Ferromagnetic Behaviors of BaTiO₃ Nano-Powder

M. Ishii, M. Uehara and Y. Kimishima

Department of Physics, Faculty of Engineering, Yokohama National University, Tokiwadai 79-5, Hodogaya-ku, Yokohama 240-8501, Japan
Fax: 81-45-339-4182, e-mail: kimi@ynu.ac.jp

BaTiO₃ (BTO) nano-particles with the diameter of 15 nm were prepared by mechanical milling using planetary ball mill from the commercial BTO. Rotation speeds were selected as 0, 100, 150, 200, 250 and 300 rpm. Magnetization measurements were performed by Quantum design's SQUID magnetometer. The 200~250 rpm samples showed the maximal saturation magnetization M_s . The 300 rpm sample showed less M_s than those of 200~250 rpm samples. The M_s of 200 rpm sample is tenth larger than the result by previous studies.

Key words: BaTiO₃, vacancy, ferromagnetism, mechanical milling

1. INTRODUCTION

The diluted magnetic semiconductors (DMS) have been studied by the present group for TM-doped non-magnetic oxides, where TM was transition metal element and non-magnetic oxides were ZnO [1,2,4], TiO₂ [1,3], SnO₂ [5] and Cu₂O [6].

In the recent years, the other candidate of room temperature ferromagnetism by vacancies were studied theoretically and experimentally for pure CaO [7], CeO₂, Al₂O₃, ZnO, In₂O₃, SnO₂, HfO₂, TiO₂, ZrO₂ [8-11] and GaN [12].

Meanwhile, much attention was paid to the addition of ferromagnetic property to the ferroelectric substance. Especially, nano-BaTiO₃ (BTO) with vacancies has been expected to be a multi-ferroic system which has the ferromagnetic and ferroelectric properties simultaneously [13-17].

In the present paper, a new method to prepare the nano-BTO (15 nm) system and the production of ferromagnetism in this system are reported.

2. SAMPLE PREPARATION AND EXPERIMENTAL

The powder specimen of commercial BTO was milled by the planetary ball mill (Fritch Pulverisette-7, Germany) with WC vials. The inner diameter and volume of each vial were 40 mm and 45 cm³, respectively, and the WC balls with 15 mm diameter were used as the grinding media. About 2 g of powder specimen of BTO was the starting material. The volume ratio of balls and powder was about 50 : 1. Rotation speed was systematically changed from 0 rpm to 300 rpm. Milling time was kept at 15 min for all of the samples.

The milled powders were characterized by CuK α x-ray powder diffraction (XRD). The superconducting quantum interference device (SQUID) were used for the magnetization measurements between 5 K and 300 K under the field between -50 kOe and 50 kOe.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Mechanical milling effect

Fig.1 XRD patterns of BaTiO₃ before milling and milled at 300 rpm for 15 minutes.

As depicted in Fig.1, the XRD pattern of BTO powder before milling corresponds to the perovskite structure with the lattice parameters of $a = 0.39945$ nm and $c = 0.40335$ nm reported by Megaw [18]. The perovskite structure was held even after milling. The diffraction peaks were broadened as the rotation speed increased from 100 rpm to 300 rpm. These results mean the decreasing of crystallographic correlation length or particle diameter.

Fig.2 shows that the lattice parameter a slightly increases between 0 and 300 rpm. The c -parameter abruptly decreased above 100 rpm and slightly increases above 150 rpm. At 150 rpm and 300 rpm, the c -values are nearly equal to a -parameter.

Fig.2 Lattice parameters of *a* and *c* between 0 rpm and 300 rpm.

These rpm-dependences of lattice parameters might be due to the formation of mechanical defects in the BTO crystal, if the vacancies induce the shrink of inter-atomic distance along *c*-direction above 150 rpm.

Fig.3 Mean crystallographic correlation length *d*.

The mean crystallographic correlation length or particle diameter *d* of BTO phase was estimated from the half widths of XRD peaks by Sherrer's formula. We think that *d* is the averaged diameter of particles. The rpm- dependence of *d* is shown in Fig.3. The *d* of commercial BTO powder was about 27 nm, and it gradually decreased as the rotation speed of ball mill increased. At 300 rpm, *d* decreased to about 15 nm.

From the above results, it was confirmed that the mechanical milling produced nano-BTO powder. Unchanged crystal symmetry of perovskite type shows that the BTO with vacancies can be expected by the mechanical milling method.

3.2 Magnetic properties of milled BaTiO₃

Temperature and field dependences of magnetizations of milled BTO are shown in Figs. 4 and 5, respectively.

Fig.4 Temperature dependences of magnetization under 10 kOe.

Fig.5 Field dependences of magnetization at 300K.

In the thermo-magnetic measurements under 10 kOe of magnetic field, negligibly small magnetizations were observed for pure BTO and the sample milled at 100 rpm. Meanwhile, visible constant magnetizations like as the saturation magnetization of ferromagnet appear between 30 K and 300 K in the samples milled above 150 rpm, as shown in Fig.4. These results show that the ferromagnetic transition temperature T_c is far above room temperature.

Fig. 5 shows the field dependences of magnetization at 300K. The pure BTO and the sample milled at 100

rpm show very small magnetization. But the milled samples above 150 rpm show ferromagnetic behaviors at 300K of room temperature, which is also supported by the results of saturation magnetization M_s , remanent magnetization M_r and coercive field H_c , shown in Figs. 6, 7 and 8, respectively.

The 200 and 250 rpm samples show the largest saturation magnetization M_s of about 1×10^{-2} emu/g which is tenth larger than the result of previous studies [13-15]. The enhancement of M_s should be due to the increasing of O-vacancies, corresponding to the reduction of particle size from 40 nm [14] to about 15 nm.

Fig.6 Rpm dependence of saturation magnetization at 300 K.

Fig.7 Rpm dependence of remanent magnetization at 300 K.

The 300 rpm sample shows less M_s than that of 200 and 250 rpm samples, which means the reduction of vacancy number by heating and oxidation effect in mechanical milling process at high rotation speed.

In Fig. 6, the M_s 's of μ_B per oxygen site are plotted for the rotation speed between 0 and 300 rpm. At 200 and 250 rpm, the M_s has the maximum value of

about $1.4 \times 10^{-4} \mu_B$. If we use the theoretical magnetization per O vacancy of $2 \mu_B$ [14], the concentration of O vacancy is estimated as about 0.007 at%. The rpm dependence of remanent magnetization M_r in Fig.7 shows nearly the same tendency as M_s .

Fig. 8 shows the rpm-dependence of coercive field H_c which is proportional to the anisotropy field. The largest H_c -value of 510 Oe appears at 250 rpm, when the mean crystallographic correlation length or particle diameter of BTO, d is about 15 nm. Since the anisotropy energy becomes largest by the formation of single magnetic domain, the particle diameter of 15 nm is thought to be a critical diameter of the single magnetic domains.

Fig. 8 Rpm dependence of coercive field at 300 K.

4. CONCLUSION

The BaTiO₃ powder was milled by WC balls and vials at 0~300 rpm for 15 minutes. The room temperature ferromagnetism was found in nearly cubic perovskite BTO nano-powder. The lattice parameter a was unchanged between 0 and 300 rpm, but the lattice parameter c steeply decreased at 100 rpm and kept constant above 150 rpm. The grain size of BTO powder was reduced to about 15 nm by the milling above 250 rpm. Enhancement of saturation magnetization M_s at 200~250 rpm might be due to the formation of vacancies. If so, the decreasing of M_s at 300 rpm may mean the reduction of vacancy number by heating and oxidation effect in mechanical milling process at high rotation speed.

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(Received January 7, 2011; Accepted December 3, 2011)