CHEMISTRY LETTERS, pp. 333-336, 1991.

Growth of Gd_2SiO_5 Crystals from MF(M=Li, Na, and K) Fluxes

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The growth of Gd_2SiO_5 crystals from MF(M=Li, Na, and K) fluxes was attempted by a slow cooling method. Crystals of Gd_2SiO_5 were grown from LiF and KF fluxes. Well-formed Gd_2SiO_5 crystals up to 0.4 mm long were grown from KF flux. Unwanted $NaGdSiO_4$ crystals were grown from NaF flux.

Crystals of Gd_2SiO_5 have been known to play host to the cerium activator.[1] Gd_2SiO_5 melts congruently at about 1900 °C.[2] The crystals of Gd_2SiO_5 have been grown by the Czochralski method.[1,3] In this method, a high temperature above the melting point of Gd_2SiO_5 is needed to grow the crystals. On the other hand, the flux growth occurs at temperatures well below the melting point of the solute phase. Formless Gd_2SiO_5 crystals have been grown from PbF_2-PbO-PbO_2 flux.[4] The crystal growth has been conducted by heating the mixture at 1250 °C for 1 h followed by cooling at a rate of 1 °C h^{-1} to 1050 °C.[4] There has been no attempt to grow Gd_2SiO_5 crystals from alkali fluoride fluxes. Y_2SiO_5 crystals have been grown from KF flux.[5] The present paper describes the attempts to grow Gd_2SiO_5 crystals from MF(M=Li, Na, and K) fluxes by a slow cooling method. Toxicity of the MF fluxes is very low although the fluxes containing lead have the disadvantage of being toxic. On the basis of the results of the flux growth experiments, the suitability of MF fluxes to grow Gd_2SiO_5 crystals is discussed.

Equimolar mixture of reagent grade Gd_2O_3 and SiO_2 was used as a solute for the flux growth runs and reagent grade LiF, NaF, or KF used as a flux. The solute contents of 3 and 5 mol% in a case of LiF or NaF flux, and of 3, 5, 7, 10, 20, and 30 mol% in a case of KF flux were prepared. The mixture (40.0 g in weight) was put into a platinum crucible of 30 cm^3 capacity. After the lid was closely fitted, the crucible was 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 10 h, and then cooled at a rate of 5 °C h^{-1} to 400 °C. When the cooling program was completed, the furnace was allowed to cool down to room temperature. Crys-

tals were separated by dissolving the flux in warm water. Grown crystals were identified by an X-ray powder diffraction method, using data given in the papers[4,6] and JCPDS cards.[7-9]

The results of flux growth experiments are shown in Fig.1. Crystals were grown from MF fluxes. Gd_2SiO_5 crystals were grown from LiF and KF fluxes. The Gd_2SiO_5 crystals grown from both the fluxes were colorless and transparent. On the basis of the X-ray powder data, Gd_2SiO_5 crystals obtained in this study had a new structure reported by Wanklyn et al.[4] They have reported on the growth of Gd_2SiO_5 crystals with the new structure from PbF_2-PbO-PbO_2 flux.[4] The Gd_2SiO_5 crystals with the new structure were obtained from only four batches of over 40.[4] Gd_2SiO_5 crystals and an unidentified powder were prepared from KF flux. Fortunately Gd_2SiO_5 crystals could be easily separated from the powder. Figure 2 shows Gd_2SiO_5 crystal coexisting with unidentified powder. Well-formed Gd_2SiO_5 crystal is shown in Fig.3. The Gd_2SiO_5 crystals grown were colorless and transparent. The Gd_2SiO_5 crystals up to 0.4 mm in length were grown from the mixture containing 5 mol% solute. The crystal size decreased with increasing the solute content. When the solute content of 30 mol% was used, Gd_2SiO_5 crystals up to 0.03 mm in length were grown. Gd_2SiO_5 crystals up to 0.4 mm in length and LiF crystals up to 3.8 mm in length were grown from LiF flux. The Gd_2SiO_5 crystals grown were not well-formed. Lithium fluoride flux also crystallized as a cubic form. Typical LiF crystals are shown in Fig.4. The LiF crystals were white and transluscent. Gd_2SiO_5 crystals were not grown from NaF flux. Unwanted $NaGdSiO_4$ crystals up to

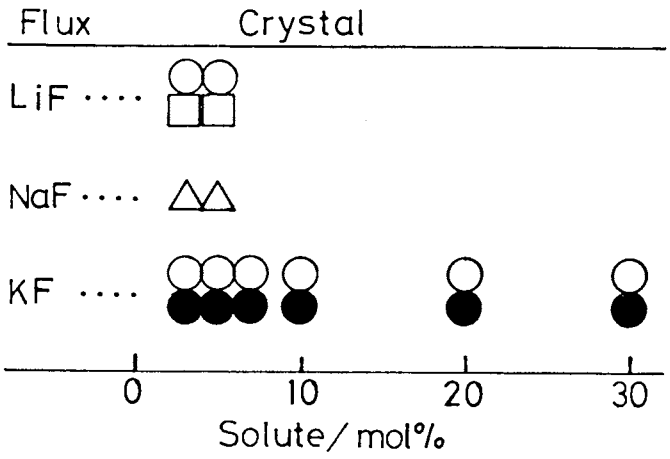

Fig.1. Crystals grown from alkali fluoride fluxes.
○: Gd_2SiO_5, □: LiF, △: $NaGdSiO_4$, ●: Unidentified powder

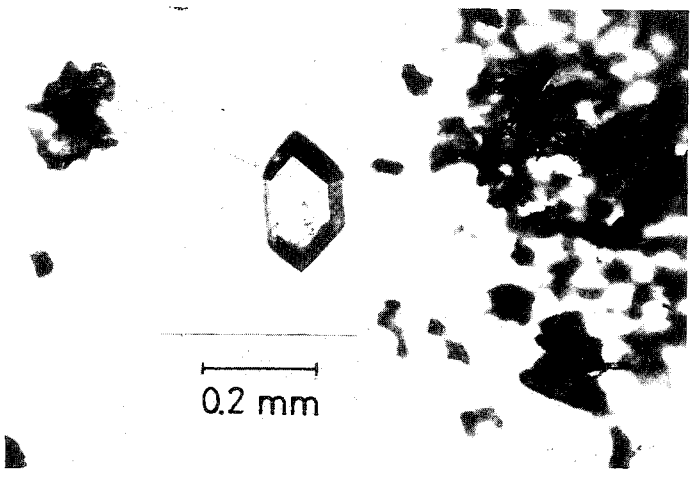

Fig.2. Gd_2SiO_5 crystal grown from KF flux and unidentified powder.

4.2 mm in length were grown from NaF flux. The reaction of solute with flux afforded the unwanted compound. Typical $NaGdSiO_4$ crystals are shown in Fig.5. The crystals grown were colorless and transparent. Shannon et al.[6] prepared $NaGdSiO_4$ crystals up to 0.2 mm in length by a hydrothermal method. There has been no report on the flux growth of $NaGdSiO_4$ crystals.

During these growth runs, the evaporation amount for each flux was less than 20 wt%. A platinum crucible was found to be undamaged after runs. The alkali fluoride fluxes did not attack a platinum crucible.

The growth of Gd_2SiO_5 crystals from alkali fluoride fluxes was attempted. Crystals of Gd_2SiO_5 were grown from LiF and KF fluxes. Well-formed Gd_2SiO_5 crystals were grown from KF flux. The obtained results showed that KF flux was superior to both LiF and NaF fluxes. It was found that KF was the most suitable to grow Gd_2SiO_5 crystals.

The present work was partially supported by a grant from the Saneyoshi Scholarship Foundation and a Grant-in-Aid for Scientific Research No.02650555 from the Ministry of Education, Science and Culture. We are indebted to Mr. Yoshifumi Kasano for technical assistance in crystal growth experiments.

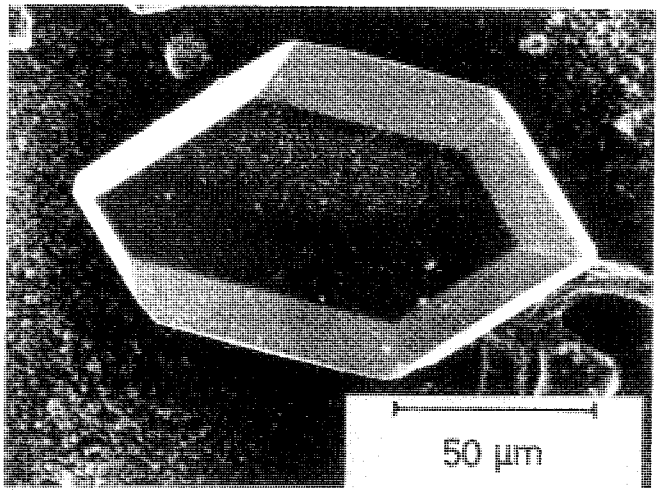

Fig.3. Gd_2SiO_5 crystal grown from KF flux.

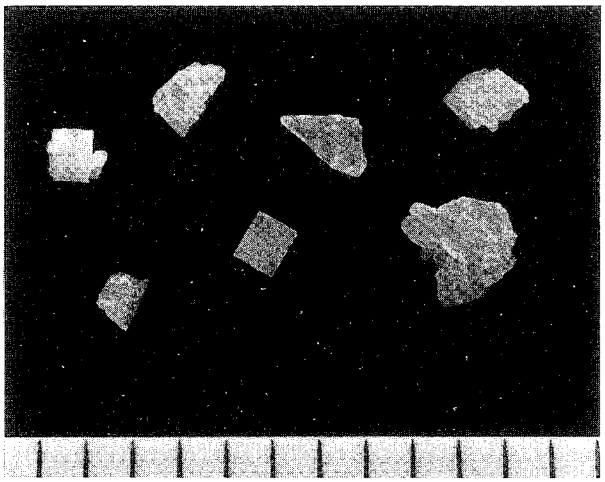

Fig.4. Grown LiF crystals (1 division=1 mm).

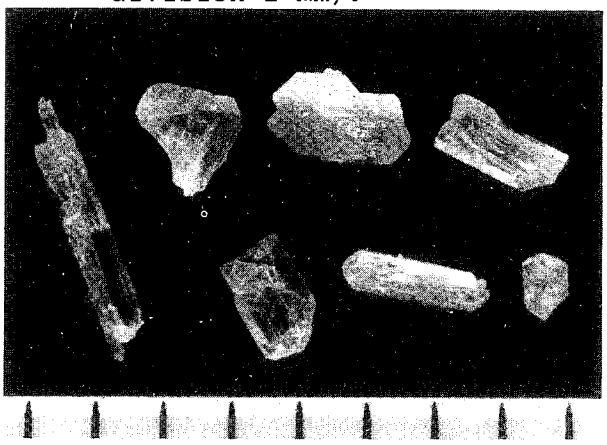

Fig.5. Grown $NaGdSiO_4$ crystals (1 division=1 mm).

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7) JCPDS card 31-534 (Gd_2SiO_5).
8) JCPDS card 4-0857 (LiF).
9) JCPDS card 35-12 ($NaGdSiO_4$).

(Received November 6, 1990)