Growth of $CaWO_4$ Crystals from M_2WO_4(M=Li, Na, and K) Fluxes

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Synopsis. Calcium tungstate crystals were grown from M_2WO_4 (M=Li, Na, and K) fluxes. Observations of the obtained $CaWO_4$ crystals showed that a high-temperature solution of Na_2WO_4 was superior to both Li_2WO_4 and K_2WO_4 solutions. It was experimentally confirmed that the Na_2WO_4 flux chosen on the basis of the guiding principle was the most suitable.

Calcium tungstate crystals were grown from the following fluxes: LiCl,[1–7] NaCl,[1,8] KCl,[1,8–11] Na_2WO_4,[1,6,12–15] and $Na_2W_2O_7$.[16] They were selected mainly on the basis of past experience. Lithium tungstate was not a suitable flux for the growth of $CaWO_4$ crystals using a traveling solvent method.[12] In the case of the usual flux method, there has been no attempt to grow $CaWO_4$ crystals from Li_2WO_4 and K_2WO_4 fluxes.

We have proposed a guiding principle to choose a suitable flux for the growth of oxide crystals.[17] On the basis of this principle, Na_2WO_4 was chosen as the flux for the growth of $CaWO_4$ crystals.[17] Octahedral crystals of $CaWO_4$, up to 4.5 mm in size, were grown from the flux.[17,18] However, there has been no experimental evidence that Na_2WO_4 is the most suitable of M_2WO_4 (M=Li, Na, and K) fluxes.

The present paper describes the growth of $CaWO_4$ crystals from M_2WO_4 fluxes. Calcium tungstate crystals were grown from M_2WO_4 fluxes by a slow-cooling method. The crystals obtained from the Na_2WO_4 flux differed clearly from those grown from the Li_2WO_4 and K_2WO_4 fluxes regarding their form, transparency, and surface features. On the basis of the results of the flux growth and the observation of $CaWO_4$ crystals, the suitability of M_2WO_4 fluxes is discussed.

Experimental

Reagent-grade $CaCO_3$, WO_3, Li_2CO_3, Na_2CO_3, and K_2CO_3 were used for the flux growth of $CaWO_4$ crystals. The starting compositions for typical mixtures prepared are shown in Table 1. The mixtures (40—50 g in weight) were put into platium crucibles of 30 cm^3 capacity. After the lids were closely fitted, the crucibles were placed in an electric furnace with silicon carbide heating elements. The furnace was heated at a rate of about 50 °C h^{-1} to 1100 °C, held at this temperature for 5 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. Crystal products were separated by dissolving the flux in warm water. The obtained crystals were identified by an X-ray powder diffraction method. The crystals were observed by the use of an optical microscope.

Results and Discussion

Calcium tungstate crystals were found to be grown not only from Na_2WO_4, but also from Li_2WO_4 and K_2WO_4 fluxes. About 25 growth runs were carried out in order to find suitable solute-flux ratios. These experiments showed that mixtures containing 10, 15, and 30 mol% solute produced the largest crystals from Li_2WO_4, Na_2WO_4, and K_2WO_4 fluxes, respectively, as shown in Table 1. The maximum sizes of the grown crystals were 4.5—6 mm. The obtained crystals were identified by their X-ray powder patterns, using data given in the JCPDS card.[19] Typical $CaWO_4$ crystals grown from the respective fluxes are shown in Fig. 1. During these growth runs, evaporation of the respective fluxes was less than 1 wt%. The influence of evaporation on crystal growth was negligible. The platinum crucibles were found to be undamaged after use. The M_2WO_4 fluxes did not attack the platinum crucibles.

As shown in Fig. 1, the Na_2WO_4 flux yielded octahedral crystals, up to 4.5 mm in size, with smooth {112} facets. These crystals were both colorless and transparent. On the other hand, the Li_2WO_4 and K_2WO_4 fluxes produced bulky crystals up to 6 mm in size. These crystals were white, translucent, and not well formed. The maximum size of crystals grown from the Na_2WO_4 flux was somewhat smaller than that of crystals grown from Li_2WO_4 or K_2WO_4 flux. From the point of view of crystal form and transparency, however, the Na_2WO_4 flux was found to be the most suitable of the three fluxes.

The surface features observed on the faces of the grown $CaWO_4$ crystals are shown in Fig. 2. The crystals grown from the respective fluxes have the characteristic surface features. The surfaces of the crystals grown from Na_2WO_4 flux are very flat. Flux inclusions are rarely found in the crystals. It therefore seems that the growth of $CaWO_4$ crystals from the Na_2WO_4 flux proceeded under stable conditions. On the other hand, the surfaces of the crystals grown from the Li_2WO_4 flux are greatly striated. It is a peculiarity of the surface features of the crystals grown from the K_2WO_4 flux that large numbers of minute crystals are

Table 1. Starting Compositions and Crystal Products

Flux used	Composition/mol%		Crystal product
	Solute	Flux	
Li_2WO_4	10	90	Bulky crystals up to 6 mm in size
Na_2WO_4	15	85	Octahedral crystals up to 4.5 mm in size
K_2WO_4	30	70	Bulky crystals up to 6 mm in size

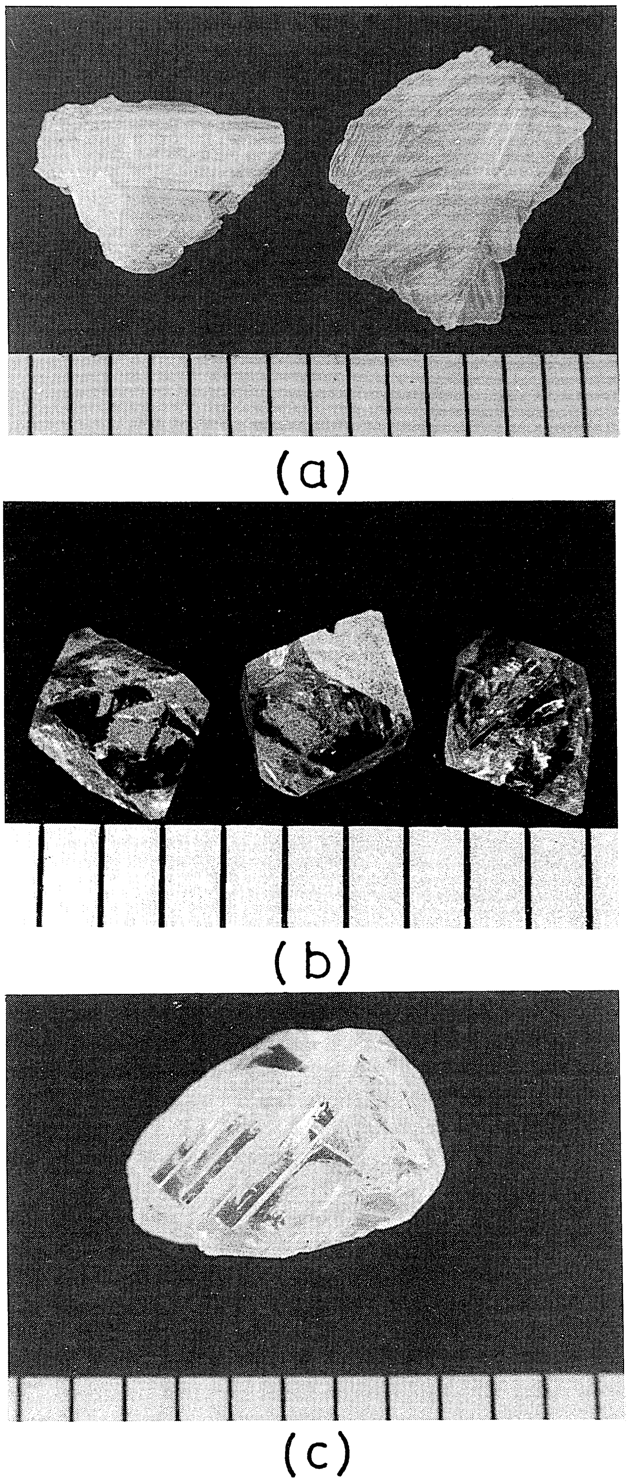

Fig. 1. $CaWO_4$ crystals grown from (a) Li_2WO_4, (b) Na_2WO_4, and (c) K_2WO_4 fluxes (1 div.=1 mm).

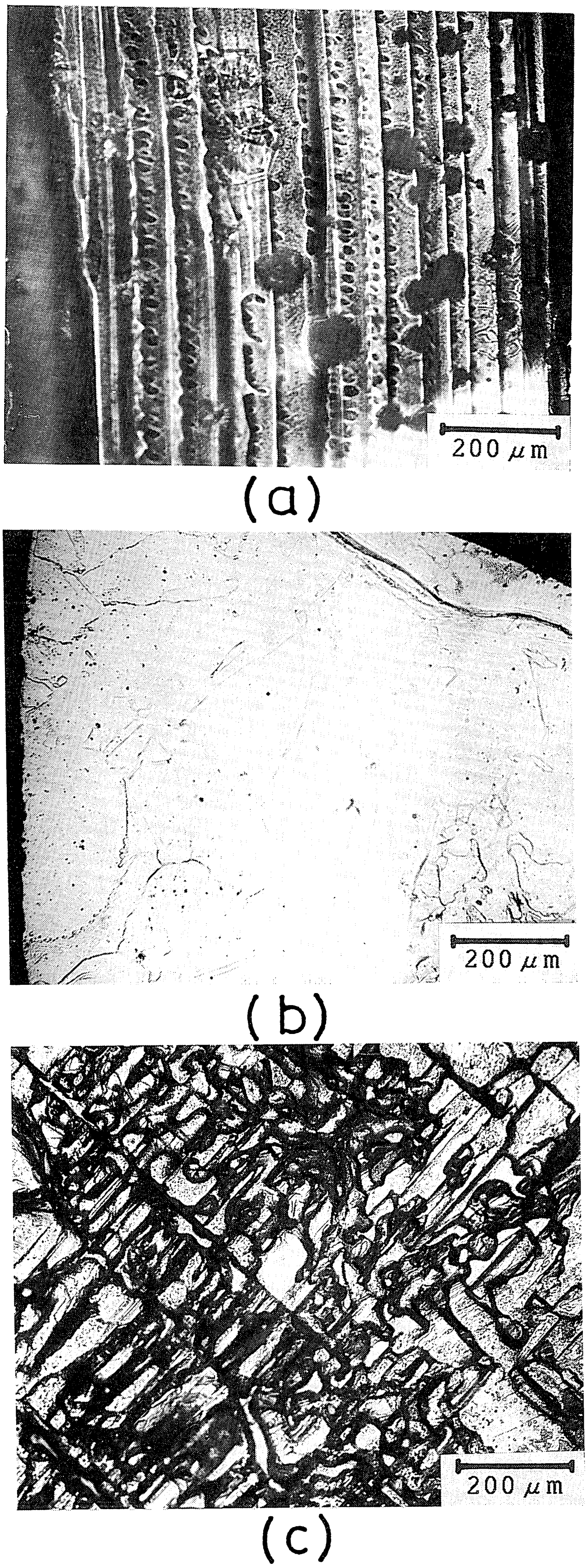

Fig. 2. Surface features observed on the faces of $CaWO_4$ crystals grown from (a) Li_2WO_4, (b) Na_2WO_4, and (c) K_2WO_4 fluxes.

observed on the faces. Flux inclusions are also found in the crystals grown from Li_2WO_4 and K_2WO_4 fluxes. The defects in these crystals are related to rapid crystal growth. It is, therefore, considered that the growth of $CaWO_4$ crystals from Li_2WO_4 or K_2WO_4 flux proceeded under unstable conditions. Evidently, the homogeneity of the crystals grown from the Na_2WO_4 flux is superior to that of the crystals grown from the Li_2WO_4 or K_2WO_4 flux. From the viewpoint of surface features, Na_2WO_4 was found to be the most suitable flux.

The three kinds of fluxes used for the growth of $CaWO_4$ crystals contain anions in common with the solute. Obvious crystal-chemical differences between the fluxes and the solute are established by differences in the valency states of the cations. Regarding M^+ ions, the ionic radius of Na^+ is the closest to that of Ca^{2+}. This similarity may contribute to the suitability of the Na_2WO_4 flux for the growth of $CaWO_4$ crystals.

We attempted to grow $CaWO_4$ crystals from M_2WO_4 fluxes. Objective crystals were grown from the respective fluxes. Regarding these fluxes, it was confirmed in observations of the obtained $CaWO_4$ crystals that Na_2WO_4 was the most suitable flux.

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