Mössbauer Study of Two Discernable Fe Sites in $CaFe_2O_4$

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Structural and magnetic properties of polycrystalline $CaFe_2O_4$ prepared by the solid state reaction method were studied using powder X-ray diffraction (XRD) and Mössbauer spectroscopy. The structure of $CaFe_2O_4$ belongs to an orthorhombic system (space group: *Pnma*) with the lattice parameters $a = 9.2373$ Å, $b = 3.0237$ Å, and $c = 10.7124$ Å. Results of structural refinement indicate, however, that there are two slightly different iron sites in the sample. The Mössbauer spectrum at 4.2 K shows a hyperfine sextet with a hyperfine magnetic field and an isomer shift of 47.3 T and 0.36 mm/s, respectively. An examination of the spectrum revealed that the line widths of the spectral lines were not uniform. The degree of asymmetric line broadening decreases with increasing temperature, suggesting that the difference in the degree of crystalline distortions between two FeO_6 octahedra is eliminated as the temperature rises.

Keywords : $CaFe_2O_4$, rietveld refinement, Mössbauer spectroscopy

1. Introduction

1:2 compounds of AB_2O_4 is one of the major series of complex oxides that has been most extensively investigated for some time in solid state chemistry [1]. A typical example among these is known as a spinel group, in which divalent and trivalent transition metal ions occupy, respectively, the octahedral and the tetrahedral sites of a cubic closest sphere packing of oxygen ions. Having the same compositional formula, $CaFe_2O_4$ crystallizes entirely differently in the orthorhombic *Pnma* structure made up of distorted FeO_6 octahedra and 8-fold coordinated calcium atoms [2]. An octahedron in the $CaFe_2O_4$-type structure shares edges and corners with adjacent octahedral, forming a very unique layered network similar to that found in the related perovskite materials.

Since the first report on the synthesis of $CaFe_2O_4$ [3], a variety of elements have been found to replace Ca and Fe with crystallizing in the same structure. While the spinel group has been studied so widely, no significant attention has been paid to this compound especially in regards to its electric and magnetic properties. $CaFe_2O_4$ was known to be an antiferromagnetic insulator below the Néel temperature of 160 K [4]. In particular, the edge- and corner-sharing FeO_6 octahedra in the $CaFe_2O_4$-type struc- ture form a very distinctive layered structure similar to that in the perovskite-like materials, in which the magnetic properties of the sample are dependent on the bonding angle and bond length in the O-Fe-O linkage. Therefore, crystallographic information plays a decisive role in better understanding the magnetic behavior of $CaFe_2O_4$. In this study, we examine the Mössbauer spectroscopic characteristics of $CaFe_2O_4$ in relation to the results of a crystallographic investigation.

2. Experiment

A polycrystalline $CaFe_2O_4$ sample was prepared by a solid-state reaction method. A stoichiometric mixture of $CaCO_3$ and Fe_2O_3 powders was intimately ground and fired at 800 °C for calcinations. After regrinding followed by press-molding into a pellet, the precursor was sintered at 1100 °C under dynamic vacuum for 48 hours.

The powder X-ray diffraction (XRD) pattern of the sample was obtained with Cu Kα radiation. The pattern was recorded at room temperature over the range of $10° \leq 2\theta \leq 80°$ with a slow scanning speed of 0.5° advance in 2θ per min. to enhance the resolution. Rietveld profile refinement was carried out using the GSAS program package [5]. A Mössbauer spectrometer of a conventional transmission type was used in the constant acceleration mode over a temperature range from 4.2 K to 300 K. A ^{57}Co source in a Rhodium matrix was used at room temperature.

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3. Results and Discussion

The measured XRD pattern for CaFe$_2$O$_4$ showed a single phase with no trace of impurity. The diffraction pattern was analyzed by the Rietveld method using the orthorhombic space group *Pnma* (No. 62). At first, only profile parameters were refined until a convergence was attained. A profile function formed by a convolution of a pseudo-Voigt shape [5] (CW profile function #3 provided in the package) was used. Once a minimum had been reached for a set of profile parameters, the atomic para-meters such as the atomic positions and isotropic thermal factors were then varied in the next process of refinement. The fractions of the atoms were fixed to the full occupancies under the assumption that there were no vacancies in either the metal sites or the oxygen sites. All the atoms were set to enter in 4c positions. Consequently, 13 profile parameters and 21 atomic parameters were refined simultaneously. The final observed and calculated profiles are illustrated in Fig. 1, and the corresponding crystallographic data are given in Table 1. Lattice para-meters were found to be a = 9.2373 Å, b = 3.0237 Å, and c = 10.7124 Å, which are consistent with those found in other literature [6]. It is possible to visualize the arrange-ment of FeO$_6$ octahedra in CaFe$_2$O$_4$ by means of the results in Table 1. In the CaFe$_2$O$_4$-type structure, FeO$_6$ octahedra were known to share edges at oxygen atoms O2 and O4, and isolated corners via oxygen atoms O1 and O3, thus forming stereoscopic linkages [7]. In particular,
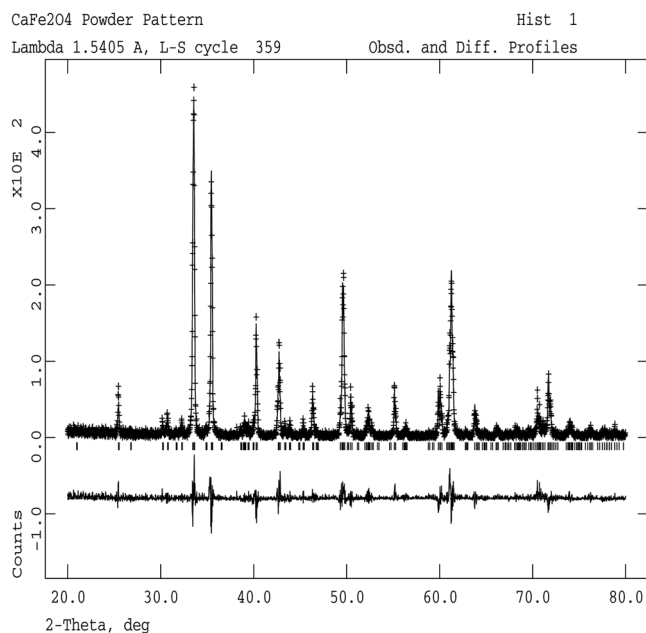
Table 1. Bond distances and bond angles obtained from XRD refinements for CaFe$_2$O$_4$

Bond distances (Å)			
Fe1 - O1	2.140(17)	Fe2 - O1	2.013(12) (×2)
Fe1 - O2	2.096(12) (×2)	Fe2 - O3	2.010(16)
Fe1 - O2	2.051(16)	Fe2 - O4	1.977(16)
Fe1 - O3	2.020(12) (×2)	Fe2 - O4	2.075(12) (×2)

O - Fe - O Bond angles (°)			
O1 - Fe1 - O2	93.6(5) (×2)	O1 - Fe2 - O1	97.3(8)
O1 - Fe1 - O2	173.9(7)	O1 - Fe2 - O3	87.2(6) (×2)
O1 - Fe1 - O3	95.9(6) (×2)	O1 - Fe2 - O4	84.1(5) (×2)
O2 - Fe1 - O2	92.3(7)	O1 - Fe2 - O4	106.2(6) (×2)
O2 - Fe1 - O2	82.2(6) (×2)	O1 - Fe2 - O4	172.4(7) (×2)
O2 - Fe1 - O3	84.6(5)	O3 - Fe2 - O4	85.3(6) (×2)
O2 - Fe1 - O3	88.1(7) (×2)	O3 - Fe2 - O4	159.3(8)
O2 - Fe1 - O3	170.2(7) (×2)	O4 - Fe2 - O4	80.5(6) (×2)
O3 - Fe1 - O3	96.9(7)	O4 - Fe2 - O4	93.5(7)

Fe - O - Fe Bond angles (°)			
Fe1 - O1 - Fe2	117.4(6)	Fe1 - O3 - Fe1	96.9(7)
Fe2 - O1 - Fe2	97.3(8)	Fe1 - O3 - Fe2	131.4(4)
Fe1 - O2 - Fe1	92.3(7)	Fe2 - O4 - Fe2	93.5(7)
Fe1 - O2 - Fe1	97.8(6)	Fe2 - O4 - Fe2	99.5(6)

the edge-sharing connection of the octahedra forms a Fe-O double-chain structure, which is a characteristic of low dimensional compound systems. Putting all of these together, networks of octahedra can be drawn as shown in Fig. 2. An examination of the bond lengths and bond angles indicates that the degrees of distortion within the two types of octahedra are slightly different. The theoretical ratio between these two crystallographic sites is 1:1.

Mössbauer spectra for CaFe$_2$O$_4$ taken at various temper-atures are depicted in Fig. 3. At 4.2 K, the spectrum is comprised of a single magnetic sextet pattern with a hyperfine magnetic field of 47.3 T and an isomer shift of
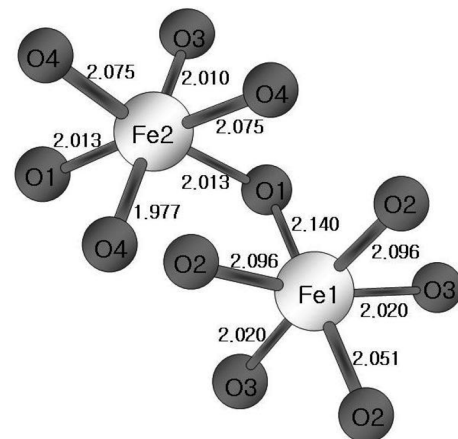

Fig. 1. Observed (⋯), calculated (—), and difference curves in the XRD profile for CaFe$_2$O$_4$ at room temperature.

Fig. 2. Detailed view of Fe octahedral environment in CaFe$_2$O$_4$.

Fig. 3. Mössbauer spectra of $CaFe_2O_4$ at various temperatures.

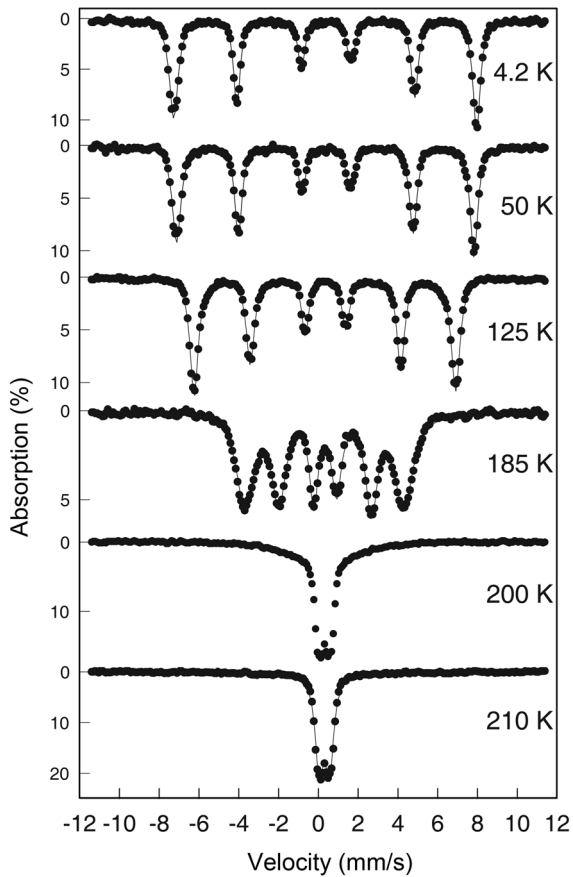**Fig. 4.** Temperature dependence of the difference in line widths between the first and sixth lines $\Gamma(1)$-$\Gamma(6)$ for Mössbauer spectra of $CaFe_2O_4$.

0.36 mm/s, respectively. This spectrum is ascribed to Fe^{3+} ions in the octahedral sites. The magnetic hyperfine field value is somehow smaller than those of the octahedral site in conventional spinels at 4.2 K, which is about 55 T [8].

It should be noted that a slight asymmetric line broadening appears in the spectrum taken at 4.2 K. An examination of the spectrum shows that the first, fifth, and fourth lines along the velocity are somehow broader compared to the sixth, second, and third lines, respectively. On the contrary, the maximum absorptions for corresponding lines show an opposite trend, thus making the formers appear to be sharper. This type of asymmetric line broadening in the Mössbauer spectra has well-known precedent examples, where they were attributed to either dynamic Jahn-Teller distortion or probability distribution for the occupation of neighboring cations around Fe ions [9]. The Fe^{3+} ion in the octahedral site, however, is not a Jahn-Teller ion; all the ions present in $CaFe_2O_4$ are only Fe ions and oxygen ions, ruling out the possibility that the asymmetric line broadening might originate for the two reasons mentioned above. Rather, this can be understood if we take into account the existence of two slightly different Fe sites identified by the XRD analysis. In order
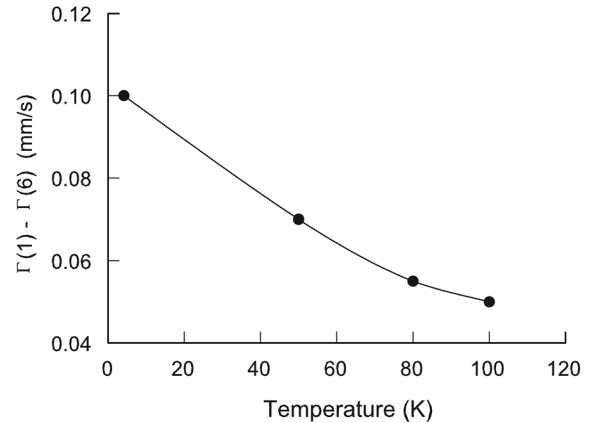
to verify this possibility, Mössbauer spectra were fitted with two sets of sextets of equal absorption areas under the restriction that the intensity of the i-th line equals that of the $(7-i)$th line. The spectra were found to consist of component spectra with the quadrupole splitting of 0.09 mm/s and -0.11 mm/s, which is consistent with the crystallographic result whereby the Fe1 site distorted prolately, and the Fe2 site distorted oblately. Therefore, the asymmetric line broadening of the Mössbauer spectra is ascribed to the difference in the degree of distortions between two FeO_6 octahedra.

Fig. 4 shows the temperature dependence of the difference in line widths between the first and sixth line, $\Gamma(1)$-$\Gamma(6)$ for $CaFe_2O_4$. It is noted that the degree of asymmetric line broadening decreases with increasing temperature up to 100 K, suggesting that the difference in the degree of crystalline distortions between both FeO_6 octahedra is eliminated as the temperature rises. The Néel temperature is determined to be 210 K, which is much higher than reported earlier. Mössbauer spectra above T_N were doublets with equal intensities, while there were no quadrupole splittings within experimental error below T_N, indicating that line broadening can take place due to the distribution of quadrupole splitting from the random orientation of electric field gradient axes.

4. Conclusion

Polycrystalline $CaFe_2O_4$ was studied in order to clarify its structural aspects by means of Mössbauer spectroscopy. Asymmetric line broadening in Mossbauer spectra was observed at low temperature, which was attributed to two different FeO_6 octahedra as identified by the XRD analysis. There might therefore be a considerable differ-

ence in local symmetry for the Fe sites at low temperature, which is discernable by Mössbauer spectroscopy.

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