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Synthesis and Physical Properties of Double Perovskite Pb_2FeReO_6

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An ordered double perovskite Pb_2FeReO_6 was prepared at 6 GPa and 1000 °C. Despite the presence of Pb^{2+} ions at the A site, its crystal structure was determined in a synchrotron X-ray powder diffraction study to be a centrosymmetric one with the space group $I4/m$ ($a = 5.62$ Å and $c = 7.95$ Å). No structural transition to the lower symmetry was observed at temperatures down to 23 K. This compound exhibited a ferrimagnetic transition at 420 K, and its saturation magnetization could be adjusted by using different heat treatments to change the degree of Fe^{3+}/Re^{5+} ordering.

Introduction

The magnetic properties of an ordered double perovskite (ODP) $A_2B'B''O_6$, where $B'O_6$ and $B''O_6$ octahedra are arranged in a rock salt configuration, depend on the combination of B′ and B″ cations. An ODP in which B′ is magnetic and B″ is nonmagnetic is antiferromagnet, but when both of these are magnetic ions, the coupling between them depends on their electronic configurations. Since the B′ and B″ ions are connected through an almost linear B′−O−B″ bond, an ODP is a good model compound for examining the Kanamori−Goodenough rules. The ferromagnetic interaction between Ni^{2+} or Co^{2+} with e_g electrons and Mn^{4+} without e_g electrons makes La_2NiMnO_6 and La_2CoMnO_6 ferromagnetic insulators.[1−4] These compounds attract attention because of their possible spintronics applications, and Azuma and his colleagues tried to synthesize an ODP that also showed ferroelectricity by replacing the La^{3+} of La_2NiMnO_6 with Bi^{3+} because they expected covalent Bi−O bonds and the $6s^2$ lone pair of the Bi^{3+} ion to stabilize a noncentrosymmetric structure.[5] Bi_2NiMnO_6 is indeed a ferromagnetic ferroelectric, with a magnetic T_C of 140 K and a ferroelectric T_C of 485 K.[5] It was first synthesized at 6 GPa and then fabricated as an epitaxial thin film, and a ferroelectric hysteresis loop was observed for the thin film sample deposited on Nb-doped $SrTiO_3$ by using a laser ablation technique.[6]

The Sr_2MReO_6 (M = Cr, Mn, Fe, Ni) compounds, on the other hand, are ferrimagnetic semiconductors.[7−10] In these compounds, the magnetic moments of the M and Re ions are coupled antiparallelly. The magnetic transition temperature and the saturation magnetization at 5 K are 635 K and 0.3 μ_B/fu for Sr_2CrReO_6 and are 400 K and 2.6 μ_B/fu for Sr_2FeReO_6. These compounds are studied intensively because of their large magnetoresistance effects.

In this context, the Pb_2MReO_6 compounds are expected to be polar ferrimagnets with magnetic transition temperatures higher than room temperature because Pb^{2+} has the same character as Bi^{3+}. Sr_2FeReO_6 is a semiconductor, but substituting the smaller Ca^{2+} ions for Sr^{2+} decreases the Fe−O−Re bond angle and thus makes Ca_2FeReO_6 an insulator.[11] Substituting stereochemical Pb^{2+} for Sr^{2+} is also expected to decrease the M−O−Re angle and make Pb_2FeReO_6 an insulator.

Pb_2FeReO_6 synthesized at an ambient pressure is an oxygen-deficient pyrochlore structure,[12] and in this paper, we report a double perovskite phase of Pb_2FeReO_6 synthesized at a higher pressure. Synchrotron X-ray powder diffraction (SXRD) showed that its crystal structure was that of

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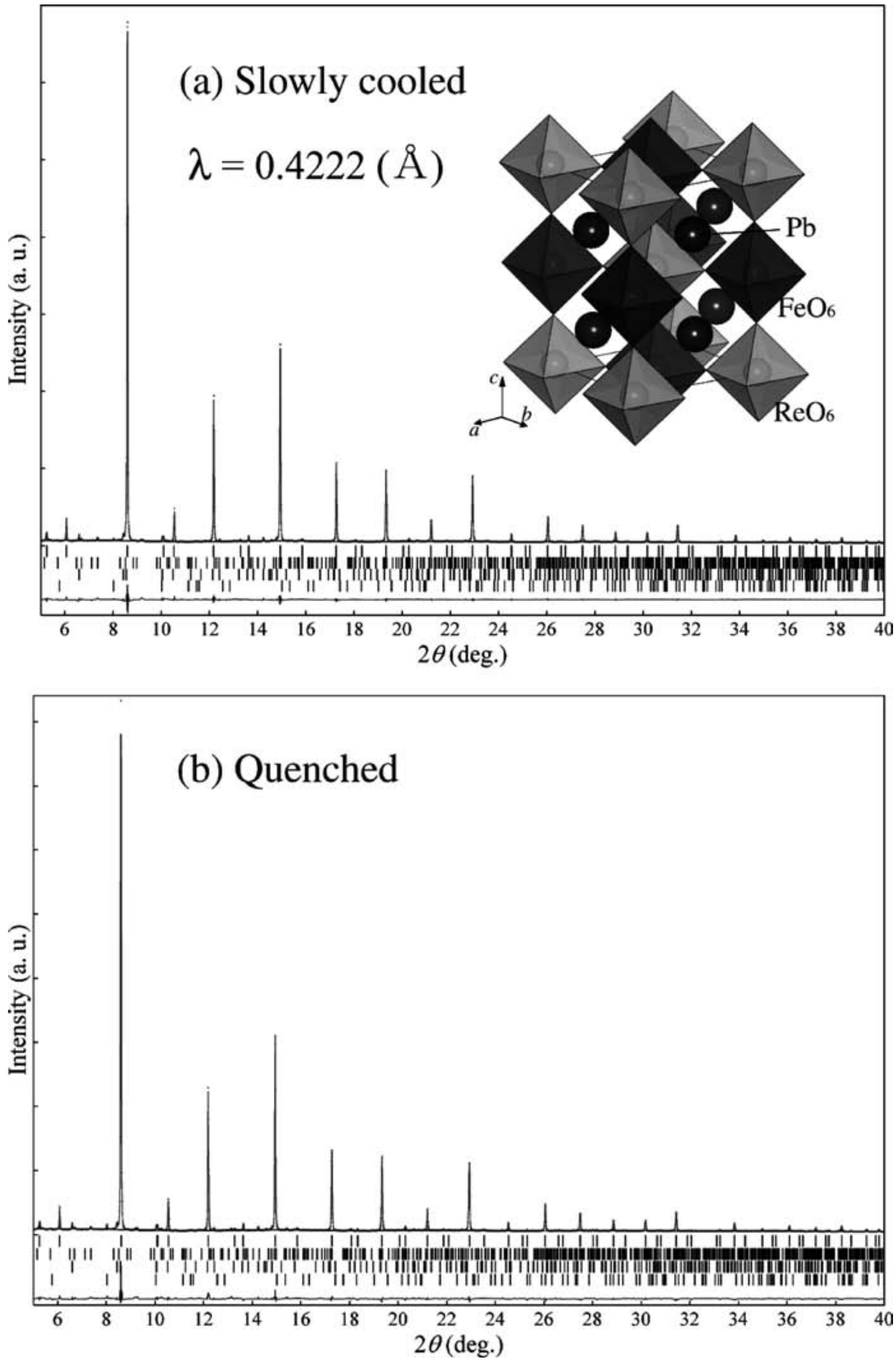

Figure 1. Observed (dots) and calculated (upper solid line) SXRD patterns of (a) slowly cooled and (b) quenched Pb_2FeReO_6 at room temperature (λ = 0.4222 Å). The lower solid line is the difference between the observed and calculated patterns, and the four rows of tick marks respectively correspond (from top to bottom) to the positions of the Bragg reflections of Pb_2FeReO_6, ReO_2, ReO_3, and $Pb(ReO_4)_2$. The inset in a shows the crystal structure of perfectly ordered Pb_2FeReO_6.

an ODP with a density higher than that of the oxygen-deficient pyrochlore. We also found that its saturation magnetization could be adjusted by using different heat treatments to change the degree of Fe/Re ordering.

Experimental Section

Stoichiometric mixtures of PbO (99.9%), ReO_3 (99.9%), Fe_2O_3 (99.999%), and Fe (99.99%) were enclosed in gold capsules that were then compressed to 6 GPa with a cubic-anvil-type high-pressure apparatus. Two samples were prepared using different heat treatments before releasing the pressure: one was kept at 1000 °C for 30 min and then slowly cooled (for 8 h) to 800 °C, whereas the other was rapidly quenched to room temperature. SXRD patterns of both samples were collected with a large Debye−Scherrer camera on beamline BL02B2 of the SPring-8 synchrotron radiation facility in Hyogo, Japan. The crystal structures of the samples were determined by Rietveld analysis with RIETAN-2000 software.[13] XRD data at temperatures between 23 and 293 K were measured with a RINT2500 diffractometer (Cu Kα radiation). The temperature dependence of the magnetic susceptibility was evaluated by using a SQUID

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magnetometer (Quantum Design, MPMS) under an external field of 100 Oe from 300 to 560 K. Magnetization data were measured under magnetic fields between −5 and +5 T at 5 K. The electrical resistivity at temperatures from 5 to 300 K was measured using a four-probe method with a Quantum Design PPMS.

Results and Discussion

SXRD Results at Room Temperature. Despite our expectation, the crystal structure of Pb_2FeReO_6 turned out to be the same as that of Sr_2FeReO_6: centrosymmetric, with the space group $I4/m$, and with a $(2)^{1/2}a \times (2)^{1/2}a \times 2a$ unit cell, where a is the lattice constant of a cubic perovskite. It should be noted that another Pb_2MReO_6 compound, Pb_2MnReO_6, is also reported to have a centrosymmetric space group of $P2_1/n$[14] and that simple perovskites $PbCrO_3$[15] and $PbMnO_3$[16] are centrosymmetric. The peak positions could also be explained assuming a $2a \times 2a \times 2a$ cell, but the refinement in the cubic space group that is allowed for an ODP ($Fm\bar{3}m$)[17] was not successful even if the splitting of the Pb position was assumed. Figure 1 shows the results of Rietveld analysis for both the slowly cooled and quenched samples. Trace amounts of impurities were found: ReO_2 (2.6%), ReO_3 (0.23%), and $Pb(ReO_4)_2$ (0.68%) for the slowly cooled sample and ReO_2 (2.8%), ReO_3 (0.57%), and $Pb(ReO_4)_2$ (0.47%) for the quenched sample. The lattice parameters of the slowly cooled sample were a = 5.6180(2) Å and c = 7.9413(1) Å, while those of the quenched sample were a = 5.6180(1) Å and c = 7.9458(2) Å. In the refinement, the position of Pb^{2+} was split into two in the c direction, as done for $PbZrO_3$,[18] because this significantly reduced the R factors. We also assumed mixing of Fe and Re in both the B′ and B″ sites. The Fe major site was named Fe1/Re1, while the Re major site was Re2/Fe2. Linear constraints $g_{\mathrm{Fe1}} + g_{\mathrm{Re1}} = g_{\mathrm{Re2}} + g_{\mathrm{Fe2}} = 1$ and $g_{\mathrm{Fe1}} = g_{\mathrm{Re2}}$, where g is the occupancy, were applied.

The g values were found to differ significantly between the slowly cooled and the quenched samples. The occupancy ratio of the Fe major site in the slowly cooled sample was Fe/Re = 0.897:0.103, while that in the quenched sample was Fe/Re = 0.704:0.296, as summarized in Table 1 with the atomic positions. This shows that the degree of the ordering in the B site improved with slow cooling. The bond lengths and the angles are summarized in Table 2. The bond valence sums (BVS)[19] for the Fe1/Re1 and Re2/Fe2 sites of the slowly cooled sample were respectively 3.24 and 4.27. Since the ionic radius of Fe^{3+} is larger than that of Re^{5+}, it is reasonable to think that the valences of the Fe and Re ions are respectively +3 and +5 and that the mixing at the sites results in the BVS overestimating the Fe valence and underestimating the Re valence.

Table 1. Refined Structural Parameters for (a) Slowly Cooled and (b) Quenched Pb_2FeReO_6[a]

(a) slowly cooled sample; space group, $I4/m$; a = 5.6180(2) Å; c = 7.9413(1) Å; R_{wp} = 4.81%; R_{I} = 1.37

atom	site	g	x	y	z	B (Å^2)
Pb	8g	0.5	0	0.5	0.2244(1)	0.8
Fe1	2a	0.897(1)	0	0	0	0.5
Re1	2a	0.103	0	0	0	0.5
Re2	2b	0.897	0	0	0.5	0.5
Fe2	2b	0.103	0	0	0.5	0.5
O1	8 h	1	0.246(15)	0.252(11)	0	1
O2	4e	1	0	0	0.247(17)	1

(b) quenched sample; space group, $I4/m$; a = 5.6180(1) Å; c = 7.9458(2) Å; R_{wp} = 6.45%; R_{I} = 5.73

atom	site	g	x	y	z	B (Å^2)
Pb	8g	0.5	0	0.5	0.2232(1)	0.8
Fe1	2a	0.704(2)	0	0	0	0.5
Re1	2a	0.296	0	0	0	0.5
Re2	2b	0.704	0	0	0.5	0.5
Fe2	2b	0.296	0	0	0.5	0.5
O1	8 h	1	0.252(19)	0.258(15)	0	1
O2	4e	1	0	0	0.235(5)	1

[a] The isotropic atomic displacement parameters (B) were fixed.

Powder XRD Results at Low Temperatures. Structural analysis based on SXRD at room temperature indicated that the high-pressure synthesis stabilized an ODP phase, but contrary to our expectation, the structure of that phase was centrosymmetric. A low-temperature XRD study was carried out in order to examine the possibility that the ferroelectric transition temperature was below room temperature. The results are shown in Figure 2. No change in the diffraction pattern was evident at temperatures down to 23 K. The lattice parameters changed monotonously (Figure 3), confirming the absence of a ferroelectric structural transition.

Magnetic Properties. The temperature dependence of the magnetic susceptibility from 300 to 560 K is shown in Figure 4. Both the slowly cooled and the quenched samples showed ferromagnetic-like inflections at about 420 K, well above room temperature.

The magnetization curves measured at 5 K are shown in Figure 5. The slowly cooled sample showed a saturation magnetization of 2.4 μ_B/fu, whereas the quenched sample showed one of 1.2 μ_B/fu. These values were considerably smaller than the 7 μ_B/fu expected for ferromagnetic ordering of Fe^{3+} and Re^{5+} magnetic moments. This suggests that the observed ferromagnetic-like behavior is the ferrimagnetic ordering. The observed saturation magnetizations were compared with the calculated values based on the refined degrees of Fe/Re ordering. The trivalent Fe ion carries 5 μ_B (S = 5/2), and the pentavalent Re ion carries 2 μ_B (S = 1). Considering the Fe1/Re1 and Re2/Fe2 ratios in the slowly cooled sample, one would expect the average magnetic moment to be $5 \times 0.897 + 2 \times 0.103 = 4.691$ on the Fe1/Re1 site and $2 \times 0.897 + 5 \times 0.103 = 2.309$ on the Re2/Fe2 site. Since these moments are coupled antiparallelly, the saturation magnetization is calculated to be $4.691 - 2.309 = 2.382$ (μ_B/fu). Similarly, the

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Table 2. Bond Lengths (Å) and Angles (deg) for (a) Slowly Cooled and (b) Quenched Pb_2FeReO_6

(a) slowly cooled sample		(b) quenched sample	
$Fe1O_6$ Octahedra		$Fe1O_6$ Octahedra	
Fe1−O1 (×4) = 1.98(7)	Fe1−O2 (×2) = 1.96(14)	Fe1−O1 (×4) = 2.0(2)	Fe1−O2 (×2) = 1.87(4)
$Re2O_6$ Octahedra		$Re2O_6$ Octahedra	
Re2−O1 (×4) = 1.99(7)	Fe1−O1−Re2 = 178.6(8)	Re2−O1 (×4) = 1.9(2)	Fe1−O1−Re2 (×4) = 179(1)
Re2−O2 (×2) = 2.01(14)	Fe1−O2−Re2 = 180	Re2−O2 (×2) = 2.10(4)	Fe1−O2−Re2 (×2) = 180

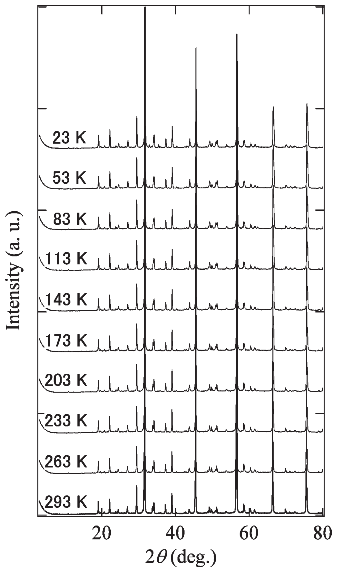

Figure 2. Powder XRD patterns for the slowly cooled Pb_2FeReO_6 measured at temperatures between 23 and 293 K.

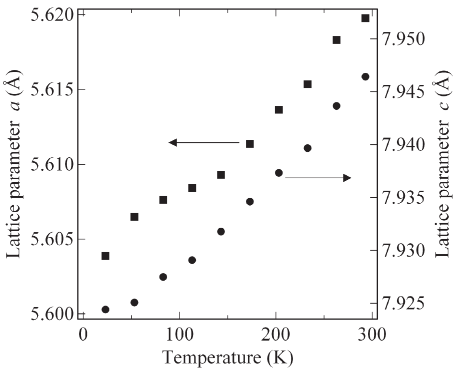

Figure 3. Temperature dependence of the lattice parameters of the slowly cooled Pb_2FeReO_6.

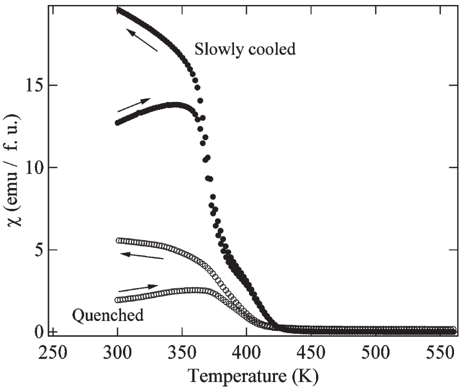

Figure 4. Temperature dependence of the magnetic susceptibility of (●) slowly cooled and (○) quenched Pb_2FeReO_6 under an external field of 100 Oe.

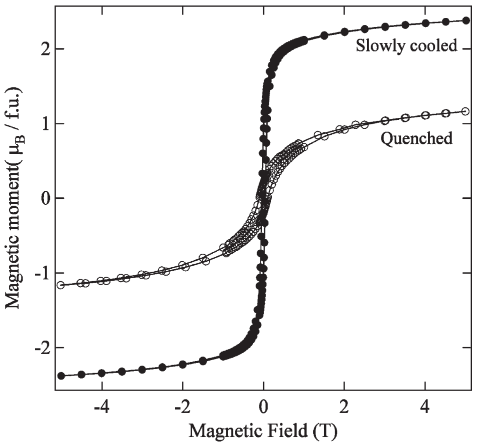

Figure 5. Magnetization curves at 5 K for (●) slowly cooled and (○) quenched Pb_2FeReO_6.

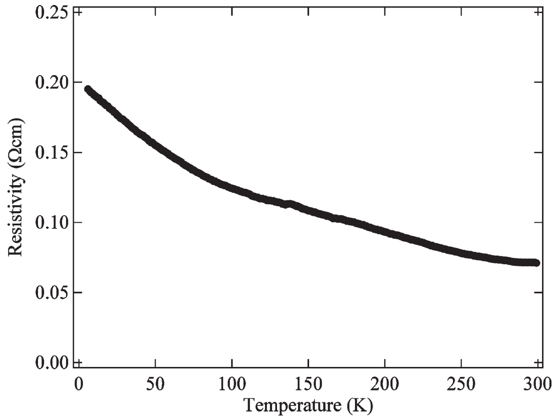

Figure 6. Temperature dependence of the electric resistivity of slowly cooled Pb_2FeReO_6.

saturation magnetization for the quenched sample is calculated to be 1.224 μ_B/fu. These values are in good agreement with the observed ones of 2.4 and 1.2 μ_B/fu. These results indicate the ferrimagnetism of Pb_2FeReO_6.

Electric Resistivity. The temperature dependence of the electric resistivity of the slowly cooled sample is shown in Figure 6. The resistivity was about 0.07 Ω cm at room temperature and showed semiconductive behavior similar to that of Sr_2FeReO_6.[20] The quenched sample showed essentially the same semiconductive behavior. Contrary to our expectation that the replacement of Sr by Pb would induce structural distortion and make the system insulating, Pb_2FeReO_6 is semiconducting. This conductivity is due to the linear Fe−O−Re bond (Table 2).

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Conclusion

The crystal structure of an ODP Pb_2FeReO_6 synthesized at 6 GPa was determined in a synchrotron X-ray powder diffraction study to be a centrosymmetric one with the space group $I4/m$, and no structural transition was found at temperatures down to 23 K. The compound was a ferrimagnetic semiconductor with a magnetic $T_C \approx 420$ K, and its saturation magnetization showed excellent agreement with the value calculated assuming partial mixing of Fe^{3+} and Re^{5+} and antiferromagentic ordering of spins at these two sites.

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