

Lead-Free Ferroelectric Materials: BaTiO₃ and Beyond

By Claire McGhee

Since its discovery in the 1880's the field piezoelectric materials has grown and the materials have been incorporated into many devices in modern technology including actuators, transducers, generators, sensors, capacitors, and oscillators.¹ Piezoelectric materials gain their unique electromechanical properties because of their non-centrosymmetric crystal structure.² This structure affords two distinct groups of materials, those which have an induced-dipole and those with a permanent dipole. Materials with a permanent dipole tend to have a stronger piezoelectric response, and are referred to as ferroelectric materials. Because of the strong piezoelectric properties ferroelectric materials exhibit, they have been well developed in the field of materials science. Of these materials, the most studied and applied materials are perovskite structure polycrystalline ceramics.³ Recent advancements in the study of perovskite thin films is continuing to further application of these classic materials. To a lesser degree, semicrystalline polymers and small-molecule single-crystals have been developed. In the past, both polymer and small-molecule ferroelectric materials tended to have a smaller piezo-response, a lower Curie temperature, and a smaller spontaneous polarization, however, recently, single-crystal small-molecule ferroelectric materials have been characterized which have properties comparable with perovskite ceramics. This talk will review one of the new applications of perovskite ultrathin films and the properties of these newly developed ferroelectric materials.

One unique aspect of ferroelectric materials is the permanent dipole within the material, the orientation of which is measured by the sign of its spontaneous polarization. When an electric field is applied to a ferroelectric material, its spontaneous polarization can be reoriented, or flipped. This ability allows thin film ferroelectrics, used as resistors in capacitors, to be read based on the orientation of their dipole in a device known as ferroelectric random access memory (FeRAM). However, this process is destructive and the memory must be rewritten after each read.⁴ Recent developments in ferroelectric ultrathin films,^{5,6} have made possible the creation of ferroelectric tunneling junctions (FTJs),⁷ which have the potential to be used as memory devices but are non-destructive. In addition, studies of ultrathin BaTiO₃ have revealed that strain properties enhance the Curie temperature and spontaneous polarization significantly.⁵ FTJs for memory application typically have an ultrathin (less than 2 nm) layer of ferroelectric material sandwiched between two metal plates and give an on/off signal difference of 100-300 times amplification.^{8,9} However, it was discovered, using a BaTiO₃ ultrathin film, that by replacing one metal plate with a heavily doped semiconductor the amplification between the on and off state of the FTJ can be amplified 10⁴ times, one hundred times greater than previous results.¹⁰

In 2010 Sachio Horiuchi *et al.* discovered that crystallized croconic acid (4,5-dihydroxy-4-cyclopentene-1,2,3-trione) had ferroelectric properties.¹¹ This oxocarbon acid has the ability to realign its dipole by undergoing solid state tautomerism (Figure 1).¹² The strong dipole combined with the acentric *Pca2*₁ crystal structure combined to a theoretical spontaneous polarization (P_s)

of $26 \mu\text{C}\cdot\text{cm}^{-2}$, confirmed by a remnant polarization (P_r) of $21 \mu\text{C}\cdot\text{cm}^{-2}$, a comparable P_r to lead-free perovskite ceramics. Though the Curie temperature (T_c) of this material has yet to be numerically defined, DSC experiments indicate that no phase transitions occur until the degradation of the compound at 450 K. Currently, the T_c is known to be greater than 400 K.

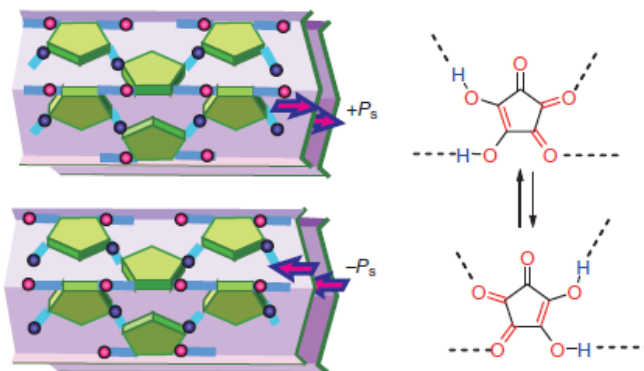


Figure 1. Croconic acid dipole switched by keto-enol proton transfer. *Left* shows the charge on the spontaneous polarization based on the dipole. *Right* shows the tautomer reaction using a single molecular unit. (This figure is adapted from Sachio Horiuchi *et al.*, 2010.)

Following this work the ferroelectric properties of single-crystal diisopropylammonium chloride (DIPAC) and diisopropylammonium bromide (DIPAB) were characterized in 2011 and 2013, respectively.^{13,14,15} Both organic crystals were selected because of their high melting points and acentric point group at room temperature.^{16,17} DIPAC showed had a T_c of 440 K, while DIPAB had a T_c of 426 K. However, the spontaneous polarization for DIPAC was lower than for DIPAB with P_s values of $8.2 \mu\text{C}\cdot\text{cm}^{-2}$ and $23 \mu\text{C}\cdot\text{cm}^{-2}$ respectively. Lastly, the domains for DIPAB were mapped and the piezoresponse was measured to be 360 pm per 1 V_{ac} , which is again similar to the response factor of some commercially used ferroelectric materials.

In conclusion, there have been several new and exciting developments within the field of ferroelectric materials within the last few years. Some of these include the development of ultrathin films and their application in FTJs, and several organic small molecule ferroelectric materials with properties similar to widely used perovskites. These studies show the continued applicability and necessity of studying ferroelectric materials, from continued study and application of perovskites, to exploring new organic and small-molecule ferroelectric materials.

References:

- 1) Tichì, J. (Eds.) *Fundamentals of piezoelectric sensorics mechanical, dielectric, and thermodynamical properties of piezoelectric materials*. Berlin ; Springer, **2010**.
- 2) Brockmann, T. H. *Theory of Adaptive Fiber Composites*, Dordrecht : Springer, **2009**.

- 3) Nelson, Wesley G., eds. *Piezoelectric Materials: Structure, Properties, And Applications*. New York : Nova Science Publishers, **2010**.
- 4) Miller, S. L. & McWhorter, P. J. Physics of the ferroelectric nonvolatile memory field effect transistor. *J. Appl. Phys.* **1992**, *72*, 5999-6010.
- 5) Choi, K. J. et al. Enhancement of ferroelectricity in strained BaTiO₃ thin films. *Science* **2004**, *306*, 1005-1009.
- 6) Fong, D. D. et al. Ferroelectricity in ultrathin perovskite films. *Science* **2004**, *304*, 1650-1653.
- 7) Tedrow, P. M. & Meservey, R. Spin-dependent tunneling into ferromagnetic nickel. *Phys. Rev. Lett.* **1971**, *26*, 192-195.
- 8) Chanthbouala, A. et al. Solid-state memories based on ferroelectric tunnel junctions. *Nature Nanotech.* **2012**, *7*, 101-104.
- 9) Pantel, D. et al. Tunnel electroresistance in junctions with ultrathin ferroelectric Pb(Zr_{0.2}Ti_{0.8})O₃ barriers. *Appl. Phys. Lett.* **2012**, *100*, 232902.
- 10) Wen, Z.; Li, C.; Wu, D.; Aidong Li, A.; Ming, N. Ferroelectric-field-effect-enhanced electroresistance in metal/ferroelectric/semiconductor tunnel junctions. *Nat. Mat.* **2013**, *12*, 617-621.
- 11) Horiuchi, S.; Tokunaga, Y.; Giovannetti, G.; Picozzi, S.; Itoh, H.; Shimano, R.; Kumai, R.; Tokura, Y. Above-room-temperature ferroelectricity in a single-component molecular crystal. *Nature*. **2010**, *463*, 789-792.
- 12) Sanz, D.; Pe´rez-Torralba, M.; Alarco´n, S. H.; Claramunt, R. M.; Foces-Foces, C.; Elguero, J. Tautomerism in the Solid State and in Solution of a Series of 6-Aminofulvene-1-aldimines . *J. Org. Chem.* **2002**, *67*, 1462-1471.
- 13) Fu , D.-W.; Zhang , W.; Cai , H.-L.; Ge , J.-Z.; Zhang, Y.; Xiong, R.-G. Diisopropylammonium Chloride: A Ferroelectric Organic Salt with a High Phase Transition Temperature and Practical Utilization Level of Spontaneous Polarization. *Adv. Mater.* **2011**, *23*, 5658–5662
- 14) Fu , D.-W.; Cai , H.-L.; Liu, Y.; Ye, Q.; Zhang , W.; Zhang , Y.; Chen, X.-Y.; Giovannetti, G.; Capone, M.; Li, J.; Xiong, R.-G. Diisopropylammonium Bromide Is a High-Temperature Molecular Ferroelectric Crystal. *Science* **2013**, *339*, 425-428.
- 15) Piecha, A.; Gagor, A.; Jakubasa, R.; Szklarza, P. Room-temperature ferroelectricity in diisopropylammonium bromide. *CrystEngComm* **2013**, *15*, 940-944.

- 16) Prince, P.; Miller, J. A.; Fronczek, F. R.; Gandour, R. D. Diisopropylammonium Chloride. *Acta Cryst.* **1990**, *46*, 336-338.
- 17) Haberecht, M.; Lerner, H.-W.; Bolteb, M. The low-temperature phase of diisopropylammonium bromide. *Acta Cryst.* **2002**, *58*, 0555-0557.