

Large frequency dependence of lowered maximum dielectric constant temperature of LiTaO_3 nanocrystals dispersed in mesoporous silicate

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A large frequency dependence of the maximum dielectric constant temperature was observed for LiTaO_3 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 LiTaO_3 . The maximum temperature in the imaginary part rose from 285 to 420 °C with increasing frequency from 10 to 1000 kHz. Since the bulk LiTaO_3 shows no relaxor behavior, such superparaelectric behavior is obviously a consequence of nanominiaturization of LiTaO_3 crystal and insignificant cooperative interactions between the nanoparticles. © 2003 American Institute of Physics.

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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 T_m for nanocrystals of BaTiO_3 and $\text{SrBi}_2\text{Ta}_2\text{O}_9$ dispersed in mesoporous silicate lowered from 130 to 60 °C and from 310 to 180 °C, respectively.^{7–9} Such lowering of T_m from the paraelectric–ferroelectric transition temperature T_c of the bulk ferroelectrics suggests that the nanocrystals have a single domain structure and the system is in the superparaelectric state. Though, there has been no report on frequency (f) dependence of T_m as an indication of the superparaelectric state for nanominiaturized ferroelectrics. In order to confirm the f dependence of lowered T_m for nanosized ferroelectrics with insignificant cooperative effects between the particles, we prepared a diluted system of LiTaO_3 nanocrystals ($\phi \approx 20$ Å) dispersed in mesoporous silicate since LiTaO_3 has a higher T_c and a larger spontaneous polarization than those of BaTiO_3 and $\text{SrBi}_2\text{Ta}_2\text{O}_9$.^{10,11} Because of the high stability of ferroelectric phase of LiTaO_3 , the LiTaO_3 nanocrystals are promising for developments of low-power non-volatile memory devices and low-field optical switching devices of Pb free ferroelectrics.^{12–14}

An assembly of LiTaO_3 nanocrystals was fabricated by using mesopores of the MCM-41 molecular sieve^{15–17} as a growth template. By filling the mesopores with nanosized LiTaO_3 crystals, we can realize a diluted system of ferroelectric nanodots with a large dielectric constant (ϵ) separated by an amorphous SiO_2 matrix with a small ϵ . For preparation of the diluted assembly of LiTaO_3 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 LiTaO_3 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 LiTaO_3 crystal. Therefore, the assembly contains no bulk particle of LiTaO_3 .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 % LiTaO_3 .

Figure 2 shows the lowering of T_m in the real part of dielectric constant $\epsilon'(T)$ by 280 °C from 645 (the bulk T_c) to 365 °C for the LiTaO_3 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

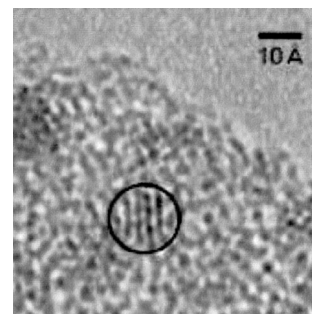


FIG. 1. Bright-field image of a LiTaO_3 nanocrystal in the amorphous SiO_2 matrix. Uncertainties exist in the measurement of the particle size due to fuzzy particle boundary.

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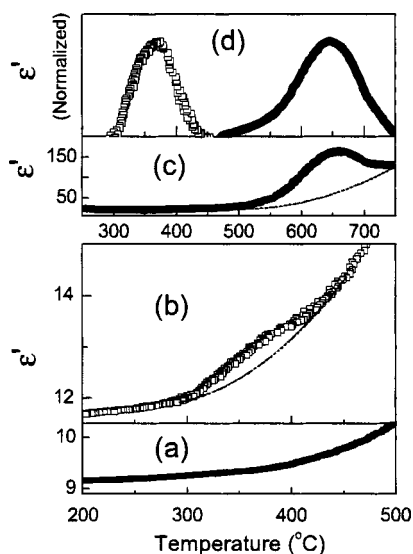


FIG. 2. Temperature dependence of $\epsilon'(T)$ at $f=100$ kHz of the matrix (a), the assembly of LiTaO_3 nanocrystals (b), the LiTaO_3 powders (c), and background subtracted and normalized $\epsilon'(T)$ of the nanocrystals and the bulk (d). Dotted lines in the panels (b) and (c) were assumed ϵ' backgrounds due to ionic conduction. Maxima of the panel (d) indicate T_m of the nanocrystals and T_c of the bulk.

below T_c and above T_m . At T_c , 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 T_c each nanocrystal has finite Landau–Ginsburg energy associated with polarization, therefore, the equilibrium temperature to the thermal energy ($k_B T$) lowers from T_c to T_m . Due to random distribution of the polarization direction of individual nanocrystals in the assembly, the system exhibits a paraelectriclike behavior above T_m .

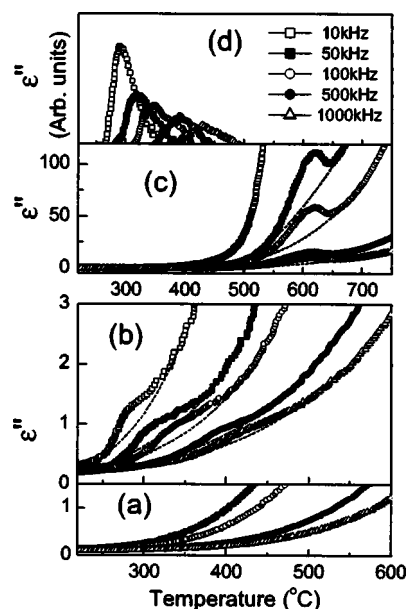


FIG. 3. Frequency dependence of $\epsilon''(T)$ of the matrix (a), the assembly of LiTaO_3 nanocrystals (b), the LiTaO_3 powders (c), and background subtracted $\epsilon''(T)$ of the nanocrystals (d). The matrix showed gradually increasing $\epsilon''(T)$ with no peak in $T=200$ – 750 °C and $f=10$ – 1000 kHz. The dotted lines in the panels (b) and (c) were assumed ϵ'' backgrounds at each f due to ionic conduction.

TABLE I. Frequency dependence of the blocking temperature and activation energy.

f (kHz)	T_b (°C)	U (eV)
10	285	0.887
50	324	0.866
100	345	0.859
500	393	0.833
1000	420	0.826

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, $\epsilon(T)$ is expected to depend on f with respect to the relaxation time τ . If $(1/f) > \tau$, the relaxation appears to be so fast and the assembly behaves like a paraelectric system. On the contrary, if $(1/f) < \tau$, the relaxation appears to be so slow that quasistatic properties are observed (blocked state). The blocking temperature T_b separating the two states is defined as T at which $(1/f) = \tau$. Thus, τ varies exponentially with the $U/k_B T$ ratio, and T_b increases with increasing f for a given ϕ . At T_b , dielectric dipoles cannot follow the ac applied field, therefore, the imaginary part of dielectric constant $\epsilon''(T)$ appears. We examined $\epsilon''(T)$ at from $f=10$ to 1000 kHz to clarify the superparaelectric state for the LiTaO_3 nanocrystals. As shown in Fig. 3, T_m in $\epsilon''(T)$ of the assembly increased with f as expected for the superparaelectric state, while the bulk LiTaO_3 powders showed no change. Thus, T_b determined as T_m in $\epsilon''(T)$ reflects slow dynamics of the dielectric dipole moments in the superparaelectric state.

The U values listed in Table I were estimated with the equation $T_b = U/k_B \ln(1/\tau_0 f)$ at the attempt time $\tau_0 = 1 \times 10^{-12}$ 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 T_b from 285 to 420 °C implies that the free energy becomes smaller as T increased.

The LiTaO_3 nanocrystals demonstrated the superparaelectric nature of single domain ferroelectrics. The large f dependence of lowered T_m of the nanocrystals was brought about only by the nanominiaturization of LiTaO_3 crystal since the bulk LiTaO_3 shows no relaxor behavior.

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- ¹⁸We 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).
- ¹⁹The 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.