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Synthesis of Fluoride Garnets $\{Na_3\}[M^{3+}{}_2](Li_3)F_{12}$ (M = Al, Cr, and Fe) from Aqueous Solution and Their Properties

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The garnet-type fluorides, $Na_3M_2Li_3F_{12}$ (M = Al, Cr, and Fe) were synthesized as the coprecipitates of ~1 to 10 μm powders from HF solutions. The garnet structures were always obtained under acidic conditions. The incorporation of water molecules into the structure of the Cr and Fe garnets was observed. After heat treatment at 300°C, very small unknown peaks were observed in the X-ray powder pattern in addition to the garnet phase which had a slightly smaller value of the lattice constant than that of hydrous garnets. From the measurement of magnetic properties and Mössbauer effects, the Fe and Cr garnets were found to be paramagnetic with both ions in the trivalent state. Presentation of infrared spectra of the garnets is also included.

Introduction

The synthesis, crystal growth, phase relations, and physicochemical properties of various fluoride compounds have previously been reported. They are typical ionic crystals and their magnetic and optical properties are easily explained by simple theoretical models (*1*). They possess interesting transparent optical properties (*2*) and promising applications such as laser host materials. The synthesis and growth of single crystals of various fluorides have been accomplished using elaborate techniques. The instability of fluorides for water at high temperatures and the strongly corrosive properties of HF gas require special attention to the apparatus and procedure (*3*). Precipitation from aqueous solutions has also been tried for preparing the complex fluorides (*4*). High-quality samples were easily obtained, but the application of this method to complex fluorides is restricted by the solubility and stability of the starting materials in water.

The fluoride garnets $Na_3M_2Li_3F_{12}$ (M = Al^{3+}, Cr^{3+}, and Fe^{3+}) have been synthesized by Garton and Wanklyn (*9*) and by de Pape et al. (*5*) by means of solid state reactions between fluorides MF_3, LiF, and NaF under vacuum or between M_2O_3 metal oxides (M = transition metals), LiF, and NaF in HF gas. On the other hand, $Na_3Al_2Li_3F_{12}$, cryolithionite, has been known as a unique natural mineral of the fluoride garnet and occurs in hydrothermal deposits associated with minerals of other alumino-fluorides (*6*). This leads us to expect that fluoride garnets can be synthesized in aqueous solution.

In a previous paper (*7*), we described the synthesis of the fluoride garnets in aqueous solution. Here, the details on the method of synthesis of the fluoride garnets and some properties of the garnets obtained are reported.

Experimental

The fluoride garnets $Na_3M_2Li_3F_{12}$ (M = Al^{3+}, Cr^{3+}, and Fe^{3+}) were synthesized as coprecipitates from aqueous solutions, prepared dissolving NaOH, $LiOH \cdot H_2O$ and $NaAlO_2$, $NaFeO_2$, or $CrCl_3 \cdot 6H_2O$. The concentration of M^{3+} in the solution was 2–4 mole%. In the cases of $NaAlO_2$ and $CrCl_3 \cdot 6H_2O$, sufficient solubility of each cation was

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obtained by using pure water, but dilute hydrochloric acid was needed for $NaFeO_2$. The aqueous solution thus prepared, which was strongly basic, was quickly stirred into the mixture of methanol and 45 wt% of hydrofluoric acid. At this point the solution was strongly acidic. The precipitates were immediately obtained. Methanol was added in order to lower the solubility of the fluoride in solution. The precipitates were filtered, washed repeatedly with methanol, and then dried on a steam bath.

The identification of the precipitates was carried out by X-ray powder patterns using Co*Kα* or Cu*Kα* radiation and by examination under the polarizing microscope. The lattice constants were measured by referring to an internal standard of silicon metal.

Differential thermal analysis (DTA) and thermogravimetry (TG) for the products were performed with a heating rate of 5°C/min up to 800°C in air. Magnetic susceptibility measurements were carried out using an automatic recording magnetic balance in the temperature range from 77 to 300°K under a magnetic field of 8 kOe. The Mössbauer effect was measured with a 400-multichannel analyzer at room temperature. For the calibration of the velocity scale of the absorption spectra, Fe foil was used as the standard absorber. The infrared spectra in the range of 4000 to 200 cm^{-1} were obtained on a grating I.S. spectrometer. The powdered samples were vacuum pressed into KBr discs. Frequencies were calibrated against a polystyrene film. The refractive index was determined by the immersion method under the light of a tungsten lamp.

Results

Synthesis

The as-precipitated samples were identified as garnet structures from their X-ray powder patterns. No extra phases were detected from the X-ray patterns nor by examination under the polarizing microscope. In Table I, the lattice constants are summarized. For the Al garnet, the measured lattice constant a_0 is the same as that reported on the sample synthesized by solid state reaction (*9*). On the Cr and Fe garnets, however, the values of the lattice constant measured are slightly larger than those on the samples synthesized by solid state reaction ($a_0 = 12.328(2)$ Å for the Cr and $a_0 = 12.393(2)$ Å for the Fe garnet) (*5*). The garnets precipitated were 1 to 10 μm powders.

When the HF solution was added to the aqueous solution containing Al^{3+}, the final percipitate obtained was a mixture of the garnet (cryolithionite), chiolite ($Na_5Al_3F_{14}$), and cryolite (Na_3AlF_6). By detailed investigation of the phases formed during precipitation, the cryolite and chiolite were found to be precipitated in the basic and neutral ranges, and the garnet was formed only in the acidic range. These results show the dependence of the phase of the precipitate on the pH of the solution.

The precipitates of the above three kinds of garnets were aged at 80°C in aqueous solution. The Fe and Cr garnets decomposed to hydroxides or oxy-hydroxides. The Al garnet showed neither decomposition nor growth of particles.

When the water was evaporated out from an aqueous solution of the mixture of NaF, LiF, and AlF_3 with the garnet composition on a steam bath, the single phase of garnet was also obtained. Because of the low solubilities of the starting fluorides in water, this method was not particularly adequate for the synthesis of the fluoride garnet.

Physical Properties

The measured refractive indexes of the garnets synthesized are listed in Table I.

The temperature dependence of magnetic susceptibility for Cr and Fe garnets was measured in the temperature range from 77 to 300°K. Both garnets were paramagnetic above 77°K and their susceptibilities obeyed the Curie–Weiss law. Their paramagnetic Curie temperature, θ_p, and the effective magnetic moment, μ_{eff}, are given in Table I. In the present result, iron and chromium ions are in a trivalent state with $3d^5$ ($d\varepsilon^3 d\gamma^2$) and $3d^3$ ($d\varepsilon^3 d\gamma^0$) electron configurations, respectively.

The Mössbauer spectrum of the Fe garnet measured at room temperature is shown in Fig. 1. The values of the isomer shift, 0.43 ± 0.02 mm/sec, and quadrupole splitting,

TABLE I

LATTICE CONSTANTS AND MAGNETIC CHARACTERISTICS OF $Na_3M_2{}^{3+}Li_3F_{12}$

	As precipitated				Heat treated at 300°C
M^{3+}	Lattice constant (Å)	Refractive index	θ_p (°K)	$\mu_{eff}(\mu S)$	Lattice constant (Å)
Al	12.119(4)	1.340(3)	—	—	12.120(4)
Cr	12.334(4)	1.418(3)	3(10)	4.1(3)	12.320(4)
Fe	12.407(2)	1.403(3)	0(10)	6.5(3)	12.396(2)

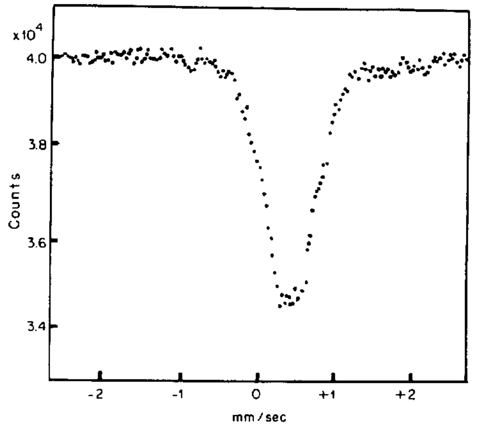

FIG. 1. Mössbauer spectrum of the Fe garnet as precipitated.

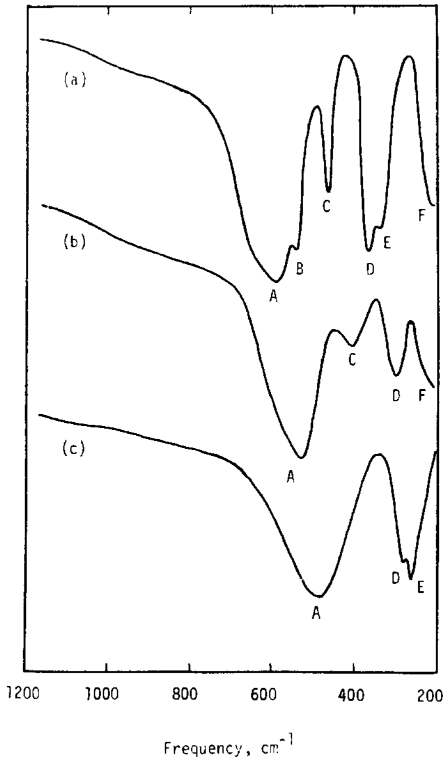

FIG. 2. Infrared spectra of the fluoride garnets as precipitated. (a) Al garnet, (b) Cr garnet, (c) Fe garnet.

0.25 ± 0.02 mm/sec, are similar to those of Fe^{3+}, which is located in the octahedral site of the oxide garnets. Therefore, it is considered that Fe^{3+} occupies the octahedral site in this fluoride garnet, as has been known for Al^{3+} in the Al garnet (*18*).

The infrared spectra observed are shown in Fig. 2. Bands A and B (at 580 and 537 cm^{-1} for the Al, at 530 cm^{-1} for the Cr, and at 478 cm^{-1} for the Fe garnet) are assigned to the asymmetrical stretching vibration ν_3 of the LiF_4 tetrahedron from the similarity in the spectra to the oxide garnets (*10–12*). Although the bands due to the AlF_6, CrF_6, and FeF_6 octahedra which are interlinked by common fluorine atoms have been observed at 660 ~ 600, 585 ~ 520, and 490 ~ 400 cm^{-1}, respectively (*13*), the bands due to isolated similar octahedra in the fluoride garnets are expected to be in a lower frequency region. In the oxide compounds the stretching frequencies of the coordinated groups interlinked by common oxygen atoms are significantly higher than those of isolated groups (*14*). This is confirmed by a semiquantitative calculation by Matossi (*15*). Therefore, the observed bands of D and E (at 365 and 337 cm^{-1} for the Al, at 290 cm^{-1}

for the Cr, and at 282 and 268 cm^{-1} for the Fe garnet) are assigned to stretching vibrations in isolated AlF_6, CrF_6, and FeF_6 octahedra.

The frequencies of each band decreased linearly with increases in the lattice constant of the three garnets. This indicates that an increase in the ionic radius of the cations from Al^{3+} via Cr^{3+} to Fe^{3+} in an octahedral site influences not only the vibrational spectra of the octahedron but also those of the tetrahedron.

Thermal Stability

The typical TG and DTA curves for the three garnets are shown in Fig. 3. For the Al garnet, two endothermic peaks appear at about 695 and 720°C, which agrees well with the decomposition temperature of $Na_3Al_2Li_3F_{12}$ (693°C) and the eutectic point of Na_2AlLiF_6 (713°C) reported by Stinton and Brown (*8*). In the sample quenched from 720°C, Na_2AlLiF_6 was detected. For the Fe and Cr garnets, an endothermic peak and weight loss are observed at about 235 and 250°C, respectively. Beyond these temperatures very small unknown peaks were observed in the powder patterns in addition to those of the garnet phase. The values of the lattice constant of the garnets that were heat treated at 300°C are listed in Table I. The lattice constants of the Fe and Cr garnets after heating at 300°C are slightly smaller than those below 230°C and are the same as those prepared by solid state reaction (*5*).

The weight loss observed in the Fe and Cr garnets (Figs. 3b and c), was attributable to water vaporization, since ir spectra of the as-precipitated garnets showed the peaks for the stretching and bending vibration of the O–H bond, but no peaks on the heat-treated garnets. Considering the amount of included water, the as-precipitated Fe and Cr garnets contain one and two molecules of water per formula unit of garnet, respectively.

At temperatures of about 645 and 690°C, the Fe and Cr garnet, respectively, showed endothermic peaks and weight losses due to decomposition to NaF, LiF, and the respective metal oxide (Fe_2O_3 and Cr_2O_3).

Discussion

Referring to the natural occurrence of cryolithionite, we have succeeded in precipitating the garnet from aqueous solution. But at a room temperature and under an atmospheric pressure, only fine particles were obtained. Aging them in water at 80°C did not lead to the growth of the particle. This may be due to the extremely low solubility of garnets for water. In order to obtain single crystals, growth under hydrothermal conditions is the most applicable. In fact, we have obtained single crystals of cryolithionite with dodecahedral shapes and with the size of 1 ~ 2 mm under hydrothermal conditions (*16*).

The synthesis of the fluoride garnets containing Mn^{3+}, Co^{3+}, and Ni^{3+} was tried by the

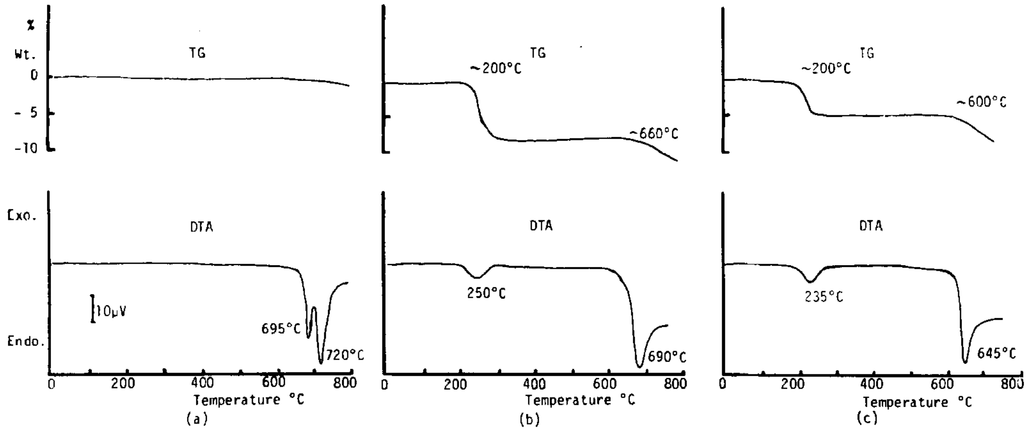

FIG. 3. TG-DTA curves of the garnets as precipitated. (a) Al garnet, (b) Cr garnet, (c) Fe garnet.

same procedure, but garnets were not precipitated. This seems to be due to the change of valency of these cations to the divalent state in aqueous solution.

In the Fe and Cr garnets, incorporation of water molecules into the structure was observed in the precipitates. Cowley and Scott (*17*) reported similar incorporation of water molecules into the cryolite and chiolite which were prepared also from aqueous solution. As the F^- ion has a radius very similar to that of the OH^- ion, it is considered to be replaced by the OH ion in a crystal lattice. We can see these two garnets as the hydrooxyfluorides such as $Na_3M_2Li_3F_{12-x}(OH)_x$. When these hydrooxyfluorides lose their water by heating, they decompose to $Na_3M_2Li_3F_{12}$ and other compounds which have not been identified in the present work. This is consistent with the experimental fact that the lattice constants of the Fe and Cr garnets heated at 300°C are the same as those of anhydrous garnets prepared by solid state reaction (*5*).

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