表層の電気結合で発生する高温のディーゼルエンジン

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

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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 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.

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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 BaTiO₃ and SrBi₂Ta₂O₉ 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 are 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 LiTaO₃ nanocrystals ($d$ ≈20 Å) dispersed in mesoporous silicate since LiTaO₃ has a higher $T_c$ and a larger spontaneous polarization than those of BaTiO₃ and SrBi₂Ta₂O₉.¹⁰¹¹ 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 ($\varepsilon$) separated by an amorphous SiO₂ matrix with a small $\varepsilon$. For preparation of the diluted assembly of LiTaO₃ nanocrystals the MCM-41 was soaked in the 0.01 mol/l 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 $T_m$ in the real part of dielectric constant $\varepsilon'(T)$ by 280 °C from 645 (the bulk $T_c$) 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.

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above assembly, the system exhibits a paraelectriclike behavior of the polarization direction of individual nanocrystals in the paraelectric state. In a single domain nanocrystal, there is no nanocrystal disappears and the system reaches the intrinsic state. During the blocking temperature \( T_b \) separating the two states is defined as \( T \) at which \((1/f) = \tau \). The \( \tau \) varies exponentially

<table>
<thead>
<tr>
<th>( f ) (kHz)</th>
<th>( T_b ) (°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>
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<tr>
<td>500</td>
<td>393</td>
<td>0.833</td>
</tr>
<tr>
<td>1000</td>
<td>420</td>
<td>0.826</td>
</tr>
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</table>

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, \( \varepsilon(T) \) is expected to depend on \( f \) with respect to the relaxation time \( \tau \). 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 slow that quasistatic properties are observed (blocked state). The blocking temperature \( T_b \) separating the two states is defined as \( T \) at which \((1/f) = \tau \). The \( \tau \) varies exponentially

\[
\tau = \frac{1}{k_B T} \exp \left( \frac{U}{k_B T} \right)
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, and \( U \) is the activation energy. The total dipole moment of the assembly of LiTaO₃ nanocrystals in a superparaelectric state for the LiTaO₃ nanocrystals. As shown in Fig. 3, \( T_m \) in \( \varepsilon''(T) \) of the assembly increased with \( f \) as expected for the superparaelectric state, while the bulk LiTaO₃ powders showed no change. Thus, \( T_b \) determined as \( T_m \) in \( \varepsilon''(T) \) 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 LiTaO₃ 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 LiTaO₃ crystal since the bulk LiTaO₃ shows no relaxor behavior.

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18 We could observe weak signals can be indexed to LiTaO$_3$ (JCPDS No. 29-0836) buried in an intense background of the amorphous SiO$_2$ by synchrotron radiation x-ray diffraction at KEK-PF (Tsukuba, Japan).
19 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.