Above-Room-Temperature molecular ferroelectric and fast switchable dielectric of Diisopropylammonium Perchlorate

Kaige Gao[a], Minqiang Gu[a], Xiangbiao Qiu[b], X. N. Ying[a], Hen-Yun Ye[c], Yi Zhang[c], Jinglan Sun[d], Xiangjian Meng[d], F.M. Zhang[a], Di Wu[b], Hong-Ling Cai[a*], and X.S. Wu[a*]

[a]National Laboratory of Solid State Microstructures and School of Physics, Nanjing University, Nanjing 210093, P. R. China

[b]Department of Materials Science and Engineering,College of Engineering and Applied Sciences, Nanjing University, Nanjing 210093, China,

[c]Ordered Matter Science Research Center, Southeast University, Nanjing 211189, P. R. China

[d]National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai 200083, P. R. China

Dielectric susceptibility of improper ferroelectric

For a proper ferroelectric the dielectric constants obey the Curie-Weiss law: $\varepsilon = C / (T - T_c)$. The dielectric behavior of IMP is distinguished character of improper ferroelectric. In the basic view of the phenomenological Landau theory of phase transition, the order parameter of phase transition of improper ferroelectric is not the polarization but another physical quantity. Spontaneous polarization acts as a secondary effect in improper ferroelectric transition. It should be noted that the first order parameter of improper ferroelectric at least has two components. Therefore, the Gibbs free energy can be written as:

$$G = G_0 + A(\eta_1^2 + \eta_2^2) + B(\eta_1^2 + \eta_2^2)^2 + B'(\eta_1\eta_2)^2 + A'P_s^2 - k\eta_1\eta_2P_s$$

If the free energy reaches the minimum value, the balance value of order parameters η_{10}, η_{20}, and P_{s0} should meet the equations as following:

$$\frac{\partial G}{\partial \eta_1} = 2A_0(T - T_0)\eta_{10} + 4B\eta_{10}^3 + (4B + 2B')\eta_{10}\eta_{20}^2 - k\eta_{20}P_{s0} = 0$$

$$\frac{\partial G}{\partial \eta_2} = 2A_0(T - T_0)\eta_{20} + 4B\eta_{20}^3 + (4B + 2B')\eta_{10}^2\eta_{20} - k\eta_{10}P_{s0} = 0$$

$$\frac{\partial G}{\partial P_s} = 2A'P_{s0} - k\eta_{10}\eta_{20} = 0$$

When $T < T_0$ and $2B' - k^2(2A')^{-1} < 0$, we get the stable solutions:

$$\eta_{20} = \pm\eta_{10}$$

$$\eta_{10}^2 = \frac{2A_0(T_0 - T)}{8B + 2B' - k^2(2A)^{-1}}$$

$$P_{s0} = \pm \frac{k}{2A'} \eta_{10}^2 \propto (T_0 - T)$$

It indicates that spontaneous polarization of improper ferroelectrics linear changes with temperature increasing, which is distinguished with proper ferroelectrics.

When there exists a homogeneous electric field E, the Gibbs free energy can be written as:

$$G = G_0 + A(\eta_1^2 + \eta_2^2) + B(\eta_1^2 + \eta_2^2)^2 + B'(\eta_1\eta_2)^2 + A'P_s^2 - k\eta_1\eta_2 P_s - EP_s$$

$$\frac{\partial G}{\partial P_s} = 2A'P_{s0} - k\eta_{10}\eta_{20} - E = 0$$

The stable solution is $\eta_{10} = \eta_{20} = 0$, $P_s = \frac{E}{2A'}$.

Therefore, dielectric susceptibility is

$\chi = \frac{P}{\varepsilon_0 E} = \frac{1}{2\varepsilon_0 A'}$, which is temperature independent.

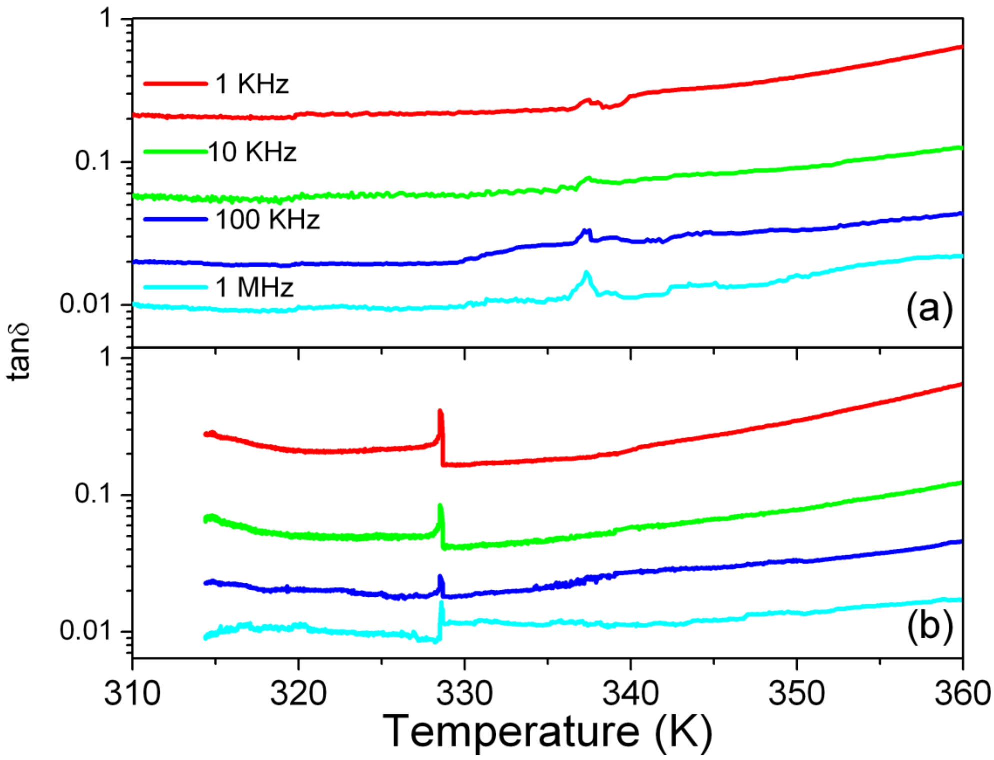

Fig.S1 The temperature dependent of dielectric loss with different frequencies in (a) heating and (b) cooling processes.

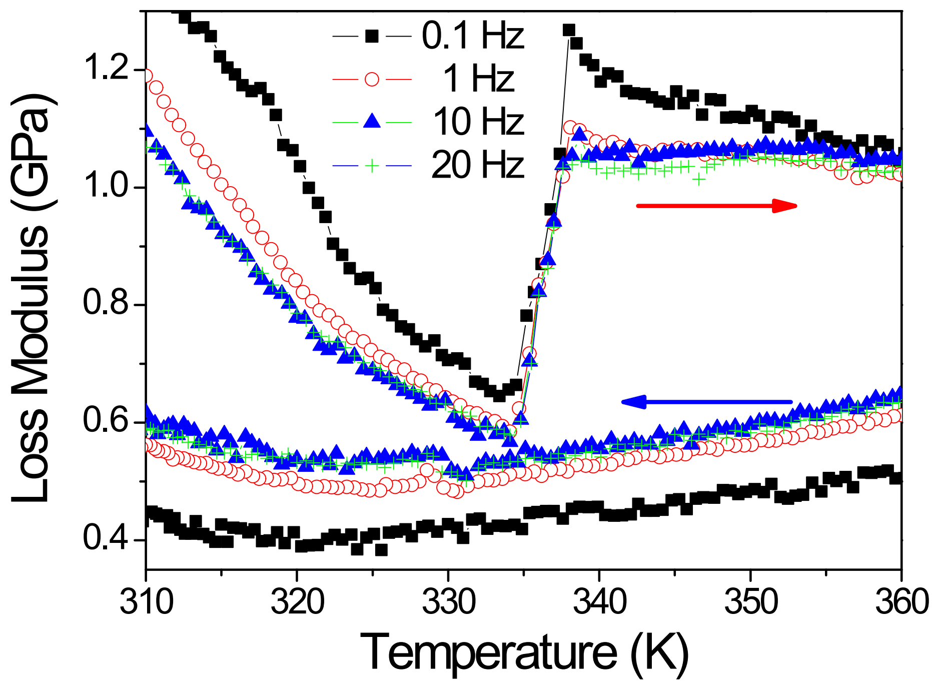

Fig.S2 The temperature dependence of Loss modulus of DMA at different frequency.

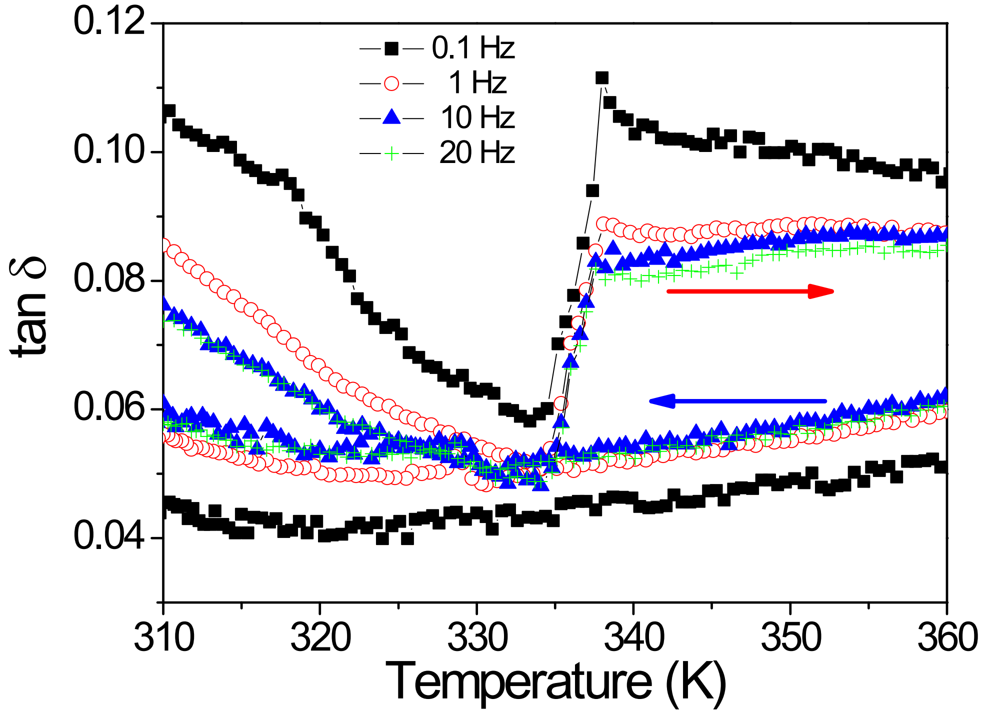

Fig. S3 The temperature dependence of dissipation tanδ of DMA at different frequency.

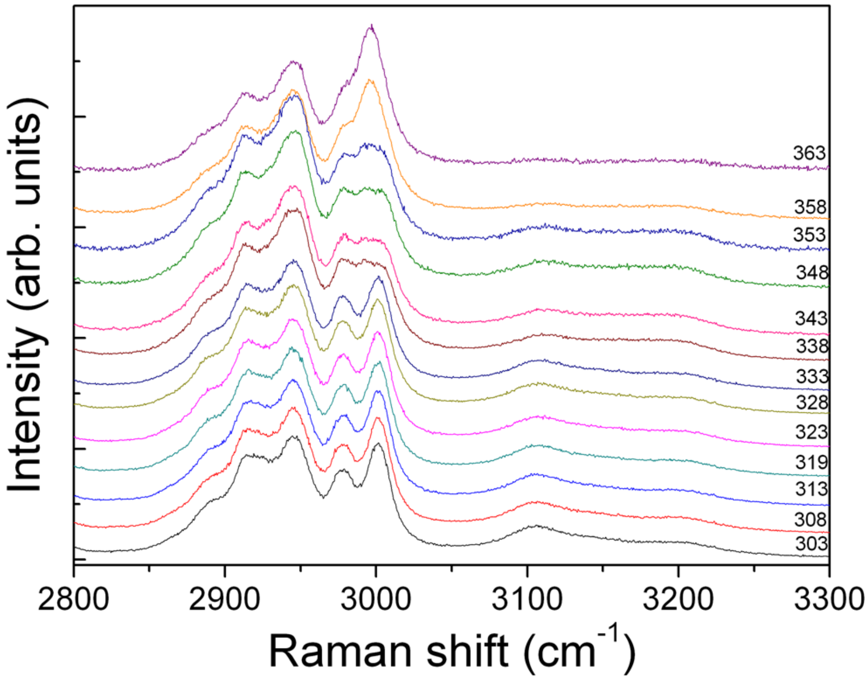

Fig.S4 Raman spectrum above wave number of 2800 cm^{-1} at different temperature.

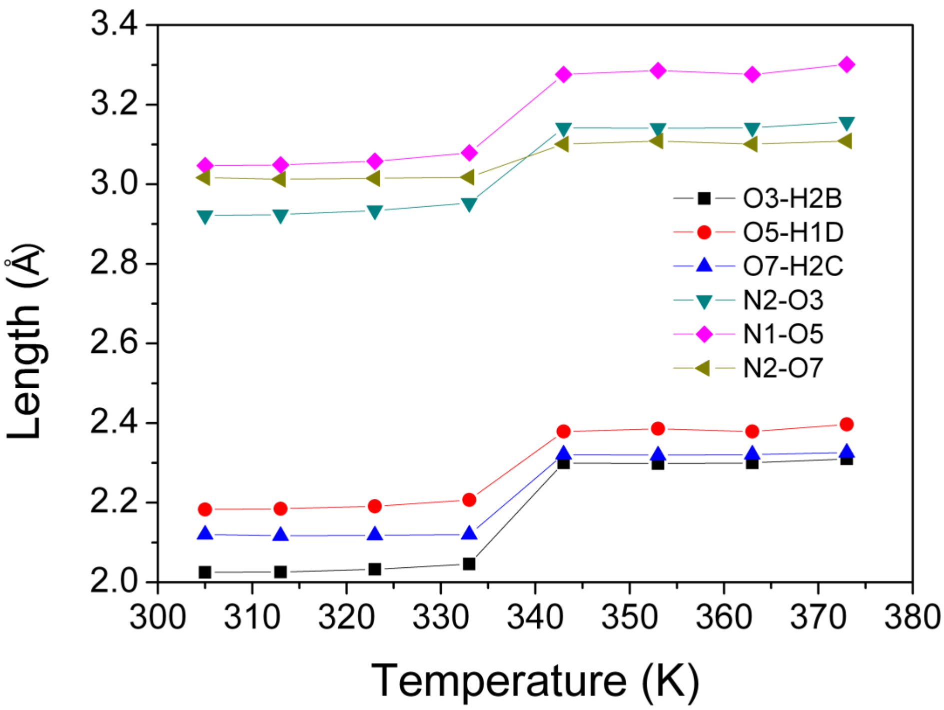

Fig.S5 Temperature dependence of some bond lengths.