Journal of Fluorine Chemistry, 13 (1979) 1 – 6

Received: August 28, 1978

SYNTHESIS OF TRANSITION-METAL FLUORIDE GARNETS

Richard H. Langley and George D. Sturgeon
Dept. of Chemistry, The University of Nebraska, Lincoln, Nebraska 68588

SUMMARY

The preparation of the fluoride garnets of the first-row transition metals ($Na_3M_2Li_3F_{12}$) has been studied. The fluoride garnets of manganese (III) and nickel (III) are reported for the first time, leaving only copper (III) garnet unachieved.

By using a guideline based on the electronic configuration of the transition metal ion and its site symmetry in the cubic structure, the ease or difficulty of preparation of these garnets is systematized.

INTRODUCTION

The characterized fluoride garnets comprise a much smaller class, to date, than do oxides with the garnet structure (space group O_h^{10}-Ia3d). Only one fluoride with the garnet structure ($Na_3M_2Li_3F_{12}$) has been observed in nature; it is the mineral cryolithionite in which the trivalent metal ion is that of aluminum. Other fluoride garnets have been synthetically prepared with M = Sc, Ti, V, Cr, Fe, Co, Rh, Ga and In, using a variety of techniques [1-5].

In a review article in 1967, Geller [6] states that, in the garnet structure, the octahedral and tetrahedral sites appear to prefer cations which have spherical or pseudospherical ground-state electronic configurations (i.e., are free of Jahn-Teller distortion). This 'rule' was based on the general lack of success in preparing garnets which involved such Jahn-Teller distorted ions. The usefulness of the 'rule' is lessened, however, by the synthesis of some garnets which are exceptional to it. In spite of these exceptions, this 'rule' may be considered as a guideline to predict the ease of preparation of new garnets.

This work was initiated in order to prepare a complete as possible series of fluoride garnets of the first-row transition-metal trivalent ions for thorough characterization and comparison, and to test and elucidate the limitations on garnet formation attributable to the electronic configuration of the metal ion.

EXPERIMENTAL PROCEDURES

For the first-row transition metals which form trifluorides, Sc to Co, direct fusions of the respective trifluorides with stoichiometric amounts of sodium and lithium fluorides were essayed. The fusion reactions were carried out on thoroughly mixed stoichiometric fluoride components, sealed in evacuated copper tubes. The ampoules were heated to 800° under vacuum and then allowed to slowly cool to ambient temperature. Copper was used because fluorides did not attack it to any significant extent.

In the case of cobalt, a 1:1 mixture of sodium and lithium hexacyanocobaltates(III) was fluorinated under two atmospheres pressure of fluorine gas at 286° for two hours. After cooling, the sample was pulverized and subjected to a repeat of the fluorination treatment.

For nickel and copper, the fluorination procedure was carried out on stoichiometric mixtures of transition metal dichlorides with sodium and lithium chlorides.

All starting materials were commercially available substances except the hexacyanocobaltates which were prepared using a literature method [7].

The identification of the various phases present in product samples was carried out using X-ray powder diffractometry with a Debye-Scherrer camera of diameter equal to 114.6 mm. As appropriate to avoid X-ray fluorescence, either CrK_α or CuK_α radiation was employed. Cubic unit cell parameters were obtained by extrapolating $\underline{a}$ versus the function $\left[\frac{\cos^2\theta}{\theta} + \frac{\cos^2\theta}{\sin\theta}\right]$ to $\theta = 90°$.

RESULTS

Direct fusion of the component substances lead to the preparation of the appropriate garnet for the first six members of the series. But in the case of cobalt, the cobalt trifluoride apparently decomposed to difluoride. The vanadium garnet was found to be especially difficult to prepare in this group. The manganese garnet was only obtained on one occasion and then only in an impure state. There was no evidence that the fluoride melt attacked the copper container. In addition, a qualitative X-ray

Fluorescence analysis of the titanium garnet indicated no significant contamination of the sample by copper.

The cobalt garnet was achieved by the fluorination of the hexacyanocobaltate(III) mixture. The nickel garnet was prepared but, again, only in the presence of major impurities. There was no evidence of a copper fluoride garnet.

In most samples, the presence of lithium fluoride and/or sodium fluoride was detected by the respective powder diffraction patterns. The vanadium garnet was contaminated by an unidentified orthorhombic phase ($\underline{a} \simeq$ 10.4 Å, $\underline{b} \simeq$ 10.8 Å and $\underline{c} \simeq$ 11.2 Å). The manganese sample displayed an unidentified tetragonal phase ($\underline{a} \simeq$ 5.63 Å, $\underline{c} \simeq$ 4.12 Å). The chromium sample also contained some chromium(III) fluoride trihydrate and the iron sample some sodium hexafluoroferrate(III).

The cobalt garnet was a light blue material; this result is in conflict with its reported color of chestnut brown ('marron' in French) [1]. Even when freshly prepared, the cobalt sample contained an unidentified unstable phase which was not characterized. In addition, we observed that the light blue cobalt sample, upon contact with air, changed to a brown material, apparently due to the formation of an oxide or hydroxide. The degeneration of the sample was followed by time interval sampling for X-ray powder diffraction. As the color changed, the intensity of the diffraction lines due to the cobalt garnet decreased and there was a corresponding appearance and intensification of lines which we ascribe tentatively to oxides and hydroxides. Because of the numerous such oxygen-containing species, the coincidence of many of their diffraction $\underline{d}$-spacings and the diffuseness of the diffraction lines we observed because of the largely amorphous nature of the decomposition product, a definite identification of the brown material could not be made.

The inappropriate color of the product iron sample is attributed to the presence of the intensely-colored oxide as a contaminant. An electronic spectrum of this powder indicated the presence of iron(III) coordinated by oxygen [8]. The oxygen may have been present before the fluorination, as elemental oxygen or adsorbed water. Or it may have entered the reaction chamber by diffusion out of, or through, the copper walls of the ampoule.

The unit cell edge lengths and colors of the transition metal garnet products are listed in Table I.

Table I. Cell edges (with standard deviations) and the color of the various fluoride garnets ($Na_3M_2Li_3F_{12}$).

M	a(Å)	color
Sc	12.637 ± 0.014	white
Ti	12.495 ± 0.011	lavender
V	12.434 ± 0.006	light green
Cr	12.340 ± 0.006	dark green
Mn	12.116 ± 0.025	brownish violet
Fe	12.404 ± 0.005	reddish brown
Co	12.290 ± 0.007	light blue
Ni	12.165 ± 0.030	tan

DISCUSSION

Our procedure for the preparation of the titanium garnet is more direct than the two-step synthesis in the literature; our preparation of the cobalt garnet is also different from that used previously [1]. Previous attempts to prepare the manganese and nickel garnets had been unsuccessful. Obtaining the manganese garnet is very difficult and depends upon extremely close control of conditions.

The light blue material resulting from the synthesis attempt for the cobalt garnet is consistent with the reported color of Co(III) in an octahedral fluoride environment [9]. The chestnut color reported for this garnet accords more readily with the presence of mixed fluoride/oxide and hydroxides of cobalt(II) which would be expected to be brown or black. The decrease in the intensity of the diffraction lines as the material changed from blue to brown indicates that the blue material is indeed the garnet and that the brown color is due to contamination. The designation of the blue material as a cobalt fluoride garnet is also supported by infrared absorption spectra [8,10].

The use of a Debye-Scherrer camera and the complications of impurities in the diffraction patterns, which caused ambiguity in the assignment of several diffraction lines, tend to increase the standard deviations in the calculated unit cell parameters in spite of the extrapolation to 90° diffraction angles.

Since the ionic radii of manganese(III) and iron(III) are similar, one would expect the lattice parameters of the corresponding garnets to be similar. However, the manganese(III) garnet has a value of a significantly smaller than the value of a for the iron garnet. This is probably a consequence of the Jahn-Teller effect expected for the manganese(III) ion. Manganese(III) ions in octahedra are known to show a significant variation in ionic radius [11].

A similar explanation may be invoked to explain the difference in the cell parameters of the cobalt and nickel fluoride garnets.

In this series of garnets, titanium, vanadium, manganese, cobalt and nickel would all appear to be exceptions to Geller's 'rule' regarding non-distorting ground-state electronic configurations of the metal ions. In fact, titanium and cobalt garnets are quite straightforward to prepare. However, if one considers the actual S_6 site symmetry of the nominally octahedrally coordinated trivalent ions, the picture clarifies. According to Ballhausen [12], the metal d-orbitals in an S_6 environment are split into the following energy levels: a_g (d_{z^2}) lowest energy, e_g ($d_{xy}, d_{x^2-y^2}$) intermediate, and e_g (d_{xz}, d_{yz}) highest energy.

Therefore, Jahn-Teller distortions would be expected only for the trivalent ions of vanadium, manganese and nickel. These are the ions for which the preparation of the fluoride garnets indeed has proved difficult so that the Geller rule may be considered applicable once the actual site symmetry of the metal ion is invoked. It must be remembered that this 'rule' does not predict whether a particular garnet can or cannot be prepared, but that it gives an indication of the ease of preparation, and, thus, can serve as a useful guide. It does imply that certain lattice types are more 'rigid' than others, and that these 'rigid' lattices resist the incorporation of ions which would require a distortion of the lattice. Conversely, certain other lattice types readily distort to accommodate other ions (i.e., perovskites). Therefore, one must not only consider the ionic radius when attempting an isomorphous substitution, but also the lattice type. This along with other similar rules can be useful aids in the field of inorganic synthesis.

ACKNOWLEDGEMENTS

The financial support of the University of Nebraska-Lincoln Research Council is gratefully acknowledged. The authors thank Mr. Victor Medina who assisted in the analysis of X-ray powder diffraction data.

REFERENCES

1 R. dePape, J. Portier, G. Gauther, and P. Hagenmuller, C. R. Acad. Sc. Paris, <u>265</u> (1967) 1244.

2 R. dePape, J. Portier, J. Grannec, G. Gauther, and P. Hagenmuller, C. R. Acad. Sc. Paris, <u>269</u> (1967) 1120.

3 S. Naka, Y. Takeda, M. Sone, Y. Suwa, Chem. Lett. <u>1975</u> 653.

4 Y. Takeda, M. Sone, Y. Suwa, M. Inagaki, and S. Naka, J. Solid State Chem. <u>20</u> (1977) 261.

5 J. Chassaing, Revue de Chimie Minerale <u>5</u> (1968) 1115.

6 S. Geller, Zeit. fur Kristall. <u>125</u> (1967) 1.

7 G. Brauer, Ed., 'Handbook of Preparative Inorganic Chemistry,' Academic Press, New York, 1963.

8 R. H. Langley, Ph.D. Dissertation, University of Nebraska, Lincoln, Nebraska (1977).

9 F. A. Cotton and M. D. Meyers, J. Am. Chem. Soc. <u>82</u> (1960) 5023.

10 R. H. Langley and G. D. Sturgeon, Spectrochemica Acta, in press.

11 R. D. Shannon, Acta Cryst., A32 (1976) 751.

12 C. J. Ballhausen, 'Introduction to Ligand Field Theory,' McGraw-Hill, New York, 1962.