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SYNTHESIS OF THE FLUORIDE GARNETS $\{Na_3\}[M_2^{3+}](Li_3)F_{12}$ (M=Al, Cr, Fe)

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The synthesis of the fluoride garnets, $\{Na_3\}[M_2^{3+}](Li_3)F_{12}$, in aqueous solution is studied. The garnet for M=Al obtained is identical with that prepared in the solid reaction. Garnets for M=Cr and Fe contain a given amount of water removable at 250° and 235°C, respectively, at temperatures of which the garnet structure remains unaltered but the color and cell constants change.

There are only a few reports on fluoride garnet corresponding to the weakened model of the oxide garnet. Cryolithionite, $\{Na_3\}[Al_2](Li_3)F_{12}$, is the only natural mineral among fluoride garnets. The crystal structure of the mineral determined by Menzer[1)] and Geller[2)] revealed an anomalous site distribution of cations, that is, Li^+ ion occupies a tetrahedral (d-) site and smaller Al^{3+} ion does an octahedral (a-) site. Syntheses of derivatives of cryolithionite $Na_3M_2Li_3F_{12}$ (M=Ti, Cr, Fe etc) were carried out by Pape et al.[3)] but they needed many elaborate laboratory techniques using the solid reaction under HF gas glow. It is expected from the conditions of occurrence of natural cryolithionite that the synthesis of the fluoride garnets should be successfully carried out in the aqueous solution, too. Various attempts for synthesis of fluoride garnets $[Na_3M_2^{3+}Li_3F_{12}]$ from the solution were made, the garnets with M=Al, Cr and Fe being obtained. In this paper, these methods and thermal stability of the garnets obtained are described.

The starting materials are NaOH, $LiOH\cdot H_2O$ and $NaAlO_2$ for $Na_3Al_2Li_3F_{12}$, NaOH, $LiOH\cdot H_2O$ and $NaFeO_2$ for $Na_3Fe_2Li_3F_{12}$ and NaOH, $LiOH\cdot H_2O$ and $CrCl_3\cdot 6H_2O$ for $Na_3Cr_2Li_3F_{12}$. Given mole ratios of the materials are dissolved in water for the first and last garnets and in HCl aqueous solution for the second one. Each resulting solution is added to a mixed solvent of 45% HF aqueous solution and methanol [$HF(45\%)/CH_3OH=1/10$(Vol)] under stirring to give a precipitate, which is filtered off, washed repeatedly with methanol and dried on a steam bath. The X-ray powder diffraction patterns of the products were completely indexed as garnet structure.

Table 1. Cell constants of $Na_3M_2Li_3F_{12}$

M	prepared in solution	heat treated at 300°C	prepared in solid reaction
Al	12.119(4) white	12.120(4) white	12.117(5) white[4)]
Fe	12.407(2) white	12.396(2) brown	12.393(2) white[3)]
Cr	12.334(4) green	12.320(4) dark green	12.328(2) green[3)]

The results of thermo-gravimetric and differential thermal analysis of the garnets prepared are shown in Fig. 1. For $Na_3Al_2Li_3F_{12}$, two endothermic peaks appear, corresponding to the incongruent melting points. For $Na_3Fe_2Li_3F_{12}$ and $Na_3Cr_2Li_3F_{12}$ endothermic peaks are observed at 235°C and 250°C, respectively, in addition to the respective peak of the melting point. When the latter two garnets are heated, weight losses and variations in cell constants and colors are observed at the temperature of the endothermic peak rather than melting point even though the structures remain unchanged. The values of cell constants and the colors of heat treated garnets are listed in Table 1. The weight loss is attributable to water vaporization, since the IR spectra of the garnets prepared in the solution show peaks of stretching and bending vibrations of O-H in water but those of the heated garnet do not. Details on the state of water in the structures of the garnets prepared in the solution are not yet known.

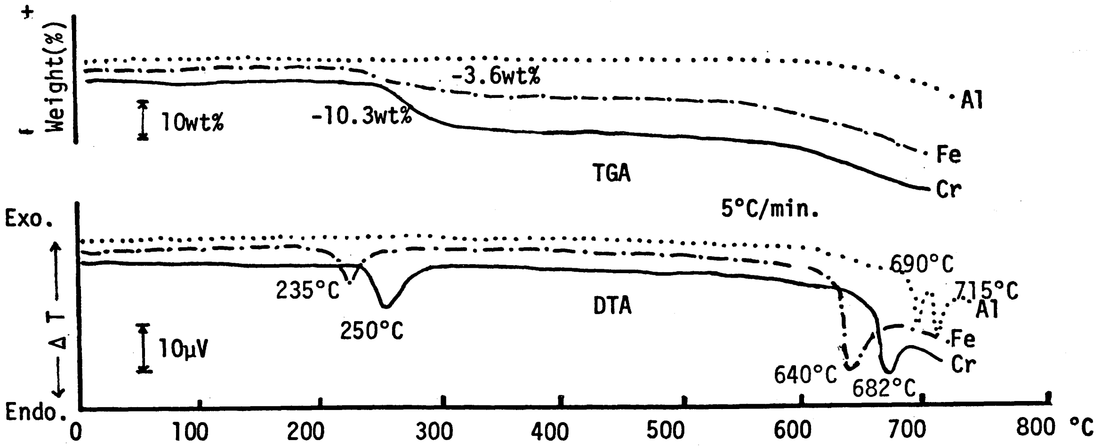

Fig. 1 TG-DTA curve of $Na_3M_2Li_3F_{12}$

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