Large frequency dependence of lowered maximum dielectric constant temperature of LiTaO3 nanocrystals dispersed in mesoporous silicate
Large frequency dependence of lowered maximum dielectric constant temperature of LiTaO₃ nanocrystals dispersed in mesoporous silicate

Shigemi Kohiki,¹ Shinichiro Nogami, Shintaro Kawakami, Syozo Takada, Hirokazu Shimooka, and Hiroyuki Deguchi
Faculty of Engineering, Kyusyu Institute of Technology, Kita-kyusyu 804-8550, Japan

Masanori Mitome
Advanced Materials Laboratory, National Institute of Materials Science, Tsukuba, Ibaraki 305-0044, Japan

Masaoki Oku
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

(Received 21 October 2002; accepted 5 April 2003)

A large frequency dependence of the maximum dielectric constant temperature was observed for LiTaO₃ nanocrystals (the diameter ≈20 Å) dispersed in mesoporous silicate. At the applied field frequency of 100 kHz, the maximum temperatures in the real and imaginary parts were 365 and 345 °C, respectively. The maximum temperature in the real part is apparently lower than the paraelectric–ferroelectric transition temperature (645 °C) of bulk LiTaO₃. The maximum temperature in the imaginary part rose from 285 to 420 °C with increasing frequency from 10 to 1000 kHz. Since the bulk LiTaO₃ shows no relaxor behavior, such superparaelectric behavior is obviously a consequence of nanominiaturization of LiTaO₃ crystal and insignificant cooperative interactions between the nanoparticles. © 2003 American Institute of Physics. [DOI: 10.1063/1.1580991]

Size effects of ferroelectrics have been of great interest in science and technology.¹−⁶ We have already reported that the maximum dielectric constant temperatures Tm for nanocrystals of BaTiO₃ and SrBi₂Ta₂O₉ dispersed in mesoporous silicate lower from 130 to 60 °C and from 310 to 180 °C, respectively.⁷−⁹ Such lowering of Tm from the paraelectric–ferroelectric transition temperature Tc of the bulk ferroelectrics suggests that the nanocrystals have a single domain structure and are in the superparaelectric state. Though, there has been no report on frequency (f) dependence of Tm as an indication of the superparaelectric state for nanominiaturized ferroelectrics. In order to confirm the f dependence of lowered Tm for nanosized ferroelectrics with insignificant cooperative effects between the particles, we prepared a diluted system of LiTaO₃ nanocrystals (ϕ≈20 Å) dispersed in mesoporous silicate since LiTaO₃ has a higher Tc and a larger spontaneous polarization than those of BaTiO₃ and SrBi₂Ta₂O₉.¹⁰,¹¹ Because of the high stability of ferroelectric phase of LiTaO₃, the LiTaO₃ nanocrystals are promising for developments of low-power nonvolatile memory devices and low-field optical switching devices of Pb free ferroelectrics.¹²−¹⁴

An assembly of LiTaO₃ nanocrystals was fabricated by using mesopores of the MCM-41 molecular sieve¹⁵−¹⁷ as a growth template. By filling the mesopores with nanosized LiTaO₃ crystals, we can realize a diluted system of ferroelectric nanodots with a large dielectric constant (ε) separated by an amorphous SiO₂ matrix with a small ε. For preparation of the diluted assembly of LiTaO₃ nanocrystals the MCM-41 was soaked in the 0.01 mol/ℓ absolute ethanol solution of lithium chloride and tantalum chloride, and then calcined at 850 °C. The assembly exhibited no peak from LiTaO₃ crystal in x-ray diffraction with a Rigaku CN2013 diffractometer using a Cu tube, while bulk powders obtained from the solution with the same conditions exhibited the diffraction peaks of LiTaO₃ crystal. Therefore, the assembly contains no bulk particle of LiTaO₃.¹⁸ A representative image shown in Fig. 1 with a JEOL JEM-3000F transmission electron microscope operated at 300 kV demonstrates that the diameter of a fine particle was ≈20 Å. Since the particle was so fine, we could not obtain a clear electron diffraction pattern, though we detected Li and Ta elements contained in the particle.¹⁹ By energy-dispersive x-ray (EDX) analysis, the assembly contained approximately 0.8 mol % LiTaO₃.

Figure 2 shows the lowering of Tm in the real part of dielectric constant ε’(T) by 280 °C from 645 (the bulk Tc) to 365 °C for the LiTaO₃ nanocrystals. Since the size of the nanocrystal is evidently smaller than the ferroelectric domain size, it is readily understood that the nanocrystals have a single domain structure and are in the superparaelectric state.

FIG. 1. Bright-field image of a LiTaO₃ nanocrystal in the amorphous SiO₂ matrix. Uncertainties exist in the measurement of the particle size due to fuzzy particle boundary.

¹Electronic mail: kohiki@che.kyutech.ac.jp
assembly, the system exhibits a paraelectriclike behavior because the polarization direction of individual nanocrystals in the assembly of LiTaO₃ nanocrystals (b), the LiTaO₃ powders (c), and background subtracted and normalized ε’(T) of the nanocrystals and the bulk (d). Dotted lines in the panels (b) and (c) were assumed ε’ backgrounds due to ionic conduction. Maxima of the panel (d) indicate Tₐ of the nanocrystals and Tₐ of the bulk.

below Tₐ and above Tₘ. At Tₐ, the dipole moment of each nanocrystal disappears and the system reaches the intrinsic paraelectric state. In a single domain nanocrystal, there is no domain-wall energy, though below Tₐ each nanocrystal has finite Landau–Ginsburg energy associated with polarization, therefore, the equilibrium temperature to the thermal energy (k_B T) lowers from Tₐ to Tₘ. Due to random distribution of the polarization direction of individual nanocrystals in the assembly, the system exhibits a paraelectriclike behavior above Tₘ.

Two polarization states, +p and −p, in a superparaelectric potential having double minima are separated by an activation energy barrier U. The total dipole moment of the nanocrystal can thermally fluctuate with overcoming of U, therefore, ε(T) is expected to depend on f with respect to the relaxation time τ. If (1/f) > τ, the relaxation appears to be so fast and the assembly behaves like a paraelectric system. On the contrary, if (1/f) < τ, the relaxation appears to be so slow that quasistatic properties are observed (blocked state). The blocking temperature Tₜ separating the two states is defined as T at which (1/f) = τ. Thus, τ varies exponentially with the U/k_BT ratio, and Tₜ increases with increasing f for a given φ. At Tₜ, dielectric dipoles cannot follow the ac applied field, therefore, the imaginary part of dielectric constant ε″(T) appears. We examined ε″(T) at from f = 10 to 1000 kHz to clarify the superparaelectric state for the LiTaO₃ nanocrystals. As shown in Fig. 3, Tₜ in ε″(T) of the assembly increased with f as expected for the superparaelectric state, while the bulk LiTaO₃ powders showed no change. Thus, Tₜ determined as Tₜ in ε″(T) reflects slow dynamics of the dielectric dipole moments in the superparaelectric state.

The U values listed in Table I were estimated with the equation Tₜ = U/k_BT ln(1/τ₀f) at the attempt time τ₀ = 1 × 10⁻¹² s. Since U is approximately equal to the product of the Gibbs free energy density and the volume, the reduction of U from 0.887 to 0.826 eV led by the increase of Tₜ from 285 to 420 °C implies that the free energy becomes smaller as T increased.

The LiTaO₃ nanocrystals demonstrated the superparaelectric nature of single domain ferroelectrics. The large f dependence of lowered Tₜ of the nanocrystals was brought about only by the nanominiaturization of LiTaO₃ crystal since the bulk LiTaO₃ shows no relaxor behavior.

<table>
<thead>
<tr>
<th>f (kHz)</th>
<th>Tₜ (°C)</th>
<th>U (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>285</td>
<td>0.887</td>
</tr>
<tr>
<td>50</td>
<td>324</td>
<td>0.866</td>
</tr>
<tr>
<td>100</td>
<td>345</td>
<td>0.859</td>
</tr>
<tr>
<td>500</td>
<td>393</td>
<td>0.833</td>
</tr>
<tr>
<td>1000</td>
<td>420</td>
<td>0.826</td>
</tr>
</tbody>
</table>

One of the authors (S.K.) thanks the support from The Murata Science Foundation for this work, and helpful discussions of Dr. S. Fukushima (AML, NIMS) on EDAX. Another author (H.D.) thanks Professor Y. Murakami for helpful discussions on SR-XD. A part of this work was supported by “Nanotechnology Support Project” of the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan.

21 We could observe weak signals can be indexed to LiTaO₃ (JCPDS No. 29-0836) buried in an intense background of the amorphous SiO₂ by synchrotron radiation x-ray diffraction at KEK-PF (Tsukuba, Japan).
22 The Li K energy-loss spectrum and the Ta L and M x-ray spectra were measured with a Gatan model-666 electron energy analyzer and ThermoNORAN VANTAGE EDX system equipped to the transmission electron microscope, respectively.