Superparaelectric State of LiTaO₃ Nanoparticles Embedded in a Mesoporous Silicate

S. Kawakami, S. Kohiki, S. Nogami, H. Shimooka, M. Okui*,
M. Mitome*, S. Fukushima*, Y. Bando*, and S. Takada**

Department of Materials Science, Kyusyu Institute of Technology, Kita-kyusyu 804-8550 Japan
Fax: 81-093-884-3300, e-mail: kohiki@che.kyutech.ac.jp
*Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044 Japan
Fax: 81-029-851-6280, e-mail: FUKUSHIMA.Sei@nims.go.jp,
e-mail: BANDO.Yoshio@nims.go.jp
**Advanced Semiconductor Research Center, National Institute of Advanced Industrial Science and Technology,
Tsukuba, Ibaraki 305-8569, Japan
Fax: 81-029-849-1533, e-mail: syozo-takada@aist.go.jp

A diluted system of LiTaO₃ nanoparticles ($\phi \approx 30$Å) embedded in amorphous SiO₂ matrix was prepared by calcination at 850 °C of the MCM–41 molecular sieve soaked in the 0.01 mol/l precursor solution. Temperature dependence of the dielectric constant was measured in the temperature range of 200 – 750 °C. The maximum dielectric constant temperature varied from 300 to 450 °C with increasing the external field frequency from 10 to 1000 kHz. The maximum dielectric constant temperature of LiTaO₃ nanoparticles was lower by 290 °C than LiTaO₃ bulk powders (655 °C). The large frequency dependence of the lowered maximum dielectric constant temperature is promising for developments of low–power driven nonvolatile memory devices and optical devices with low–field switching.
Key words: Nanoparticles, Frequency dependence, Superparaelectric

1. INTRODUCTION

It is of great interest to clarify the size effects of ferroelectrics [1–6], though the reported sizes for BaTiO₃ were not sufficiently small to demonstrate the nanominiaturization effect on the dielectric properties of ferroelectric nanoparticles. The reported nanominiaturization effect on the dielectric property of BaTiO₃ and SrBi₂Ta₂O₉ was lowering of the maximum dielectric constant temperatures (T_m) [7,8]. For BaTiO₃ and SrBi₂Ta₂O₉, T_m decreased from 130 to 60°C and from 310 to 180°C, respectively. Though, there has been no report on the frequency dependence of T_m for ferroelectric nanoparticles.

It is well known that LiTaO₃ is a ferroelectric material with the spontaneous polarization of $50\mu C/cm^2$, the coercive field E_c of 160kV/cm at room temperature, and T_c of 655°C [9,10]. LiTaO₃ exhibits good piezoelectric and pyroelectric properties. Furthermore, it is one of the most promising materials for use in optic devices because of its excellent electro–optic and nonlinear optical properties [11]. LiTaO₃ is advantageous for optical wave–guide applications using a high–powered laser because of its less sever laser–induced optical damage [12,13]. The crystal structure of LiTaO₃ is rhombohedral $R3c$ at room temperature. The rhombohedral unit cell of LiTaO₃ (a =5.4740Å, α=56.175°) [14] contains two formula units for total ten atoms. Li and Ta ions are on the c–axis and form triangular layers in the x–y plane. O ions also form approximate triangular layers but are slightly off–center to the c–axis. The off–center O ions are believed to be the source of ferroelectricity and its large optical nonlinearity. We have observed a large frequency dependence of lowered T_m for LiTaO₃ nanoparticles with the diameter of ≈ 30Å dispersed in mesoporous silicate [15].

At present, it is requested to use the Pb free ferroelectrics for the developments of ferroelectric random access memories and of high–frequency optical switches. And, it is also indispensable to drive the devices with a low–power. The lowered and frequency dependent T_m of the LiTaO₃ nanoparticles should lead to new developments of low–power nonvolatile memory devices and low–field optical switching devices of Pb free ferroelectrics.

2. EXPERIMENT

The diluted system of LiTaO₃ nanoparticles was prepared by using mesopores of the MCM–41 molecular sieve as a growth template. It is well known that the MCM–41 has uniform columnar periodic hexagonal pores ranging 15–100Å and separated by 8–9Å wall [16–18]. By filling the mesopores with nano–sized LiTaO₃ crystals we can realize a diluted system of ferroelectric quantum dots with larger dielectric constant separated by an amorphous SiO₂ matrix with
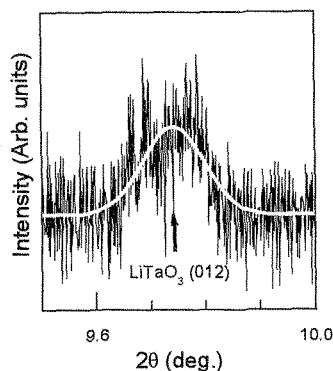
Fig. 1 Background subtracted SR–XD signal of the diluted system of LiTaO₃ nanoparticles. The peak (white line) was obtained by fitting to the Gaussian function.
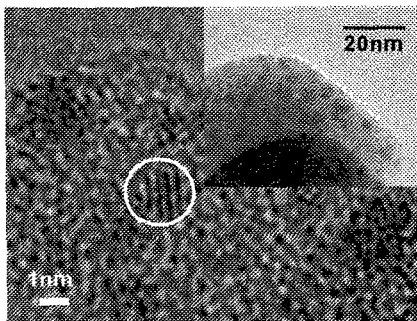

Fig. 2 Bright field TEM image of the LiTaO₃ nanoparticles in amorphous SiO₂ matrix. Uncertainties exist in the measurement of the particle size due to fuzzy particle boundary. Inset : Typical example of the nanoparticle distribution in a large area.

lower dielectric constant. The MCM–41 molecular sieve was synthesized from a mixture of SiO_2 1.00: dodecyltrimethylammonium chloride 0.70: NaOH 0.24: H_2O 62.2 in the molar ratio. The mixture was stirred at room temperature and then heated at 140°C for 48 h. After washing at 80°C for 24h and thermal dehydration at 80°C for 24h, the dried sample was calcined at 700°C for 6h in flowing oxygen to remove the organic molecules incorporated during the templating process from the mesopores. For preparation of the LiTaO₃ nanoparticles the MCM–41 was soaked in the 0.01 mol/l absolute ethanol solution of lithium chloride and tantalum chloride for 24h with stirring. The soaked sample was dried in a vacuum and then calcined in flowing oxygen at 850°C for 3h.

In X–ray diffraction (XD) measurement with a Rigaku CN2013 diffractometer using a Cu tube, the diluted system exhibited no peak from any crystal lattices, though the LiTaO₃ bulk powder prepared under the same conditions exhibited the peaks of the LiTO₃ crystal lattice. We could observe a weak signal buried in an intense

background (Fig. 1), which is corresponding to the (012) reflection of the LiTaO₃ crystal lattice [19], by using synchrotron radiation (SR) [20] as an X–ray source at BL15XU (SPring–8, Japan).

We performed transmission electron microscopy (TEM) to reveal more clearly the formation of LiTaO₃ nanoparticles in amorphous SiO_2 matrix. A JEOL JEM–3000F transmission electron microscope operated at 300 kV was employed for the observation of the samples dispersed on a carbon film. A representative TEM image demonstrates that the diameter of a fine particle was ≈ 30Å. The nanoparticles distributed randomly in the matrix as shown by the inset. (Fig. 2)

By energy–dispersive x–ray analysis (EDAX), the system contained approximately 0.8 mol % LiTaO₃.

3. DIELECTRIC PROPERTY

We examined the temperature dependent dielectric constant, $\varepsilon_r(T)$, at the external field frequency (f) of 10, 50, 100, 500, and 1000 kHz to clarify the nanominiaturization effect. (Fig. 3) T_m for the nanoparticles rose from 300 to 450°C with an increase of f from 10 to 1000 kHz, though that of the bulk powders remained at a constant despite the variation of f. At f = 100 kHz, T_m of the LiTaO₃ nanoparticles was 365 °C, which is lower than the paraelectric–ferroelectric transition temperature (T_c: 655°C) of LiTaO₃ bulk powders. The SiO_2 matrix showed gradual increase of $\varepsilon_r(T)$ in T = 200 – 750 °C and f = 10–1000 kHz. So, nanominiaturization of LiTaO₃ crystal brought about an extension of the paraelectric state temperature from T_c to T_m. Both the paraelectric–like behavior below T_c ($>T_m$) and the frequency dependence of lowered T_m suggest that below T_c the polarization directions of the single domain LiTaO₃ nanoparticles distributed randomly in the matrix and the nanoparticles were in the superparaelectric state, and at T_m the random polarization of the nanoparticles was blocked and aligned parallel to the direction of the external field. $\varepsilon_r(T)$ showed apparent f dependence of T_m, which is peculiar for the superparaelectric state of single domain ferroelectric nanoparticles.

As it is expected for the superparaelectric state, T_m shifted to the higher temperature side with increasing f. Thus, T_m reflects slow dynamics of the dielectric dipole moments in the superparaelectric state. The rate at which individual moments of the nanoparticles jump across the anisotropic energy barrier U is proportional to the Arrhenius factor, $\exp(-U/k_BT)$. At low T, the total polarization P in the direction of external filed E is rather small since the all moments of the nanoparticles are randomly oriented and frozen. As the T goes up, the nanoparticles unfreeze and align their moments parallel to the field and then P along E increases. Above T_m, moments of most of the nanoparticles are unfrozen and $\varepsilon(T)$ approaches the Curie's law.
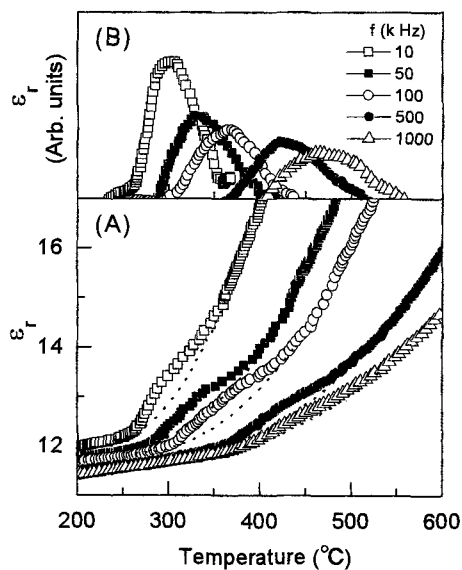
Fig. 3 Frequency dependence of $\varepsilon_r(T)$ of the diluted system of LiTaO$_3$ nanoparticles (A) and quadratic background (dotted line) subtracted $\varepsilon_r(T)$ of the nanoparticles (B).

In order to estimate the U value, the frequency dependence was fitted to the equation $T_m = U/k_B \ln(1/\tau_0 f)$ with the attempt time $\tau_0 = 1 \times 10^{-10} s$. The fitted value of U/k_B was approximately 7300K (0.63eV) for the LiTaO$_3$ nanoparticles ($\phi < 30$Å).

4. CONCLUTIONS

The LiTaO$_3$ nanoparticles, synthesized by heating at 850°C the MCM–41 molecular sieve soaked to a precursor solution, showed the superparaelectric nature of single domain ferroelectrics such as lowered and frequency dependent T_m. The higher T_m was obtained for the higher f. All the dielectric dipole moments are blocked at T_m. The polarization reversal energy E_{rev} for single domain nanoparticles below T_m should be smaller than that of the bulk since the energy for domain wall motion of the bulk is unnecessary for the nanoparticles. A small E_{rev} is

advantageous for developments of high–frequency recording and switching devices driving with a low–power. The large frequency dependence of lowered T_m of the nanoparticles was brought about only by the nano–miniaturization of LiTaO$_3$ crystal since the bulk LiTaO$_3$ shows no relaxor behavior.

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