing prismatic crystals of $\mathrm{Ca_5Cl(PO_4)_3}$ grown from NaCl flux.

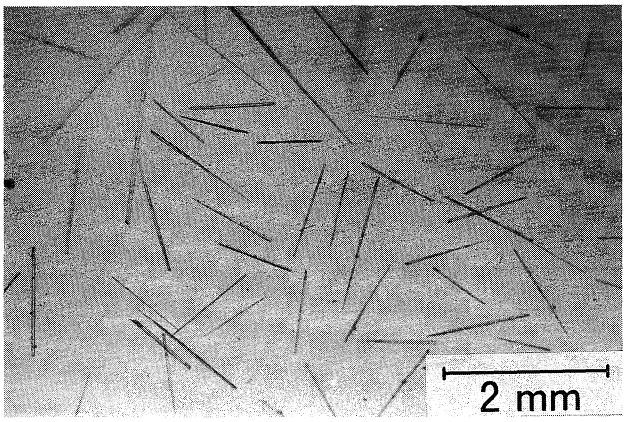

Fig. 3. Optical micrograph showing needle crystals of $Ca_5Cl(PO_4)_3$ grown from NaCl flux.

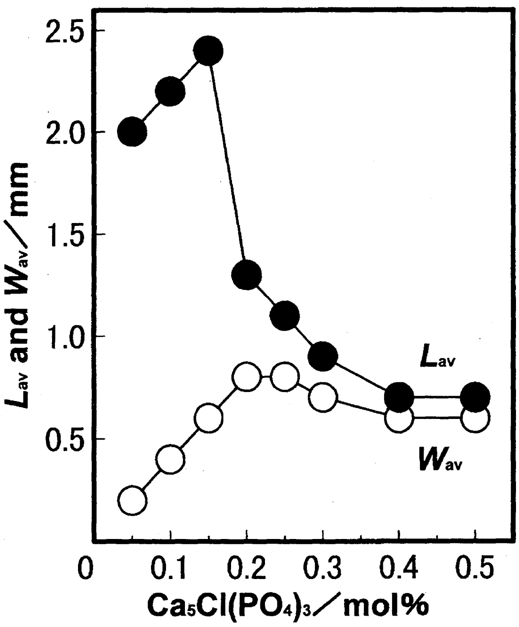

Fig. 4. Variation in average length, L_{av}, and width, W_{av}, of prismatic crystals of $Ca_5Cl(PO_4)_3$ with solute content.

were grown from a mixture containing 0.15 mol% solute. Any further increase in the solute content resulted in a decrease in the L_{av} value. This indicates that the solute was consumed during the formation of nuclei in preference to the crystal growth. Crystals of 0.8 mm in W_{av} value were grown from mixtures containing 0.2 and 0.25 mol% solute. The W_{av} value decreased with either increasing or decreasing the solute content. Mixtures containing a solute of 0.15—0.5 mol% produced crystals with W_{av} values of 0.6—0.8 mm. There is no marked difference among the W_{av} values. The aspect ratios (L_{av}/W_{av}) of the crystals were in the region of 1.2 —10. The values decreased with solute content. The forms of the prismatic crystals varied from long prismatic to short prismatic. Crystals of $Ca_5Cl(PO_4)_3$ grown from $CaCl_2$ flux were also prismatic.[9] The optimum solute content for the growth of prismatic crystals was 0.15 mol%.

Needle crystals of $Ca_5Cl(PO_4)_3$, up to $L = 2.1$ mm and $W = 55$ μm, were grown from mixtures containing solute of 0.05—0.3 mol%. L_{av} and W_{av} of the needle crystals are plotted against the solute content in Fig. 5. A mixture containing 0.1 mol% solute produced large crystals with $L_{av} = 1.1$ mm and $W_{av} = 45$ μm. Any further increase or decrease in the solute content resulted in a decrease in the size of needle crystals. The aspect ratios of the crystals were in the region of 25—65. The values increased along with the solute content. The yields of the needle crystals decreased along with increasing solute content. The optimum solute content for the growth of needle crystals was 0.1 mol%.

A mixture containing 0.15 mol% solute produced 0.30 g crystals. About 75 mass% of the solute (0.40 g) employed was recovered in the form of prismatic and needle crystals. In a calculation using the starting composition and eutectic composition, the masses of $Ca_5Cl(PO_4)_3$ crystals grown and a powder contained in eutectic mixture were 0.32 and 0.08 g, respectively. The mass of the obtained crystals was about 94% of the calculated value. The agreement between the found and calculated mass of grown crystals is good.

During these growth runs, evaporation of the NaCl flux was less than 30 mass%. The evaporation had a more or less influence on the growth of $Ca_5Cl(PO_4)_3$ crystals. In practice, a combination of slow cooling with evaporation of the flux produced crystals of $Ca_5Cl(PO_4)_3$. The platinum crucibles were found to be undamaged after use. The NaCl flux did not attack the crucibles. The resulting crystals could be readily separated from the flux in warm water because NaCl was easily soluble.

Characteristics of the $Ca_5Cl(PO_4)_3$ Crystals. Many $Ca_5Cl(PO_4)_3$ crystals of good quality were obtained up to a size of 4.0 mm in length and 1.2 mm in width, which were colorless and transparent. The obtained crystals were divided into two distinct morphological types: prism, from long to

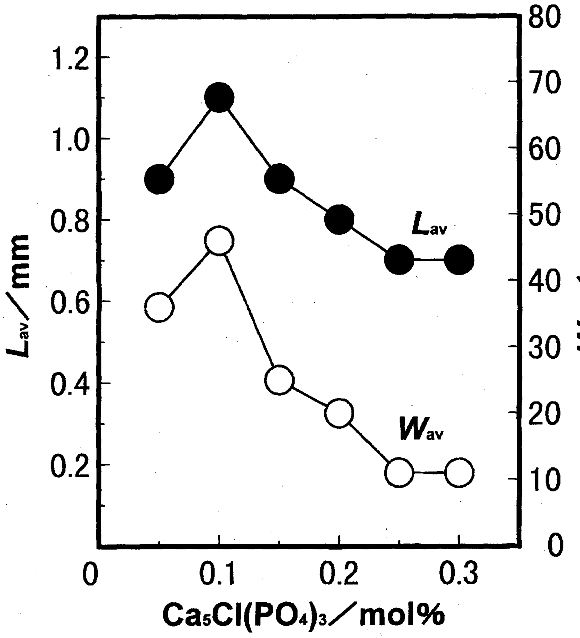

Fig. 5. Variation in average length, L_{av}, and width, W_{av}, of needle crystals of $Ca_5Cl(PO_4)_3$ with solute content.

short, and needle. They were identified as $Ca_5Cl(PO_4)_3$ by their XRD patterns, using data given on the JCPDS card (hexagonal system).[4]

The prismatic crystals of $Ca_5Cl(PO_4)_3$ had a form of hexagonal prism with pyramidal end faces. The surfaces of these crystals were very flat. A typical example is shown in Fig. 6. In order to determine the Miller indices of the crystal faces, the orientated crystals were investigated by the XRD method. The diffraction intensity of the $(30\bar{3}0)$ plane was predominant. The indices of prismatic faces were $\{10\bar{1}0\}$. The interfacial angles between prismatic faces and pyramidal faces were 51±1°. This value was in good agreement with the calculated interfacial angle (51.0°) between the $\{10\bar{1}0\}$ and $\{10\bar{1}1\}$ faces. On the basis of the XRD data and interfacial angle measurements, it was found that the prismatic crystals were bounded by the $\{10\bar{1}0\}$ and $\{10\bar{1}1\}$ faces. The prismatic crystals were elongated in the $\langle 0001\rangle$ directions. This morphology was similar to those of the $Ca_5Cl(PO_4)_3$ crystals grown from a $CaCl_2$ flux[9] and fluorapatite, $Ca_5F(PO_4)_3$, crystals grown from a KF flux by a slow-cooling method.[11] In addition, the needle crystals of $Ca_5Cl(PO_4)_3$ were also bounded by well-developed six-sided faces. Typical examples are shown in Fig. 7. On the basis of the XRD pattern of orientated needle crystals, the diffraction intensity of the $(30\bar{3}0)$ plane was predominant. The indices of side faces were $\{10\bar{1}0\}$. The needle crystals elongated in the $\langle 0001\rangle$ directions. The indices of six-sided faces of needle crystals were the same as those of prismatic crystals.

The variations in the concentration of the major constituents in the grown $Ca_5Cl(PO_4)_3$ crystals were investigated by the use of EPMA. Calcium, chlorine, phosphorus, and oxygen were almost homogeneously distributed. Sodium from the NaCl flux was not detected. The chief disadvantage of the flux-growth technique is the incorporation of ions from the flux into the lattice of crystals. However, no Na^+ ions were incorporated into the crystals obtained in this work. This can be ascribed to the difference in cationic valency between Na^+ and Ca^{2+}. Flux inclusions were rarely found in the crystals. Impurity incorporation of Pt from the crucible material was also not detected in the crystals.

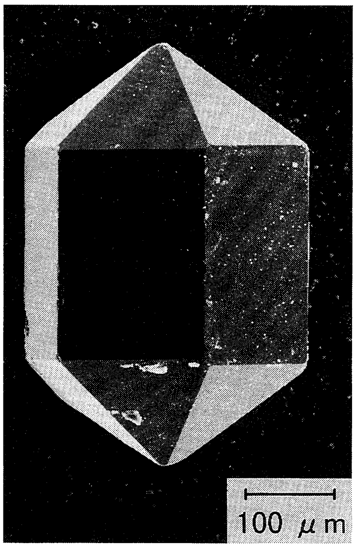

Fig. 6. SEM photograph showing a hexagonal prism with pyramidal end faces of $Ca_5Cl(PO_4)_3$ crystal.

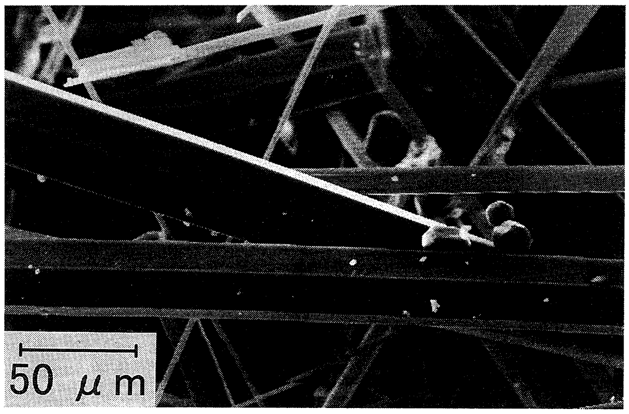

Fig. 7. SEM photograph showing six-sided needles of $Ca_5Cl(PO_4)_3$ crystals.

The density of the $Ca_5Cl(PO_4)_3$ crystals was pycnometrically determined to be 3.18±0.02 $g\,cm^{-3}$. This was in good agreement with the literature value (3.173 $g\,cm^{-3}$).[4] The observed density was independent of the crystal forms.

Conclusions

Colorless and transparent chlorapatite, $Ca_5Cl(PO_4)_3$, crystals were grown for the first time from an NaCl flux. The solubility of $Ca_5Cl(PO_4)_3$ in NaCl increased with increasing temperature. Many $Ca_5Cl(PO_4)_3$ crystals having lengths of up to 4.0 mm and widths of 1.2 mm were obtained from high-temperature solutions containing a solute of 0.05—0.5 mol%. The obtained crystals were of two morphological types: prism and needle. The crystal sizes and forms were dependent on the solute content. The quality of the obtained crystals was high. Sodium chloride was found to be a suitable flux to grow the crystals.

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