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Mössbauer study of polycrystalline multifermoic Ba-doped BiFeO$_3$ compound

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Recently, both ferroelectricity and ferromagnetism in Bi$_{0.7}$Ba$_{0.3}$FeO$_3$ compound were observed at room temperature by $P$-$E$ and $M$-$H$ loop measurements, respectively.[1,2] We prepared a Bi$_{0.7}$Ba$_{0.3}$FeO$_3$ sample by a rapid two-stage solid state reaction method. An analysis of x-ray diffraction pattern by Rietveld refinement method using FULLPROF program shows that the sample has a rhombohedrally distorted perovskite structure with the lattice constant $a = 4.2389$ Å, $c = 13.4256$ Å. The Bi$_{0.7}$Ba$_{0.3}$FeO$_3$ compound have two different crystal sites for iron ions, i.e. the octahedral sites and the oxygen-deficient tetrahedral sites. Mössbauer spectra of Bi$_{0.7}$Ba$_{0.3}$FeO$_3$ was obtained at various absorber temperatures from 4.2 K to the Néel temperature. The Mössbauer spectrum at 4.2 K was fitted to two magnetic components of the magnetic hyperfine fields $H_{hf} = 549$ kOe for octahedral sites and $H_{hf} = 521$ kOe for oxygen-deficient tetrahedral sites. The isomer shift value at room temperature is found to be 0.27 and 0.23 mm/s relative to the Fe metal, which is consistent with high-spin Fe$^{3+}$ charge states. The electric quadrupole splittings ($\Delta E_Q$) are observed with large values of 0.13 mm/s for oxygen-deficient tetrahedral sites compared to 0.03 mm/s for octahedral sites. The Néel temperature ($T_N$) and the Debye temperature are found to be 750 ± 5 K and 321 ± 1 K, respectively. Plots of the reduced magnetic hyperfine field $H_{hf}(T)/H_{hf}(0)$ against reduced temperature $T/T_N$ for octahedral sites of Bi$_{0.7}$Ba$_{0.3}$FeO$_3$ sample showed Brillouin curve $B(S)$ for $S = 5/2$. But it showed the deviation from the Brillouin variation for oxygen-deficient tetrahedral sites. It might be due to spatially complicated spin structure. Magnetization measurements indicate ferromagnetic behavior with hysteresis loops at room temperature. The coercivity value ($H_c$) is 2485 Oe. The strong coercivity force may result from the magnetic anisotropy.