$Ba_3NbFe_3Si_2O_{14}$: A New Multiferroic with a 2D Triangular Fe^{3+} Motif

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Single crystals of the new multiferroic $Ba_3NbFe_3Si_2O_{14}$ have been synthesized and characterized via X-ray diffraction, magnetic susceptibility, NMR, and electric polarization measurements. The underlying topology of the Fe^{3+} spins is composed of isolated triangular units stacked in 2D layers along the *c*-direction of the trigonal lattice. Magnetic susceptibility experiments verify the spin state of the iron moments ($S = 5/2$), and large antiferromagnetic interactions with $\theta = -190$ K. A cusp in the susceptibility and lambda-like feature in the specific heat indicate a magnetic phase transition at $T_N = 26$ K, resulting in a frustration index of $f = 7$. A significant amount of spin entropy is released at higher temperatures, suggestive of short-ranged magnetic correlations developing at 50 K (as evidenced by features in the specific heat and thermal conductivity). The development of a spontaneous electric polarization below 26 K verifies that $Ba_3NbFe_3Si_2O_{14}$ is a multiferroic.

1. Introduction

The promise of functional devices based on new multiferroics (materials that possesses both ferroelectricity and magnetically ordered phases)[1] has fueled much recent interest in the synthesis of many new transition metal oxides, such as orthorhombic $RMnO_3$ (R = Tb, Dy),[2,3] hexagonal $RMnO_3$ (R = Ho−Lu, Y),[4−6] $CoCr_2O_4$,[7] $MnWO_4$,[8] $Ba_2Mg_2Fe_{12}O_{22}$,[9] and CuO.[10] Many of these materials are composed of geometrically frustrated spin networks, which in general inhibit the formation of conventional Néel ground states for antiferromagnetically coupled spins. Most of these geometrically frustrated multiferroics ("GF multiferroics") possess 2D layered spins with an underlying triangular motif, such as the hexagonal $RMnO_3$. For example, $YMnO_3$ exhibits a ferroelectric transition at very high temperature $T_C \approx 900$ K. At the same time, the Mn ions in $YMnO_3$ form a natural 2D network of corner-sharing triangles and exhibits an antiferromagnetic transition at a much lower temperature $T_N \approx 70$ K (which leads to a frustration factor $f = \theta_{cw}/T_N = 8.7$). Near this magnetic transition, the sample shows multiferroic properties. Recently, high-resolution neutron diffraction experiments on hexagonal $RMnO_3$ samples show that there is a giant magneto-elastic coupling around the transition, whereas the atoms undergo significant displacements to allow for electric dipole formation.[11] The role of magneto-elastic coupling, and strong short-ranged spin fluctuations inherent to the magnetic frustration, are still being explored in the unraveling of the mechanism of multiferroicity.

Because of the relative scarcity of functional multiferroics with room-temperature applications, there is a considerable effort in the solid state community to find new interesting GF multiferroics. The recent work on the langasite $Ba_3NbFe_3Si_2O_{14}$, first reported in a preliminary set of measurements by Marty et al.[12] has caught our attention as a new example of this class of materials. In this sample, the Fe^{3+} ions, (the only magnetic species) form a network of isolated triangular units in the *ab* plane (Figure 1a), which is a geometrically frustrated spin arrangement. At the same time, the Nb^{5+} cations, with an octahedral coordination of oxygen anions, are located above or beneath these Fe^{3+} triangles along the *c* axis to separate the Fe^{3+} layers (Figure 1b). These structural arrangements are very similar to the arrangements of Mn and rare earth ions (R) in hexagonal $RMnO_3$. A preliminary neutron scattering experiment sug-

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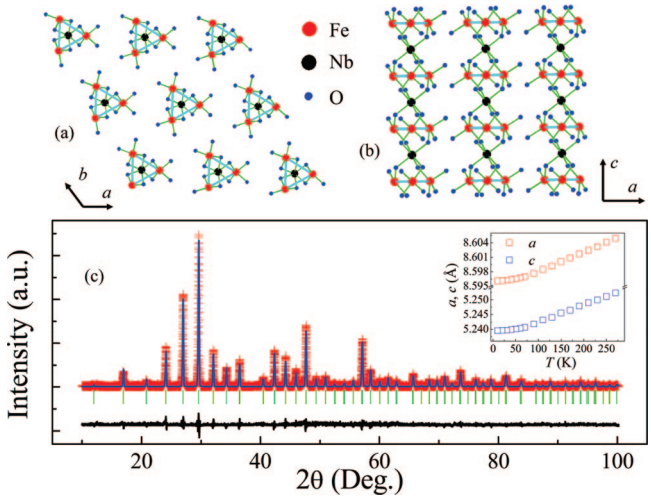

Figure 1. (a) Two-dimensional Fe^{3+} triangles in the *ab* plane for $Ba_3NbFe_3Si_2O_{14}$; (b) along the *c* axis, the NbO_6 octahedra separate the Fe^{3+} layers; (c) room-temperature XRD pattern (plus marks). The solid curves are the best fits from the Rietveld refinement using FullProf. The vertical marks indicate the position of Bragg peaks, and the bottom curves show the difference between the observed and calculated intensities. Inset: the temperature dependence of the lattice parameters.

gested that an incommensurate ordering appears at $T_N = 26$ K,[12] but there have been no published reports in the literature concerning the possibility of multiferroicity in this compound. In this paper, we detail the synthesis of single-crystalline $Ba_3NbFe_3Si_2O_{14}$, with detailed magnetic, transport, and electric property measurements to show that the sample has antiferromagnetic ordering and electric polarization change simultaneously near 26 K, heralding a new GF multiferroic.

2. Experimental Section

Single crystals of $Ba_3NbFe_3Si_2O_{14}$ were grown by the travel-solvent floating-zone (TSFZ) technique. The feed and seed rods for the crystal growth were prepared by solid-state reaction. Stoichiometric mixtures of $BaCO_3$, Nb_2O_5, Fe_2O_3, and SiO_2 were ground together and calcined in air at 950 °C for 24 h. The sample was reground and sintered at 1100 °C for another 24 h in air and cooled to room temperature. It was then reground again into a powder and pressed into a 6 mm diameter 60 mm rod under 400 atm hydrostatic pressure. The rods were finally sintered at 1150 °C. Growth was carried out in air in an IR heated image furnace equipped with two halogen lamps and double ellipsoidal mirrors. The feed and seed rods were rotated in opposite directions at 25 rpm during crystal growth at a rate of 4 mm/h.

The X-ray powder diffraction (XRD) patterns were recorded by a HUBER Imaging Plate Guinier Camera 670 with Cu $K_{\alpha 1}$ radiation. XRD patterns down to 10 K were obtained with a closed cycle cryostat. The XRD data was fit using the program FullProf with typical $R_p \approx 7.0\%$, $R_{wp} \approx 8.0\%$, and $\chi^2 \approx 1.8$. X-ray Laue diffraction was used to confirm the quality of the crystal. DC susceptibility measurements were made with a Quantum Design superconducting interference device (SQUID) magnetometer, with an applied field of 1 T along the *c*-direction. The specific heat and thermal conductivity measurements were performed on a PPMS (Physical Property Measurement System, Quantum Design). ^{93}Nb NMR experiments were completed down to 4 K on oriented single crystals. For the polarization experiments, two electrodes were painted onto the largest surfaces of the single crystals with silver epoxy. The dielectric constant was obtained by measuring the

Table 1. Crystallographic Parameters at Room Temperature for $Ba_3NbFe_3Si_2O_{14}$ with $a = 8.6049(2)$ Å and $c = 5.2523(3)$ Å

site	*x*	*y*	*z*	*B* (Å ^{2})
Ba 3 *e*	0.4343(2)	0	0	1.43(4)
Nb 1 *a*	0	0	0	1.51(7)
Fe 3 *f*	0.7476(7)	0	0.5	1.80(3)
Si 2 *d*	1/3	2/3	0.5428(10)	1.90(7)
O1 2 *d*	2/3	1/3	0.7681(53)	2.05(3)
O2 6 *g*	0.4908(28)	0.8036(24)	0.6639(31)	2.10(2)
O3 6 *g*	0.2118(21)	0.0874(20)	0.7654(35)	2.05(2)

capacitance of our samples as a function of temperature with a manual capacitance bridge, an excitation signal of 30 V at 5 kHz, and a lock-in amplifier. To obtain the temperature dependence of the electric polarization, we measured the pyroelectric current with an electrometer at a rate of 3 K/min after cooling the specimens from 40 to 1.5 K in a static poling electric field ($E_{pol} = 5$ kV/m). The polarization was measured after removing the poling field. Polarization−electric field hystresis loops were measured using a ferroelectric tester (Radiant Technologies Premier II) under the virtual ground mode. Two consecutive sawtooth waves of electric fields (with 1 ms period) were applied. All of the dielectric constant and polarization were measured along the (001) direction.

3. Results and Discussion

The room-temperature XRD pattern (Figure 1c) of $Ba_3NbFe_3Si_2O_{14}$ shows that the sample is single phase with a hexagonal noncentrosymmetric *P*321 structure. The lattice parameters and atomic positions are listed in Table 1.

The DC susceptibility measurement (Figure 2a) on a single-crystalline sample shows a sharp drop at $T_N = 26$ K, which indicates the antiferromagnetic character of the transition. The fit of high-temperature susceptibility to the Curie−Weiss law gives a Weiss temperature $\theta = -190$ K. Clearly, the Fe^{3+} spins on the triangular lattice order at much lower temperature than θ, which demonstrates the presence of geometrically frustration with $f = 7.3$. The calculated effective moment of 5.58 μ_B is slightly smaller than that of

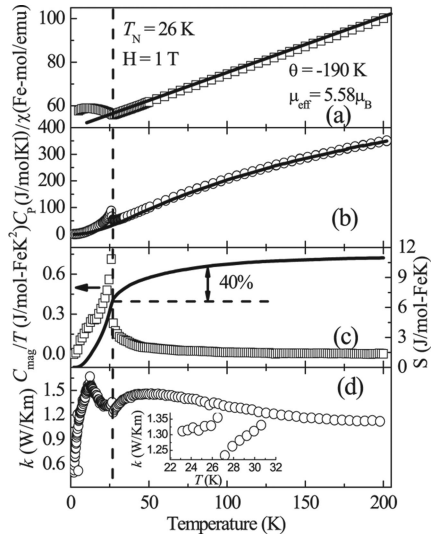

Figure 2. (a) Inverse of the DC susceptibility (open squares). The solid line is the fit by Curie−Weiss law. (b) Temperature dependence of the specific heat for $Ba_3NbFe_3Si_2O_{14}$ (open circles) and $Ba_3Nb(Fe_{0.5}Ga_{0.5})_3Si_2O_{14}$ (solid line). (c) Temperature dependence of the magnetic contribution of specific heat (C_{mag}/T) and the calculated magnetic entropy. (d) Temperature dependence of the thermal conductivity. The inset shows the thermal conductivity near the magnetic transition.

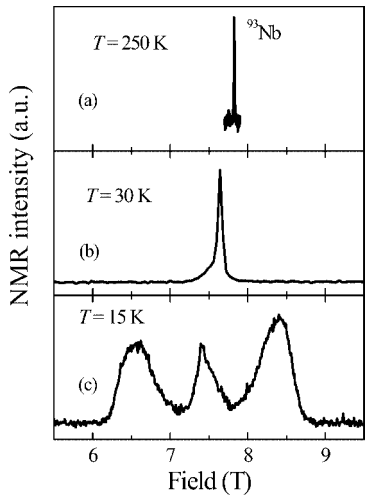

Figure 3. ^{93}Nb NMR signal for $Ba_3NbFe_3Si_2O_{14}$ at (a) 250, (b) 30, and (c) 15 K. The broad spectrum that develops at low temperatures is consistent with an incommensurate magnetic structure below $T_N = 26$ K.

single ion Fe^{3+} ($S = 5/2$, 5.9 μ_B), but this is typical of geometrically frustrated systems.[13]

The specific heat measurement shows a λ-shape peak at $T_N = 26$ K. In order to isolate the magnetic contribution to the specific heat of $Ba_3NbFe_3Si_2O_{14}$, the sample $Ba_3Nb(Fe_{0.5}Ga_{0.5})_3Si_2O_{14}$ was synthesized with the same technique as the parent compound and measured. With 50% substitution of Ga on the Fe sites, the spin interaction of the Fe^{3+} spins has been reduced and the sample shows no magnetic ordering down to 2 K. The resultant magnetic specific heat C_{mag} calculated by treating the specific heat of $Ba_3Nb(Fe_{0.5}Ga_{0.5})_3Si_2O_{14}$ as the lattice contribution is plotted as C_{mag}/T in Figure 2c. The calculated magnetic entropy $S = 11.2$ J/(mol K) is around 80% of the theoretical value 14 J/(mol K) $= R\ln(6)$ for Fe^{3+} ($S = 5/2$). The magnetic component of the specific heat begins to rise above the background at temperatures as high as around 100 K, and the calculated fraction of entropy loss above T_N in the total magnetic entropy denoted as $S(T > T_N)/S$ is around 40%. This large release of entropy above T_N likely arises from the formation of strong spin fluctuations or short-range ordering above T_N. A caveat is needed in the case of $Ba_3Nb(Fe_{0.5}Ga_{0.5})_3Si_2O_{14}$ as a lattice standard: this material is significantly diluted with respect to the magnetic lattice, but the remaining magnetic spins may still contribute toward the entropy. The total magnetic entropy may be slightly underestimated in the parent compound $Ba_3NbFe_3Si_2O_{14}$.

The thermal conductivity $\kappa(T)$ of $Ba_3NbFe_3Si_2O_{14}$ (Figure 2d) shows several features: (i) at high temperatures, $\kappa(T)$ exhibits a relatively weak temperature dependence and a broad maximum at $T \approx 50$ K, and then decreases in magnitude approaching the antiferromagnetic transition; (ii) there is an abrupt jump in $\kappa(T)$ at the antiferromagnetic transition $T_N = 26$ K; (iii) the low-temperature peak of $\kappa(T)$ below T_N shows that long-range magnetic order restores the phonon contribution $\kappa_{ph}(T)$ and may introduce a magnon contribution. The magnitude of the peak of $\kappa(T)$ reflects the high quality of our crystal.[14] Above T_N, the thermal conductivity is dominated by the phonon contribution and should approach a $1/T$ law at high temperatures, typically observed for $T > \theta_D/4$ (θ_D is the Debye temperature), as is seen in $\kappa(T)$ for the diamagnetic insulator $LaGaO_3$.[14] The nearly temperature-independent and suppressed $\kappa(T)$ for $Ba_3NbFe_3Si_2O_{14}$ obviously deviates from the $1/T$ law. This behavior is not unusual for geometrically frustrated spin systems such as $HoMnO_3$ and $YMnO_3$.[6] Sharma et al.[15] have suggested that regions of short-range magnetic order above T_N of $YMnO_3$ can lead to a nanoscale inhomogeneous strain that scatters acoustic phonons. The thermal conductivity calculated by their model with enhanced spin fluctuations above T_N for $YMnO_3$ shows a broad peak above T_N. In a similar manner, the 50 K peak observed here for $Ba_3NbFe_3Si_2O_{14}$ could also be due to spin fluctuations above T_N, which is also consistent with the specific heat data.

The magnetic structure of $Ba_3NbFe_3Si_2O_{14}$ below $T_N = 26$ K has been suggested to a be a long-ranged incommensurate spiral along the *c*-direction (from recent powder neutron diffraction data), with the moments residing within the *ab*-plane.[12] Measurements on single crystals have not been completed yet to verify this claim. However, ^{93}Nb NMR experiments on our single crystals show the development of a broad spectrum beneath 26 K. This is suggestive of many inequivalent Nb sites experiencing different internal magnetic fields. Such a spectrum is not in consistent with an incommensurate ordering, because there is crystallographically only one Nb site per unit cell.

The dielectric constant and polarization measured with the electric field along the *c* direction are plotted in Figure 4a. The dielectric constant shows a broad drop, which begins around 30 K. At the same time, the polarization sharply increases around 24 K. Figure 4b shows the polarization-electric field hysteresis at 40 and 10 K. The appearance of a hysteresis loop at 10 K, which is not shown at 40 K, clearly shows that a spontaneous polarization develops below T_N but the polarization is not saturated for our applied fields. The magnitude of this polarization, nearly 0.6 μC/cm ^{2} at 50 kV/cm, is comparable to the polarization of other studied multiferroics, which is typically on the order of 1×10^{-2} μC/cm ^{2}. These kinds of anomalies which appear near the magnetic transition clearly show that $Ba_3NbFe_3Si_2O_{14}$ is a potential geometrically magnetic frustrated multiferroic system. The polarization changes at 24 K, which is a little lower than $T_N = 26$ K. It is possible that the electronic transition is separated from the magnetic transition, which occurs for many other multiferroic systems.[16]

In the geometrically frustrated multiferroic system $HoMnO_3$, the reason for the appearance of the electric polarization near the magnetic ordering temperature is due to the displacement of Ho atoms along the *c* axis caused by the magneto-lattice coupling. Drawing an analogy with this mechanism we note that in $Ba_3NbFe_3Si_2O_{14}$, the large Nb^{5+} ions separate the Fe^{3+} triangular layers along the *c* axis. A possible bulking or tilting of the NbO_6 octahedra with

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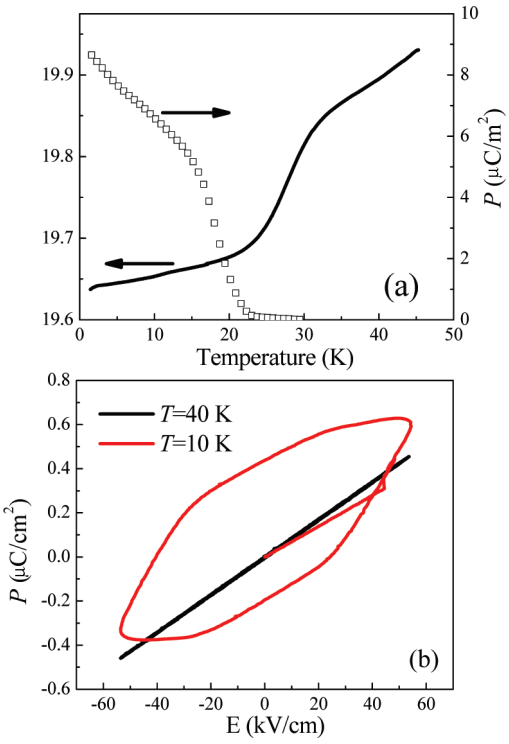

Figure 4. (a) Temperature dependences of the dielectric constant and polarization for $Ba_3NbFe_3Si_2O_{14}$; (b) polarization−electric field hysteresis at 40 and 10 K.

some component along the *c* direction (caused by magneto-lattice coupling) could be the reason for the dielectric constant drop and appearance of the electric polarization at the magnetic transition. Recent studies of $HoMnO_3$ have demonstrated that the magnitude of these atomic displacements are ~0.05−0.09Å, which could be observed by high resolution neutron diffraction but not by conventional powder X-ray diffraction. In the case of $Ba_3NbFe_3Si_2O_{14}$, low-temperature X-ray diffraction patterns have been measured down to 10 K, but no structural phase transition or structural distortion was observed around T_N. The lattice parameters show a smooth variation with decreasing temperature (inset of Figure 1c). The possibility of a lattice distortion on the order of <0.1 Å needs further neutron diffraction measurements to confirm.

4. Conclusions

In summary, the new multiferroic system $Ba_3NbFe_3Si_2O_{14}$ has been synthesized and characterized with a magnetic ordering temperature of $T_N = 26$ K. The coupling of the electric and magnetic degrees of freedom below T_N has been demonstrated through the formation of a spontaneous electric polarization. Future studies of the spin excitation spectrum, along with high resolution structural determinations, would be highly desirable for a complete picture of the mechanism for multiferroicity. As well, the substitution of various transition metal ions to replace the Fe^{3+} spins should result in a new class of materials to explore as geometrically frustrated magnets, or as new candidates for functional magnetic oxides.

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