Effects of cation distribution for $A\text{FeO}_3$ ($A=$Ga,Al)

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(Submitted on 26 December 2006; published online 3 May 2007)

Piezoelectric and ferrimagnetic $A\text{FeO}_3$ ($A=$Ga,Al) samples have been prepared by various annealing conditions and then their hyperfine structures have been investigated by x-ray diffraction and Mössbauer spectroscopy. From the analysis of the x-ray diffraction patterns by Rietveld refinement method, the crystal structure of samples was found to be an orthorhombic structure ($P2_1/n,Pnma_2$) with four different cation sites which are labeled A1 and A2 (predominantly occupied by gallium and aluminum ions) and Fe1 and Fe2 (predominantly occupied by Fe ion). The crystal structure is not changed between the samples, but the occupancies of Fe ions in four cationic sites show slight difference. We notice that the occupancies of Fe ion in A1 tetrahedral site of the samples have an effect on the magnetic properties. From the x-ray diffraction results, the ratios of occupied Fe ions in A1 site were determined to be 9.0%, 9.5%, and 7.8% for slow-cooled GaFeO$_3$, quenched GaFeO$_3$, and AlFeO$_3$, respectively, which accord with the result of Mössbauer spectroscopy. We found that the Néel temperature range decreases from 265 to 250 K, with decreasing the Fe–O–Fe bond angles between GaFeO$_3$ and AlFeO$_3$. Also, external field dependence of magnetic moment curve shows a several-stepped shape which is similar with the exchange-spring magnet. It could be explained distinctly by an effect of Fe ion distribution in hyperfine structure.


I. INTRODUCTION

The orthorhombic AlFeO$_3$ compound is piezoelectric, magnetoelectric, and ferrimagnetic at low temperature and it shows an extremely high magnetic anisotropy. GaFeO$_3$ compound was also reported to show the same properties as AlFeO$_3$ with piezoelectric and ferrimagnetic properties. It has been proposed that the piezoelectric effect originates in the bond arrangement of the metal atoms located on the tetrahedral sites in the cell. From the viewpoint of multiferroics combining ferroelectric and magnetic parameters in the same phase, these AlFeO$_3$ and GaFeO$_3$ compounds have attracted much interest in magnetoelectric materials. The structure of AlFeO$_3$, which is isomorphous to that of GaFeO$_3$, has hexagonal and cubic closed packing of oxygen ions. In the case of Ga and Al doped hematite single crystals, magnetic crystalline anisotropy depends on the angle between the component of a sublattice’s magnetization. The radius of Ga$^{3+}$ (0.62 Å) is almost the same as the Fe$^{3+}$ radius (0.64 Å), but that of the Al$^{3+}$ ion (0.53 Å) is about 10% smaller. On this basis alone, one would anticipate that aluminum would cause more distortion of the lattice than gallium. The large difference between the radii of Fe$^{3+}$ and Al$^{3+}$ ions together with the disorder in the occupation of cation sites, especially for octahedral sites, leads to a local deformation of the lattice. To understand the origin of magnetoelectric effect, the studies about the magnetic structure and correct cation distribution of Fe in each sublattice are inevitable. In this work, we have investigated the magnetic hyperfine structure especially at low temperature and cation distribution of Fe on each crystallographic site of $A\text{FeO}_3$ ($A=$Ga,Al) by Mössbauer spectroscopy and x-ray diffraction. Also, we have studied the change in cation distribution by different heat treatment methods and their magnetic hysteresis curves.

II. EXPERIMENT

The GaFeO$_3$ samples were prepared by solid-state reaction. Powders of high purity (99.999%) of Ga$_2$O$_3$ and Fe$_2$O$_3$ were mixed, ground, pressed into cylindrical pellets, and sintered at 1200–1400 °C for 12–30 h in air. The slow-cooled specimen was finally fired at 1400 °C, and then cooled to room temperature at a rate of 1 °C/min. The quenched specimen was obtained by rapidly quenching at 1400 °C into ice water. AlFeO$_3$ sample has been prepared by the sol-gel method. Iron nitrate nonahydrate ([Fe(NO$_3$)$_3$]·9H$_2$O, 99.9%) and aluminum nitrate nonahydrate [Al(NO$_3$)$_3$·9H$_2$O, 99.99%] were used as starting materials. These were dissolved in mixed solvent system. The solution was refluxed for 24 h at 70 °C and it was dried at 120 °C and calcined for 4 h at 400 °C. Then, the single phase of AlFeO$_3$ was obtained by sintering at 1400 °C for 1 h in air. Crystalline structures of the samples were examined by x-ray diffraction with Cu Ka radiation. Magnetic properties were measured by using a vibrating sample magnetometer (VSM) and Mössbauer spectroscopy. Mössbauer spectra were recorded using a $^{57}$Co source (50 mCi) in Rh matrix with the spectrometer moving at constant acceleration.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction (XRD) pattern for slow-cooled GaFeO$_3$, quenched GaFeO$_3$, and AlFeO$_3$.