J. Chosun Natural Sci.
Vol. 12, No. 4 (2019) pp. 101 – 104
https://doi.org/10.13160/ricns.2019.12.4.101

Synthesis and Characterization of a Strontium Iron Fluoride Hydrated, $Sr_2Fe_2F_{10}(H_2O)$

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Abstract

A hydrated strontium iron fluoride, $Sr_2Fe_2F_{10}(H_2O)$ has been synthesized and characterized. The material was synthesized through mild hydrothermal reaction using an aqueous CF_3COOH solution. The material exhibits a one-dimensional structure consisting of chains of corner-shared $Fe^{3+}F_6$ octahedra, isolated $Fe^{3+}F_5(H_2O)$ octahedra, chains of SrF_{10} polyhedra and isolated SrF_8 polyhedra, respectively. Magnetic property measurements on $Sr_2Fe_2F_{10}(H_2O)$ reveals an antiferromagnetic order at T_N of ~2.5 K with a Weiss temperature (θ) of -61.51 K.

Keywords : Fluoride, Hydrothermal Synthesis, Crystal Structure, Antiferromagnet

1. Introduction

Mixed-metal fluoride materials have been studied extensively attributable to their important functional properties such as magnetic, electric, multiferroic, and optical properties[1-3]. Specifically, multiferroic fluoride materials, where at least two primary ferroic- ferroelectric, ferromagnetic, ferroelastic, etc - properties occur in the same material are of topical interest attributable to their applications in advanced devices[4-7]. However, limited researches have been done compared to oxide materials attributable to difficulties of synthesis of new mixed metal fluoride materials. Also well-defined crystal structures as well as characterization of fluoride materials are rarely reported. Thus, new synthetic methods or strategies are required to make new fluoride materials and investigate their physical properties.

Previously, Le Meins et.al., reported crystal structure of $Sr_2Fe_2F_{10}(H_2O)$, which exhibit low-dimensional structure consisting of chains of corner-shared $Fe^{3+}F_6$ octahedra, isolated $Fe^{3+}F_5(H_2O)$ octahedra, chains of SrF_{10} polyhedra and isolated SrF_8 polyhedra. (see Fig. 1)[8]. However, detailed characterization and physical properties of this material were not investigated. Also, their preparation method was quite dangerous because it needs high temperature as well as HF as a solvent.

Recently, we have developed a new synthetic method to synthesize complex fluoride materials using CF_3COOH aqueous solution instead of aqueous HF via a hydrothermal route. We have previously demonstrated that this method can be used to synthesize phase-pure and polycrystalline $BaMF_4$ (M = Mg, Mn, Co, Ni and Zn)[9], $RbFe_2F_6$[10], and $K_4Fe_3F_{12}$[11]. The synthetic method could be applied to synthesize other complex fluoride materials. In this paper, utilizing a similar syn-

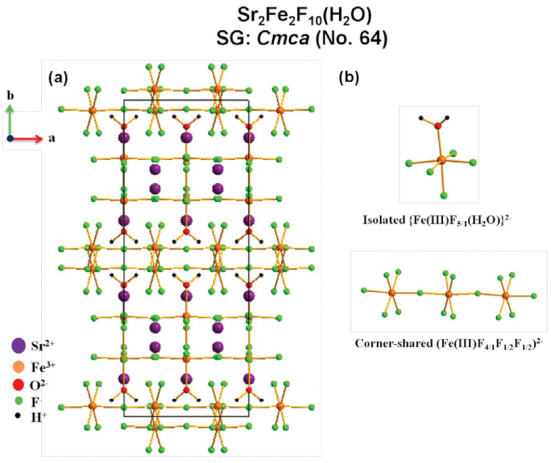

Fig. 1. Crystal structure of $Sr_2Fe_2F_{10}(H_2O)$[8]: (a) ball-and-stick diagram along the *ab*-plane and (b) illustration of two types of Fe(III) octahedra in $Sr_2Fe_2F_{10}(H_2O)$.

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(Received : November 8, 2019, Revised : November 26, 2019, Accepted : December 16, 2019)

thetic technique, we report the successful synthesis and characterization of a hydrated strontium iron fluoride material, $Sr_2Fe_2F_{10}(H_2O)$.

2. Experimental Section

2.1. Reagents

SrF_2 (Alfa Aesar, 99.99 %), FeF_3 (Alfa Aesar, 98 %) and CF_3COOH (Alfa Aesar, 99%) were used without further purification.

2.2. Synthesis

$Sr_2Fe_2F_{10}(H_2O)$ was obtained by a hydrothermal method using a diluted CF_3COOH solution. Polycrystalline $Sr_2Fe_2F_{10}(H_2O)$ was obtained by mixing 0.1432 g (1.14×10^{-3} mol) of SrF_2, 0.3859 g (3.42×10^{-3} mol) of FeF_3 and 3 ml (3.90×10^{-2} mol) of CF_3COOH with 5 ml of H_2O. The resultant solution was placed in a 23-mL Teflon-lined stainless autoclave that was subsequently sealed. The autoclave was gradually heated to 230ºC, held for 24 h, and cooled slowly to room temperature at a rate 6ºC h^{-1}. The mother liquor was decanted from the only solid product, pinkish white polycrystalline powder of $Sr_2Fe_2F_{10}(H_2O)$, was recovered by filtration and washed with distilled water and acetone. The yield was ~50% on the basis of SrF_2. The powder X-ray diffraction pattern on the synthesized phase is in good agreement with the generated pattern from the reported single-crystal data of $Sr_2Fe_2F_{10}(H_2O)$ (see Fig. 2).

2.3. Powder X-ray Diffraction

The PXRD data of $Sr_2Fe_2F_{10}(H_2O)$ were collected on PANalytical X'Pert pro diffractometer using Cu-Ka radiation in the 2θ range of 5 - 70°. A step size of 0.008 degrees (deg) with a scan time 0.3 s/deg was used. No impurities were observed, and the calculated and experimental PXRD patterns are in good agreement.

2.4. Thermal Analysis

Thermogravimetric analysis of $Sr_2Fe_2F_{10}(H_2O)$ were carried out on an EXTAR TG/DTA 6300 (SII NanoThechnology Inc.). About 10 mg of the sample was placed into a platinum crucible and heated under nitrogen atmosphere at a rate of 10ºC min^{-1} to 900ºC.

2.5. Magnetic Measurement

The dc magnetic susceptibility (χ) of $Sr_2Fe_2F_{10}(H_2O)$ was measured as a function of temperature from 2 to 300 K under a field of 100 Oe. All measurements were carried out using Quantum Design Physical Property Measurement System (PPMS).

3. Results and Discussion

3.1. Synthesis

Previously, single crystals of $Sr_2Fe_2F_{10}(H_2O)$ were obtained by a high temperature hydrothermal method using SrF_2, Fe_2O_3 and 11 M HF aqueous solution at 700ºC[8]. However, its preparation was quite dangerous because it needs high temperature as well as HF as a solvent. On the other hand, we were able to synthesize $Sr_2Fe_2F_{10}(H_2O)$ through a mild hydrothermal method using SrF_2, FeF_3 and diluted CF_3COOH aqueous solution at 230ºC for 24 h. Our preparation is quite simple, time-efficient, and highly reproducible. We have previously demonstrated that this method can be used to synthesize other complex fluoride materials[9-11].

3.2. Thermal Analysis

The thermal behavior of $Sr_2Fe_2F_{10}(H_2O)$ was investigated using thermogravimetric analysis (TGA) under nitrogen atmosphere (see Fig. 3).

The decomposition started around 300ºC, which is likely attributable to the loss of crystalline water and/or fluorides. The DTA also showed one endothermic peak at ~400ºC possibly due to the decomposition of the framework. Finally, the powder XRD pattern of the

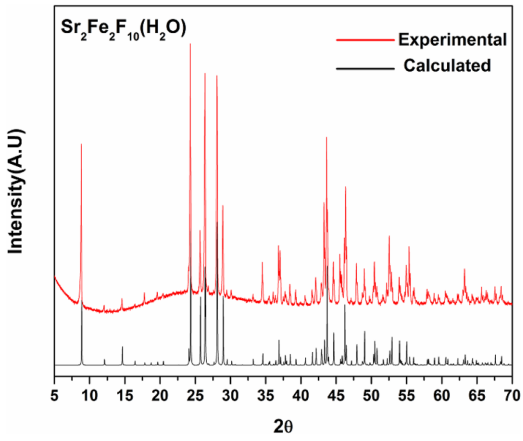

Fig. 2. Experimental and calculated powder X-ray diffraction patterns for $Sr_2Fe_2F_{10}(H_2O)$.

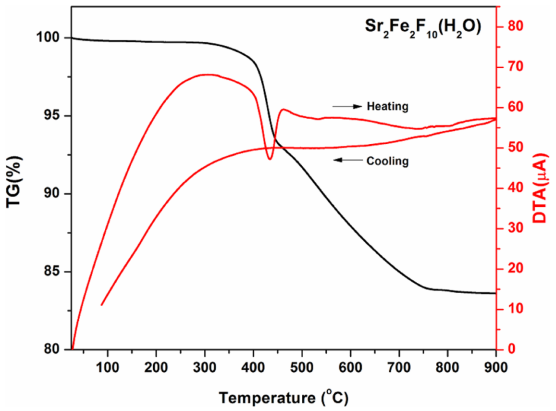

Fig. 3. Thermogravimetric analysis (TGA) diagram for $Sr_2Fe_2F_{10}(H_2O)$.

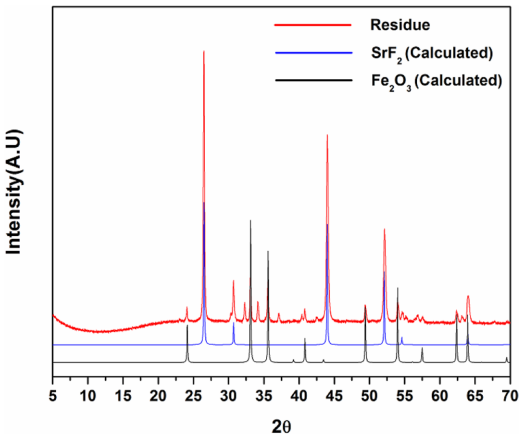

Fig. 4. Powder X-ray diffraction data for final residuals after TGA experiment: $Sr_2Fe_2F_{10}(H_2O)$.

final residue product after TGA experiment showed SrF_2, Fe_2O_3 and unknown phase (see Fig. 4).

3.3. Magnetic Property

The dc magnetic susceptibility of $Sr_2Fe_2F_{10}(H_2O)$ was measured under 100 Oe in the temperature range 2-300 K and is shown as χ and χ^{-1} versus T plots in Fig. 5 and Fig. 6, respectively. $Sr_2Fe_2F_{10}(H_2O)$ exhibits antiferromagnetic behavior with a sharp Néel transition temperature (T_N) at ~ 2.5 K. No significant divergence between ZFC (zero field cooling) and FC (field cooling) magnetization curves is observed.

From the inverse susceptibility versus temperature shown in Fig. 6, the susceptibility data were fit to the Curie-Weiss law, $\chi = C / (T - \theta)$ for T > 100 K, where

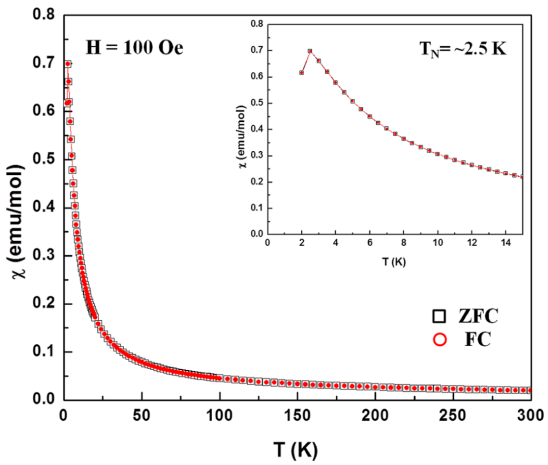

Fig. 5. Temperature dependence of the magnetic susceptibility of $Sr_2Fe_2F_{10}(H_2O)$ measured in 100 Oe. The inset shows a close up of the low-temperature region revealing the ~ 2.5 K Néel temperature.

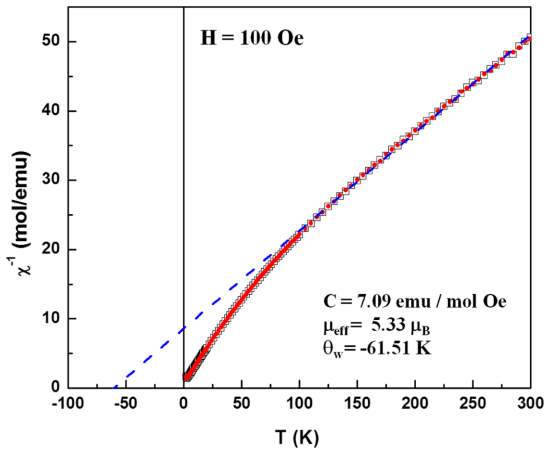

Fig. 6. The inverse magnetic susceptibility of $Sr_2Fe_2F_{10}(H_2O)$ with a Curie-Weiss fit (dash line).

C is the Curie constant and q is the Weiss constant. The Curie constant is 7.09 emu K mol^{-1} and the Weiss constant is -61.51 K, which are extracted from the curve fitting. On the basis of fit, the effective magnetic moment is 5.33 m_B/f.u. The theoretical spin only value is 5.92 μ_B/f.u.(Fe^{3+}), which is in good agreement with the data. The negative Weiss constant indicates AFM interactions, which could arise from the 180° type superexchange couplings between Fe^{3+} and Fe^{3+} connected by F_{2p} orbitals (Fe^{3+} - F_{2p} - Fe^{3+}) according to the Goodenough-Kanamori rule.[12-14]

4. Conclusion

We have synthesized and characterized a hydrated strontium iron fluoride material, $Sr_2Fe_2F_{10}(H_2O)$. This material shows a sharp antiferromagnetic transition at ~2.5 K with θ = -61.51 K. Further compositional modification studies of $Sr_2M(III)_2F_{10}(H_2O)$ (M = Al, Cr, Mn) series are in progress and will be reported elsewhere.

Acknowledgments

This study was supported by research funds from Chosun University, 2018.

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