SrZrO_3 -25% $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$ was chosen as the best composition in the ternary system SrZrO_3 - LaFeO_3 - SrFeO_3 for use as a super-hot-wall type MHD electrode. This material was subjected to a surface temperature of 1800°C in an MHD simulation facility, and was found to perform well. The details of the test results were reported elsewhere^{1), 20)}.

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論文・Paper

Preparation and Magnetic Properties of Strontium Hydrogarnets, $\text{Sr}_3\text{Fe}_2(\text{OH})_{12}$ and $\text{Sr}_3\text{Cr}_2(\text{OH})_{12}$

Shoichi OKAMOTO

(Technological University of Nagaoka
1603-1, Kamitomioka-cho Nagaoka-shi 949-54)

Two strontium hydrogarnets, $\text{Sr}_3\text{Fe}_2(\text{OH})_{12}$ and $\text{Sr}_3\text{Cr}_2(\text{OH})_{12}$, have been prepared under hydrothermal conditions up to 300°C. It has been revealed that very weak negative net magnetic interactions are observed between magnetic ions separated by two oxygen ions. Sr-Fe-hydrogarnet was easily hydrolyzed to form a noncrystalline magnetic substance which resembles to the so-called amorphous ferric hydroxide.

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ストロンチウムハイドロガーネット, $\text{Sr}_3\text{Fe}_2(\text{OH})_{12}$ 及び $\text{Sr}_3\text{Cr}_2(\text{OH})_{12}$ の合成と磁性

岡 本 祥 一

(長岡技術科学大学)

300°C 以下の水熱条件で、2種のストロンチウムハイドロガーネット、 $\text{Sr}_3\text{Fe}_2(\text{OH})_{12}$ 及び $\text{Sr}_3\text{Cr}_2(\text{OH})_{12}$ を合成した。2個の酸素により隔てられた磁性イオン間に、非常に弱い負の磁氣的相互作用が観測された。Sr-Fe-ハイドロガーネットは容易に加水分解されて、いわゆる非晶性水酸化第二鉄によく似た非晶性磁性体に変化した。

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Key-words : $\text{Sr}_3\text{Fe}_2(\text{OH})_{12}$, $\text{Sr}_3\text{Cr}_2(\text{OH})_{12}$, Hydrothermal synthesis, Magnetic properties, Hydrolysis

1. Introduction

Hydrothermal synthesis has been successfully applied for obtaining new types of magnetic compounds^{1)~4)}. Among them, new barium ferrite, $\text{BaO} \cdot 2\text{Fe}_2\text{O}_3$, has been found to be crystallized by the reaction between ferric oxide and barium hydroxide solution²⁾. In making use of strontium hydroxide instead, Sr-Fe-hydrogarnet was crystallized. Further, Sr-Cr-hydrogarnet was crystallized under similar conditions. The present paper describes the preparation and characterization of these two hydrogarnets and related phenomena.

Hydrogarnet, $\text{A}_3\text{B}_2(\text{OH})_{12}$, is cubic, of the space group $\text{O}_h^{10}-Ia\bar{3}d$ with eight molecules in the unit cell, where A represents Ca^{2+} or Sr^{2+} , and B represents Al^{3+} , Ga^{3+} , In^{3+} , Cr^{3+} or Fe^{3+} . There are 16(a) sites where B atoms see octahedral $\bar{3}$ symmetry, and 24(c) sites where A atoms see 222 symmetry. Oxygen atoms or hydroxyl ions are placed on the general positions 96(h) specified by oxygen parameters, x , y and z . Among a group of isomorphous hydrogarnets, oxygen parameters are determined only for Ca-Al-hydrogarnet to be $x=0.035$, $y=0.055$ and $z=0.65^{5)}$.

2. Experimental

2.1 Syntheses and identification

The syntheses involved solid-liquid type reaction between ferric or chromium oxide and aqueous strontium hydroxide solution under hydrothermal conditions.

Sr-Fe-hydrogarnet : To a solution of 0.17 mol of NaOH dissolved in 40 ml of water, 0.02 mol of ferric nitrate dissolved in 20 ml of water was added to form a reddish brown precipitate of ferric hydroxide. Into the suspension thus formed, 0.03 mol of strontium nitrate was added. A 100 ml teflon beaker containing the suspension was placed in an autoclave and heated to 175°C for 48 h, followed by quenching. After the treatment, the pH of the supernatant solution was 13.6.

The solid product was washed with absolute ethyl alcohol and dried at 50°C in air. Washing the product with water should be avoided, because it causes hydrolysis to form an unexpected X-ray amorphous phase, as is described later.

The product contained single crystals up to about 60 μm in diameter together with finer crystals. The crystals were almost transparent and colored light brown in transmission. The crystalline product gave a single phase X-ray diffraction pattern characteristic in hydrogarnet. The lattice constant was $13.225 \pm 0.003 \text{ \AA}$ and agreed fairly well with the value reported⁶⁾.

Sr-Cr-hydrogarnet : A 100 ml teflon beaker containing 0.02 mol of CrCl_3 and 0.08 mol of strontium hydroxide dissolved in 22 ml of water, was placed in an autoclave vessel. The vessel was heated to 275°C for 48 h and quenched to room temperature. Prior to the treatment the vessel was filled with 2 kg/cm² of N_2 gas to protect the chromium ion from oxidation by oxygen in the air. The product was washed with ethyl alcohol and dried at 50°C in air. It was dendrite, colored green in transmission, and gave a single phase X-ray diffraction pattern characteristic in hydrogarnet. The lattice constant was $13.150 \pm 0.005 \text{ \AA}$ and agreed with the value reported⁶⁾.

2.2 Magnetic measurements

Magnetic susceptibility was measured with a magnetic torsion balance in the temperature range from 4.2 K to 300 K. Calibration was made by using pure Gd_2O_3 . The necessary correction for diamagnetism was carried out.

Mössbauer spectra were obtained using a source of ^{57}Co in Cu and a constant acceleration electromagnetic drive in combination with a 400 channel pulse-height analyser operated in time mode. Measurements were carried out at 4.2 K, 77 K and 300 K. Relative velocity was calibrated by the spectrum of $\alpha\text{-Fe}$ at 300 K.

3. Results and discussion

Temperature dependences of the reciprocal molar susceptibility are shown in **Figs. 1** and **2**. The paramagnetic Curie temperatures are observed to be -16 K for Sr-Fe-hydrogarnet, and -8 K for Sr-Cr-hydrogarnet. The weak negative net exchange interactions are observed for both crystals. Their magnetic ordering temperatures, T_N , were lower than 4.2 K. The effective magnetic moments of Fe^{3+} and Cr^{3+} in the hydrogarnet structure are 6.1 and $4.0 \mu_B$, respectively, in good agreement with the theoretical high spin values of 5.9 ($S=5/2$) and $3.8 \mu_B$ ($S=3/2$).

Mössbauer spectra of Sr-Fe-hydrogarnet gave only a single peak down to 4.2 K as is

Fig. 1. Temperature dependence of the reciprocal molar susceptibility of Sr-Fe-hydrogarnet.

Fig. 2. Temperature dependence of the reciprocal molar susceptibility of Sr-Cr-hydrogarnet.

Fig. 3. Mössbauer spectra of Sr-Fe-hydrogarnet.

Fig. 4. A part of the structure model of hydrogarnet.

shown in **Fig. 3**. Slight broadening was observed at 4.2 K. The isomer shift at room temperature is 0.36 mm/s as referred to α -Fe, and is in agreement with the value characteristic of high spin Fe^{3+} surrounded octahedrally by six oxygen ions. The spectra showed no quadrupole splitting. This indicates that the Fe^{3+} in the structure is located in the center of a very regular oxygen octahedron. The slight increase in isomer shift with decreasing temperature is due to the second order Doppler shift.

The structure of hydrogarnet is schematically shown in **Fig. 4**, where the oxygen parameters are chosen to be those given for Ca-Al-hydrogarnet. Structural feature of the hydrogarnet is found to be almost linear Al^{3+} -

$O^{2-}-O^{2-}-Al^{3+}$ arrangement along the cube edges. On the assumption that the whole structure of Sr-Fe-hydrogarnet is analogous to that of Ca-Al-hydrogarnet, the almost linear $Fe^{3+}-O^{2-}-O^{2-}-Fe^{3+}$ arrangement along the cube edges is expected. This expectation is verified by the fact that half the cube edge of Sr-Fe-hydrogarnet, 6.61 Å, is very close to the sum of the ionic sizes of $Fe^{3+}-O^{2-}-O^{2-}-Fe^{3+}$, 6.9 Å ($=0.65+2.80+2.80+0.65$). Zigzag $Fe^{3+}-O^{2-}-O^{2-}-Fe^{3+}$ arrangement, on the contrary, can be seen in the structure along the body diagonals. A similar argument can also be applied to Sr-Cr-hydrogarnet.

Goodenough has suggested that when a pair of magnetic ions is separated by two anions, super exchange is still possible, though very much weakened⁷⁾. For Sr-Fe- and Sr-Cr-hydrogarnets, in which a pair of magnetic ions is separated by two oxygen ions, very weak negative net magnetic interactions are observed.

It was noticed that when Sr-Fe-hydrogarnet samples were washed by water, spontaneous magnetization was observed even at room temperature, as is shown in Fig. 5. Careful examination of the X-ray diffraction pattern revealed no trace amount of crystalline substances other than the hydrogarnet. Further, it was found that light brown color of the crystal turned to reddish brown immediately after contact with water. Mössbauer spectra of the sample also showed hyperfine splitting at 4.2 K, as is shown in Fig. 6. The Mössbauer parameters are listed in Table 1.

These magnetic and Mössbauer data to-

Fig. 5. Magnetic properties of a partly hydrolyzed Sr-Fe-hydrogarnet.

Fig. 6. Mössbauer spectra of a partly hydrolyzed Sr-Fe-hydrogarnet.

Table 1. Mössbauer parameters of Sr-Fe-hydrogarnet samples.

		I.S. (Fe) ^a (mm/sec)	ΔE (mm/sec)	HI (kOe)	β ^a (mm/sec)	Population (%)
Sr ₃ Fe ₂ (OH) ₁₂	R.T.	0.36	0	0	0.036	100
	Liq. He Temp.	0.51	0	0	0.046	100
Partly Hydrolyzed Sr-Fe Hydro- garnet	R.T.	0.36	unresolved	0	0.83	--
	Liq. He Temp.	0.52	0	0	0.036	26.0
		0.56	0	492	0.82	74.0

^aβ; half width

gether with X-ray analysis suggest mixing of a noncrystalline magnetic substance in the sample after water treatment. It seems that Sr-Fe-hydrogarnet is hydrolyzed by water and a part of strontium ions in the crystal is dissolved in the water to form the noncrystalline magnetic substance. Similar phenomena are observed when α- or β-NaFeO₂ crystals are placed in water at room temperature⁸⁾.

It is well known that there exists noncrystalline magnetic ferric compound, so-called amorphous ferric hydroxide gel, Fe(OH)₃, which is obtained by precipitation from ferric solution with addition of alkaline solution. Characterization of the hydroxide has been carried out by the present author⁹⁾. Referring to the X-ray, magnetic as well as Mössbauer data, it can be deduced that the noncrystalline substance formed by hydrolysis of Sr-Fe-hydrogarnet is quite similar to ferric hydroxide.

The hydrothermal reaction products of various trivalent metal oxides in alkaline earth

Table 2. Reaction products in alkaline earth hydroxide solutions under hydrothermal conditions up to 300°C.

	Al ₂ O ₃	Ga ₂ O ₃	In ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃
Ca(OH) ₂	H.G. ¹⁰⁾	—	—	H.G. ⁶⁾	H.G. (?) ¹²⁾
Sr(OH) ₂	H.G. ⁶⁾	H.G. ⁶⁾	H.G. ¹³⁾	H.G. ⁶⁾	H.G. ⁶⁾
Ba(OH) ₂	X*	X ¹⁴⁾	H.G. ¹⁴⁾	X*	Ba.Fe ²⁾ , 4)

H.G.; Hydrogarnet (Cubic, Ia3d)

Ba.Fe; BaO·2Fe₂O₃ (Hexagonal, P6₃/m)

X; No reaction was observed.

*; Present author.

hydroxide solutions are summarized in **Table 2**. Although strontium hydrogarnets are formed widely, barium hydrogarnets have not yet been found to be formed except Ba-In-hydrogarnet. Barium ion may be too large to go into dodecahedral site formed by eight hydroxyl ions and have a trend toward forming hexagonally packed or hexagonally close-packed layers together with nine or twelve oxygen ions, as is seen in the structure of BaAl₂O₄¹⁰⁾ or BaO·2Fe₂O₃²⁾, respectively. It was found also that when chromium hydroxide gel is heated with barium hydroxide solution at 350°C, the formation of barium chromate, BaCr₂O₄, was observed.

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論文・Paper

Preferred Orientation of Plate-like Particles in Reflection-type Powder Diffractometry

Yoshito TAKAKI and Hiroshi YAMAGUCHI*

(Department of Physics, Osaka Kyoiku University
4-88, Minami-Kawahori-cho, Tennoji-ku, Osaka-shi, 543
* Department of Earth Science (Mineralogy), Osaka Kyoiku University)

A distribution function characterizing orientation of plate-like powder particles is presented for a usual reflection-type diffractometry when the crystal structure of the specimen has been known. An application of the treatment to the case of Li₂MSiO₄ (M=Mg, Fe, Co, Zn) powders is given, and it is found that the orientation distribution function can be well approximated by an expression of the form, $N(\alpha) = C_0 + C_1 \{1/[1 + p\alpha^2] + 1/[1 + p(\pi - \alpha)^2]\}$, where p , C_0 , C_1 are parameters and α is an angle between the plane of preferred orientation of a particle and that of the sample-holder. It is also shown that the observed diffraction intensities for Li₂MSiO₄ powders are satisfactorily corrected for preferred orientation by using the above expression.

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