Ferromagnetism of Nano-KNbO₃

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KNbO₃ (KNO) nano-particles with the diameter of about 20 nm were prepared by mechanical milling using planetary ball mill from the commercial KNO powder. Rotation speeds of ball mill were 0 to 300 rpm, where the milling time was kept at 15 minutes. Magnetization was measured by SQUID magnetometer. The 250 rpm milled sample showed a tenth larger saturation magnetization than that of BaTiO₃ with vacancies.

Key words: LiNbO₃, vacancy, ferromagnetism, magnetization

1. INTRODUCTION

The diluted magnetic semiconductors (DMS) has 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. These magneto-electric multi-ferroics are expected to be very useful for device applications.

The various approaches have been done for the production of multi-ferroics. For example, there are TM doping into ferroelectric substance, and usage of exchange interactions at the interface between a ferromagnet and the ferroelectric antiferromagnet [13]. It has been reported that the nano-BaTiO₃(BTO) system with vacancies showed a multi-ferroic property [14-18], where the ferromagnetism might be induced from vacancies at the nano-grain surface. The room temperature ferromagnetism was also observed for the ferro-electric LiNbO₃(LNO) [19].

The KNbO₃ (KNO) is one of the ferro-electric material which can be applied for the acoustic wave transducers, acoustic delay lines, filters and optical phase modulator. The KNO shows a large room temperature dielectric constant of about 10³, and the ferroelectric transition temperature is 708 K [20].

Since there is no report on the induced ferromagnetism from the vacancies in KNO, we report a method to prepare the nano-KNO system and the appearance of ferro-magnetism in this system.

2. SAMPLE PREPARATION

The powder specimen of commercial KNO 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 0.5 g of powder specimen of KNO was the starting material. Rotation speed was systematically changed from 0 rpm to 300 rpm. Milling time was kept at 15 min for all of the samples.

3. EXPERIMENTAL

The milled powders were characterized by CuK α x-ray powder diffraction (XRD). The Quantum Design's SQUID magnetometer was used for the magnetization measurements between 5 K and 300 K under the field between -10 kOe and 10 kOe.

4. RESULTS AND DISCUSSION

4.1 Mechanical milling effects

Fig.1. XRD patterns of KNbO₃ before milling and milled at 250 rpm for 15 minutes.

As shown in Fig.1, XRD pattern shows that of the orthorhombic perovskite type structure [21]. The diffraction peaks of milled LNO were broadened at high rotation speed of 250 rpm. These results mean the decreasing d of the crystallo-graphic correlation length or particle diameter.

Fig.2. Lattice parameters a, b and c of KNbO₃ milled between 0 and 300 rpm.

Fig.2 shows the lattice parameters a , b and c of the KNO powder whose values before milling are 0.571 nm, 0.567 nm and 0.396 nm, respectively. Though the a and b had no systematic variation, the c slightly increased above 250 rpm. This behavior may be due to the formation of mechanical defects in the KNO crystal, because the vacancies shall induce the enlargement of inter-atomic distance along c -direction by the Coulomb repulsive force between the ions with same sign of electric charge.

Fig.3. Mean crystallographic correlation length d of KNbO₃.

The mean crystallographic correlation length or particle diameter d of KNO 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 KNO powder was about 50 nm, and it gradually decreased with the rpm-value. Above 250 rpm, d decreased to about 20 nm.

From the above results, it was expected that the mechanical milling produced fine powder with vacancies.

4.2 Magnetic properties of milled KNbO₃

Temperature and field dependences of magnetizations M of milled KNO are shown in Figs. 4 and 5, respectively, where the diamagnetic magnetization of KNO before milling was subtracted from the measured magnetization. The experimental results of milled sample at 300 rpm were nearly same as those of milled one at 250 rpm, we will show the magnetic behaviors of the milled samples below 250 rpm.

Fig.4. Temperature dependences of magnetization under 10 kOe.

Fig.5. Field dependences of magnetization at 300K.

The thermo-magnetic curves under 10 kOe in Fig.4 shows that the samples milled below 200 rpm have small magnetization, while the relatively large magnetization appear in the samples milled at 250 rpm.

Fig.5 shows the field dependences of magnetization M at 300K. The M of milled samples at 100 and 150 rpm had nearly same magnitudes as that of milled sample at 200 rpm. The samples milled below 200 rpm show paramagnetic magnetization, but 250 rpm milled one shows a ferromagnetic hysteresis curve. Thus the saturation magnetization M_s , remanent magnetization M_r and coercive field H_c appeared only in the 250 rpm sample as shown in Fig. 6.

The 250 rpm sample shows the saturation magnetization M_s of about 1.7×10^{-1} emu/g which is comparable to 1.4×10^{-1} emu/g of LiNbO_3 [19] and tenth larger than that of BaTiO_3 with vacancies [14-18]. The ferromagnetic behaviors in this sample may be due to the increasing of the number of O-vacancies, corresponding to the reduction of particle size.

Fig.6. Rpm dependence of saturation magnetization M_s , remanent magnetization M_r and coercive field H_c at 300 K.

Fig.7. Magnetization curves of 250 rpm milled sample and successively sintered one at 773 K for 3 hours in air.

The Magnetization curves of 250 rpm milled sample and successively sintered sample at 500 K for 3 hours in air are shown in Fig.7. The M of sintered sample is smaller than that of non-sintered one. The decreasing of magnetization shows the possibility of decreasing oxygen vacancy due to oxidation through the sintering.

5. CONCLUSION

The KNbO_3 (KNO) powder was milled by WC balls and vials at 0~300 rpm for 15 minutes. The room temperature ferromagnetism was found in the KNO nano-powder sample milled at 250 rpm, which showed a tenth larger saturation magnetization than that of BaTiO_3 with vacancies.

The lattice parameter c scarcely increased and the grain size of KNO powder was reduced to about 20 nm above 250 rpm. The appearance of saturation magnetization M_s and the decreasing M_s of by sintering in 250 rpm sample may show the increasing and decreasing of oxygen vacancies, respectively.

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