

Synthesis, Crystal Structure, Mossbauer Spectrum, and Magnetic Susceptibility of New Pyrochlore Compound $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$

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Received April 5, 2000; in revised form June 15, 2000; accepted July 13, 2000; published online September 30, 2000

A new pyrochlore compound $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ was synthesized by a wet chemical method. The Rietveld method is used to determine the crystal structure of the compound. The crystal structure of $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ belongs to cubic system with a cubic face-centered cell and $a = 1.04138$ nm. Mossbauer spectrum of the ^{57}Fe nucleus in the compound shows the absence of the internal magnetic field in the compound and the low spin state of the trivalent iron ion. The temperature dependence of the magnetic susceptibility indicates the paramagnetic property of $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$. There may be translation from the Fe^{III} ion in a low spin state to the Fe^{3+} ion in a high spin state in the compound when the temperature is higher. © 2000 Academic Press

Key Words: pyrochlore compound; wet chemical synthesis; crystal structure; Mossbauer spectrum; magnetic susceptibility.

1. INTRODUCTION

The general formula of the pyrochlore compound is $\text{A}_2\text{B}_2\text{O}_7$ and the crystal structure of most pyrochlore compounds belongs to a cubic system (1). Some pyrochlore compounds with more complex composition possess a special property, for example, the catalytic activity for the

carbon monoxide oxidation (2). Synthesizing the pyrochlore compounds with complex composition and studying their crystal structure and physical or chemical properties are useful for exploring the new pyrochlore compound with special physical or chemical properties. A lot of pyrochlore compounds with complicated compositions have been synthesized (3–6). We also synthesized a new pyrochlore compound, $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ with simultaneous substitutions of different metal ions for the ion at the A and B sites and determined the crystal structure of the compound by Rietveld refinements. To understand the magnetic property of the $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$, we measured the temperature dependence of the magnetic susceptibility of the compound in the range of 294–1170 K. Mossbauer spectroscopy can give useful information about the valence and spin state of the Mossbauer ion and the structure and magnetic property of the compound. In this paper, we shall give some preliminary results about the synthesis, crystal structure, and Mossbauer spectrum of the ^{57}Fe nucleus and magnetic susceptibility of $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$.

2. EXPERIMENTAL

All the chemicals used in the synthesis are analytical reagent grade. First, the aqueous solution of calcium nitrate,

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neodymium nitrate, iron nitrate, and niobium oxalate is prepared and the concentration of metal ion in the solution is calibrated. The corresponding volumes of the solutions of the calcium nitrate, neodymium nitrate, iron, nitrate and niobium oxalate in an accurate stoichiometric ratio Ca:Nd:Fe:Nb = 1:1:0.5:1.5 are mixed. A certain amount of ethylenediamine and citric acid are added into the above mixed solution. Then, water is evaporated from the mixed solution with stirring at 90°C until a viscous sol is obtained. The sol is dehydrated and heated at 300°C in a muffle furnace to yield an amorphous precursor. At last, the precursor is decomposed at 500°C for 3 h and calcined at 950°C for 8 h. The result is polycrystalline powder.

The powder X-ray diffraction pattern of the sample is recorded by a *D/max-YB* X-ray diffractometer, *CuK α* radiation; Ni filter, the range of 2θ is from 10° to 110° and the scanning step is 0.02°, at room temperature. The whole diffraction pattern is refined according to the Rietveld method by the general structure analysis software (GSAS) (7). The variables and parameters used in the refinement process are the background coefficients, profile coefficients, histogram scale, lattice parameters, zero parameter, linear absorption coefficients, the coordination parameter or oxygen parameter (*X*) for O(48*f*), and the isothermal parameters for five kinds of atoms. The random distribution model is used. The Ca²⁺ and Nd³⁺ ions occupy the 16*d* site with 0.5 occupancy and the Fe³⁺ and Nb⁵⁺ ion occupy the 16*c* site with 0.25 and 0.75 occupancy, respectively. The experimental data and calculated results of Rietveld refinements are listed in Tables 1, 2, and 3, respectively. The experimental diffraction pattern and fitting curve are shown in Fig. 1.

TABLE 1
The Results of Rietveld Refinement for a New Pyrochlore Compound

Formula	CaNdFe _{1/2} Nb _{3/2} O ₇
Crystal system	Cubic
Space group	<i>Fd-3m</i> (No. 227)
<i>Z</i>	8
<i>D</i>	5.45g.cm ⁻³
Cell parameter	<i>a</i> = 10.4138 (3) Å <i>V</i> = 1129.3 Å ³
Step scan increment (°2θ)	0.02
2θ range	10–110°
No. of reflections (CuK α _{1,2})	4299
No. of structure parameters	21
No. of profile parameters	16
<i>R</i> _{wp}	13.2%
<i>R</i> _p	7.8%

Note. $R_{wp} = \sum |Y_o^i - Y_c^i| / \sum Y_o^i$, where Y_o^i and Y_c^i are the observed and calculated intensities, respectively. $R_p = \{ \sum w_i (Y_o^i - Y_c^i)^2 / \sum w_i Y_o^i \}^{1/2}$, where w_i is the weight assigned at each intensity step.

TABLE 2
Site, Occupancy, and Thermal Displacement Factor of the Atoms in CaNdFe_{1/2}Nb_{3/2}O₇

Atom	Site	Occupancy	100 × <i>U</i> _{iso}
Ca	16 <i>d</i>	0.5	1.71
Nd	16 <i>d</i>	0.5	1.21
Fe	16 <i>c</i>	0.25	0.78
Nb	16 <i>c</i>	0.75	0.45
O1	48 <i>f</i>	1.0	0.6
O2	8 <i>b</i>	1.0	0.1

Note. The fractional atomic coordinates of the atoms in the cubic pyrochlore have been given in Ref. 1. The oxygen parameter in CaNdFe_{1/2}Nb_{3/2}O₇ is $x = 0.3228$ for O1(48*f*).

Mossbauer spectrum of the ⁵⁷Fe nucleus in CaNdFe_{1/2}Nb_{3/2}O₇ is recorded by using an Oxford MS-500 Mossbauer spectrometer with a Model 1024 multi-channel analyzer at room temperature. A xenon (methane) proportional counter is used as a detector. The radiation source is ⁵⁷Co/Rh. The velocity is calibrated by an α -Fe foil. Mossbauer spectrum of the ⁵⁷Fe nucleus in CaNdFe_{1/2}Nb_{3/2}O₇ is shown in Fig. 2 and Mossbauer parameters are listed in Table 4.

The temperature dependence of the magnetic susceptibility of CaNdFe_{1/2}Nb_{3/2}O₇ over the range from 294 to 1170 K is measured by a MB-2 automatically recording magnetic balance and the applied magnetic field: $H = 1.2$ T and $HdH/dx = 1.3 \times 10^7$ Oe*Oe/cm. The weight of the sample is 57.2 mg. The temperature dependence of the magnetic susceptibility per gram of CaNdFe_{1/2}Nb_{3/2}O₇ and the plot of the reciprocal susceptibility vs the absolute temperature is shown in Figs. 3 and 4, respectively.

TABLE 3
The Selected Atom Distances and Bond Angles in CaNdFe_{1/2}Nb_{3/2}O₇

Bond	Atom distance (Å)	Bond angle (degree)
Ca–O1	2.6066	
Ca–O2	2.2547	
Nd–O1	2.6066	
Nd–O2	2.2547	
Fe–O1	1.9909	
Nb–O1	1.9909	
O1–O1	2.7146	
O1–O1	2.9132	
O1–O2	3.1471	
O1–Ca(Nd)–O1		62.76
O1–Nb(Fe)–O1		85.96
O1–Nb(Fe)–O1		94.04
O1–Ca(Nd)–O2		80.33
O1–Ca(Nd)–O2		99.67

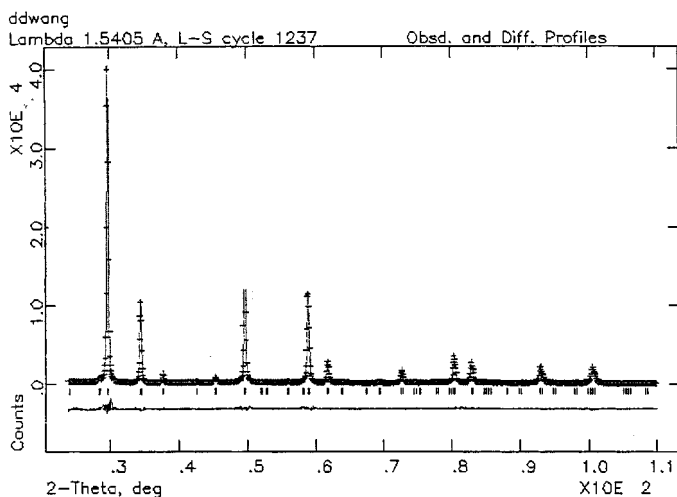


FIG. 1. The experimental powder X-ray diffraction pattern and fitting curve of $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$.

3. RESULTS AND DISCUSSIONS

The results in Table 1 show that the crystal structure of $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ belongs to a cubic system. We have also performed the indexing for main diffraction peaks in the X-ray diffraction pattern of $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ and found that the characteristic reflections (h, k, l) for a typical cubic pyrochlore compound (1), such as (311), (222) (400), (331), (422), (511), (440), (622), (444), (731), (733), and (800), appear and the values of $h, k,$ and l for all the reflections can obey the systematic absences for a cubic face-centered cell; that is, the values of $h, k,$ and l are either odd or even (1). Therefore, $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ possesses the pyrochlore structure although the composition of the compound is more complex. Obviously, the synthesis temperature and calcination time for $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ in a wet chemical process are lower and shorter.

In the pyrochlore compound $\text{A}_2\text{B}_2\text{O}_7$, the A and B ions are surrounded by eight and six large oxygen anions, respec-

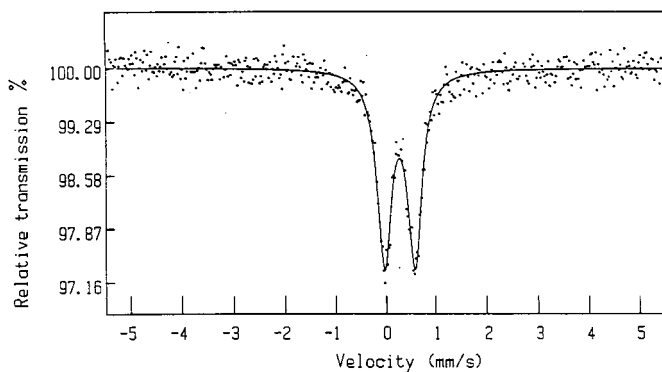


FIG. 2. Mossbauer spectrum of the ^{57}Fe nucleus in $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$.

TABLE 4
Mossbauer Parameters of the ^{57}Fe Nucleus
in $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$

Isomer shift, IS (mm/s)	Quadrupole splitting, QS (mm/s)	Linewidth, W (mm/s)
0.38 ± 0.03	0.61 ± 0.05	0.18 ± 0.05

tively. When the oxygen parameter $X = 0.3125$, the B ion will have a perfect octahedral coordination, whereas, when $X = 0.375$, the B ion is at the center of a highly distorted octahedron (1). In $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$, the Nd^{3+} and Ca^{2+} ions occupy the A site and the Fe^{3+} and Nb^{5+} ions occupy the B site in the lattice. Because the oxygen parameter (0.3225) of $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ is very close to 0.3125, the Fe^{3+} ion may possess a more perfect octahedral coordination in the lattice.

From Fig. 2, we can find that there is only a doublet from the electric quadrupole splitting of the ^{57}Fe nucleus in the Mossbauer spectrum. The absence of the sextets from the magnetic splitting in the Mossbauer spectrum of the ^{57}Fe nucleus implies that there is no internal magnetic field in $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ or the direction of the magnetic moments of all the magnetic ions in the lattice is random. So, the compound must be paramagnetic. As Table 4 shows, the linewidth of two subpeaks from the doublet in the Mossbauer spectrum is not very large. The narrower linewidth indicates that all the Fe^{3+} ions must occupy same site in the lattice or that the coordination environment about all the Fe^{3+} ions in the lattice is very similar. This supports the determination of the crystal structure for $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$. There is a relationship between the isomer shift (IS) and the valence state, spin state, or coordination number of the iron ion. For the trivalent iron ion

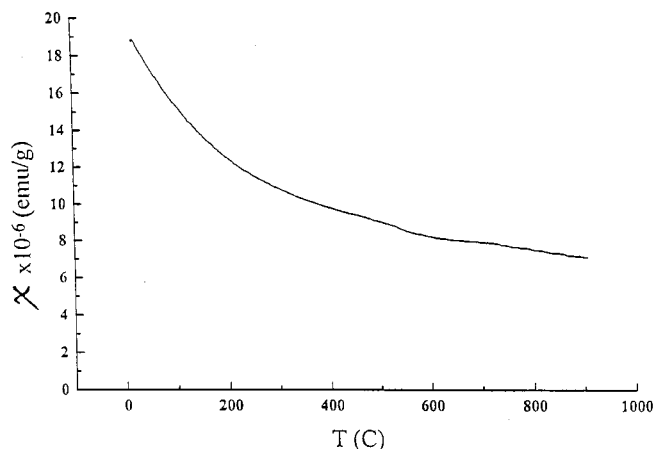


FIG. 3. Temperature dependence of the magnetic susceptibility of $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$.

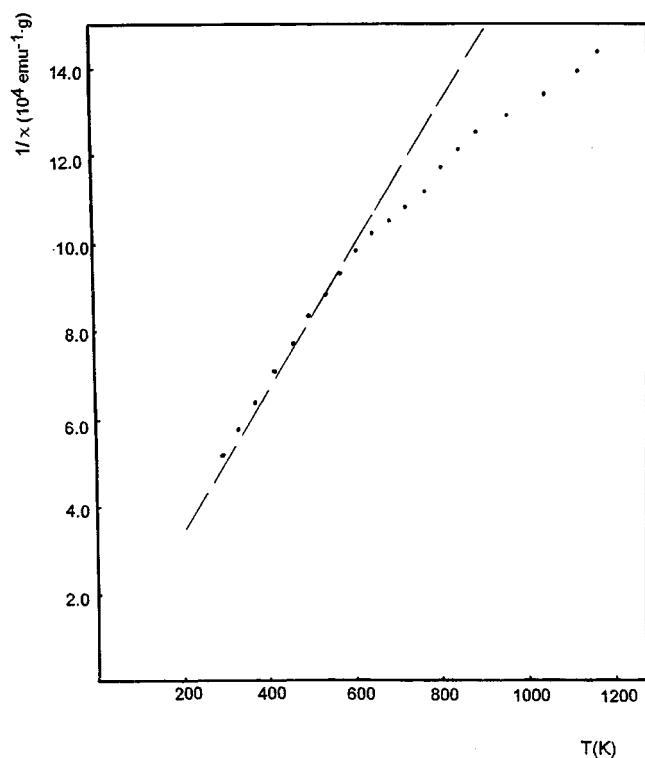


FIG. 4. The plot of the reciprocal susceptibility ($1/x$) of $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ vs the absolute temperature (T).

with six-coordination, IS of the Fe^{3+} ion in high spin state is more than 0.4 m/s (to $\alpha\text{-Fe}$) and IS of the Fe^{III} ion in low spin state is less than 0.4 mm/s. IS (0.38 mm/s) of the ^{57}Fe nucleus in $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ is just less than 0.4 mm/s. However, in some oxides of iron, the isomer shift of the ^{57}Fe nucleus can also be in the region of 0.2–0.6 mm/s for the Fe^{3+} ion with $S = 5/2$ and $-0.15\text{--}0.4$ mm/s for the Fe^{III} ion with $S = 1/2$ at room temperature. Obviously, the observed IS (0.38 mm/s) of the ^{57}Fe nucleus in $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ may belong either to the region of the isomer shift with $S = 5/2$ or to the region of the isomer shift with $S = 1/2$. Hence, we cannot rule out the possibility of the trivalent iron ion in high spin state. However, we have noted that the quadrupole splitting ($QS = 0.61$ mm/s) of the ^{57}Fe nucleus is also just in the range of 0.6–1.7 mm/s for QS of the Fe^{III} ion in low spin state (8). Therefore, the iron ion in $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ may be in a low spin state. As mentioned above, the trivalent iron ion at the B site possesses a perfect octahedral coordination. The five $3d$ orbitals of the iron ion in the crystal field with perfect octahedral coordination will be split into the threefold degenerate t_{2g} orbitals with lower energy and the twofold degenerate e_g orbitals with higher energy. The five d -electrons of the trivalent iron ion may occupy only three t_{2g} orbitals with lower energy and the electron configuration of the Fe^{III} ion in low spin state is $t_{2g}^5 e_g^0$.

As Fig. 3 shows, the temperature dependence of the magnetic susceptibility of $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ decreases monotonously with increasing temperature and the magnetic susceptibilities of the compound in the whole temperature range are very small. This indicates that the compound is paramagnetic. This is also consistent with the results from the Mossbauer spectrum of the ^{57}Fe nucleus in $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$. For the paramagnetic compound, the temperature dependence of the magnetic susceptibility will obey the Curie law or Curie–Weiss law (9). However, we have found that the plot of the reciprocal susceptibility ($1/x$) of $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ vs the absolute temperature (T) is a better straight line only below about 650 K. When the temperature is above 700 K, $1/x$ appears to be too small or the magnetic susceptibility of the compound slightly large. The magnetic susceptibility of the compound always decreases gradually with increasing temperature when the temperature is above T_C or T_N . $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ is synthesized at 950°C (1223 K). So, the above experimental phenomenon cannot be attributed to the thermal decomposition of the compound. There are two kinds of the magnetic ions in $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$: the neodymium and the iron ions. The niobium and calcium ions are not the magnetic ion. The neodymium and iron ions occupy the A and B sites in the lattice, respectively. The A and B ions are very well separated by the larger oxygen anions and there cannot be any direct magnetic interaction between the neodymium and iron ions. The magnetic superinteraction between the Nd^{3+} and Fe^{III} ions through the $\text{Nd}^{3+}\text{--O}^2\text{--Fe}^{\text{III}}$ link may also be rather weak. Because the $4f$ orbitals of the Nd^{3+} ion have been very well shielded by the outer electron shells ($5s^2$ and $5p^6$) and the $4f$ orbitals do not take part in the bonding with the oxygen anion in the $\text{Nd}^{3+}\text{--O}^2\text{--Fe}^{\text{III}}$ link. The Mossbauer spectrum of the ^{57}Fe nucleus in $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ at room temperature has indicated that the iron ion is in low spin state. To explain the above experimental phenomenon, we can assume that the translation of the Fe^{III} ion in low spin state to the Fe^{3+} ion in high spin state may occur at higher temperature due to the thermal excitation. The five $3d$ electrons in the Fe^{III} ion occupy the lower energy levels. When the temperature is higher, the $3d$ electrons can be excited to the higher energy levels due to the thermal excitation. This leads to the translation from the Fe^{III} ion to the Fe^{3+} ion. The magnetic susceptibility of a compound is from the various magnetic ions in the compound. The contribution of the Nd^{3+} ion to the magnetic susceptibility of $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ does not vary with temperature. The contribution of the iron ion to the magnetic susceptibility of the compound will vary with the translation of the Fe^{III} ion to the Fe^{3+} ion. The effective magnetic moment ($1.8 \mu_B$) of the Fe^{III} ion in low spin state is much less than that ($5.9 \mu_B$) of the Fe^{3+} ion in high spin state (9). The increase of the number of the Fe^{3+} ion in the compound must lead to increase of the magnetic

susceptibility of the compound and this partly compensates the decrease of the magnetic susceptibility of the compound with increasing temperature due to other causes. In the case, $1/\chi$ must appear smaller. To excite the Fe^{III} ion to the Fe^{3+} ion needs a certain energy; this is just why the plot of the reciprocal susceptibility of $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ vs the absolute temperature begins obviously to deviate from a straight line only when temperature is above about 700 K.

4. CONCLUSION

$\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ can be synthesized by a wet chemical method at lower temperature. $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ is a new cubic pyrochlore compound with a cubic face-centered cell. Mossbauer spectrum of the ^{57}Fe nucleus in $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ indicates that the trivalent iron ion is in low spin state at room temperature and the compound is paramagnetic. The temperature dependence curve of the magnetic susceptibility of $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ demonstrates the paramagnetic property of the compound. When temperature is higher, the deviation of the plot of the recip-

rocal susceptibility of $\text{CaNdFe}_{1/2}\text{Nb}_{3/2}\text{O}_7$ vs the absolute temperature from the straight line may be mainly attributed to the translation of some trivalent iron from a low spin state to a high spin state due to the thermal excitation.

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