Organic - inorganic Interface Engineering Towards Better Pyroelectric Materials

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Our Pyroelectric Model System: The Surface of $Li_2B_4O_7$

Surface-scientific investigation

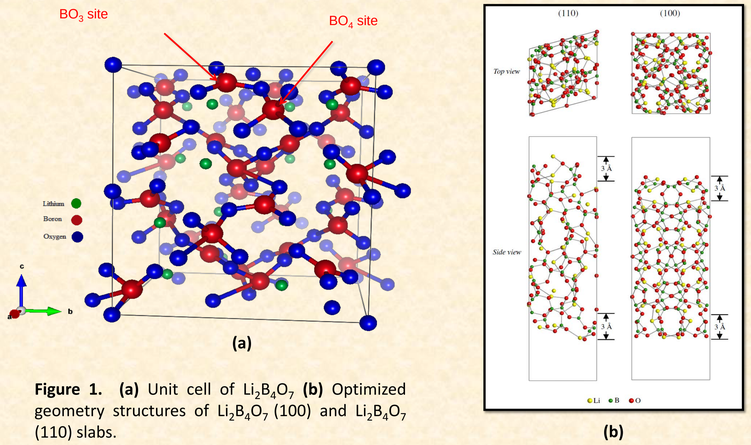


Figure 1. **(a)** Unit cell of $Li_2B_4O_7$ **(b)** Optimized geometry structures of $Li_2B_4O_7$ (100) and $Li_2B_4O_7$ (110) slabs.

NEXAFS studies of Mn-doped $Li_2B_4O_7$ show that Mn dopants occupy both Boron sites in Mn^{2+} and and Mn^{3+} with very few dopants in interstitial Lithium sites

The Surface Pyroelectric Effect in $Li_2B_4O_7$

Studies about explicit dependence of surface states and pyroelectric effects in lithium tetraborate are rare. Our work is not only an effort to remedy this deficiency but an effort to exploit the surface to make better devices.

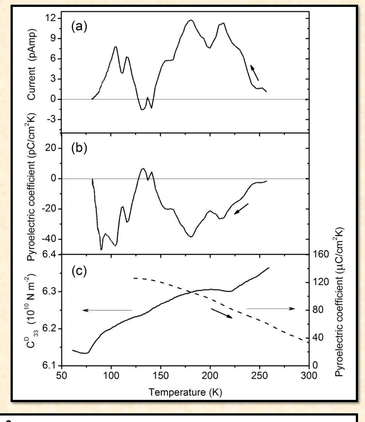


Figure 2. (**a**) Pyroelectric current for $Li_2B_4O_7$ single crystal along (110) direction; (**b**) Temperature dependence of pyroelectric coefficient along (110) direction; (**c**) temperature dependence of elastic stiffness constant along the polar *c*-axis (solid line) and the (001) pyroelectric coefficient (dashed line).

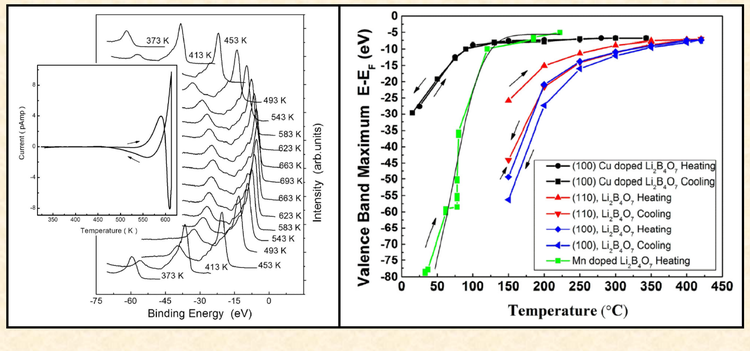


Figure 3. **(a)** Photoemission spectra from $Li_2B_4O_7$(110) surface for a succession of temperatures in a heating-cooling cycle. **(b)** Photovoltaic charging as measured from the valence band maximum.

Pyroelectric coefficient shows different temperature dependence along the (110) and the (001) direction, which is also confirmed by photovoltaic charging at higher temperatures.

INTRODUCTION

We investigate two pyroelectric materials – $Li_2B_4O_7$ and $BaTiO_3$, to enhance their pyroelectric properties by metal doping and interface engineering using dipolar molecules. We observe surface pyroelectric effects in $Li_2B_4O_7$ using photoemission technique, and increase in polarization for Dipolar molecules-$BaTiO_3$ system using Piezo-Force Response Microscopy.

Device Characterization for $Li_2B_4O_7$ and $BaTiO_3$

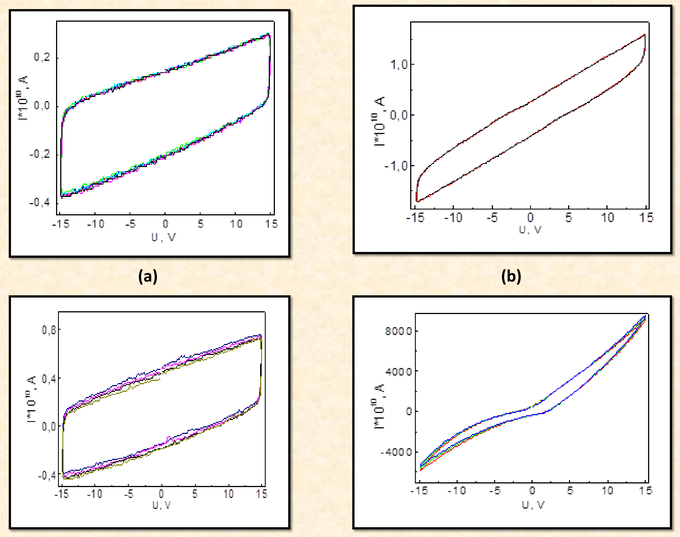
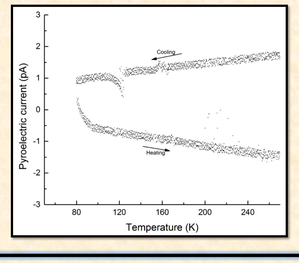


Figure 4. CVC of Pt-$Li_2B_4O_7$-Pt structures for **(a)** X-cut (100) at 292 K; **(b)** X-cut (100) at 411 K; **(c)** Z-cut (001) at 117 K; **(d)** Z-cut (001) at 400 K.

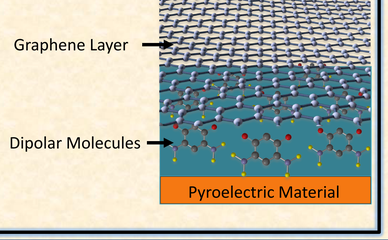
- ***Temperature dependence of CV of Pt-$Li_2B_4O_7$-Pt structures for (001) direction***
- ***Strong directional dependence of CV for (100) direction and (001) direction at highest temperatures.***

Device structures have been fabricated from thin Barium titanate films with gold electrodes. The pyroelectric current has been measured in a cryostat as a function of temperature change (right).



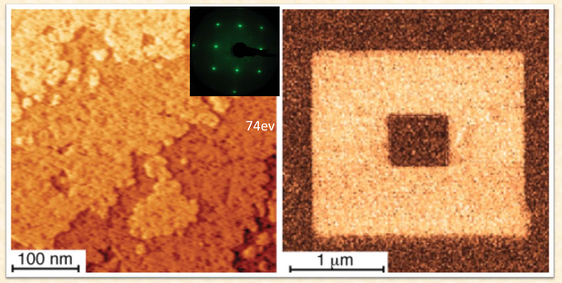
Conclusions/Future Research

- $Li_2B_4O_7$ presents small pyroelectric current along the [110] direction such that the pyroelectric coefficient is 10^3 smaller than along the [001] direction of spontaneous polarization.
- Polarization in BTO can be enhanced by depositing dipolar molecules on surface.
- We will use graphene layer to trap dipolar molecules on the surface to stabilize the polarization and do the local probe measurements using Piezo-Force Response Micoscopy.



Ultra-Thin Films of $BaTiO_3$: A Second Model System for Surface Pyroelectric Effect:

Surface-scientific investigation



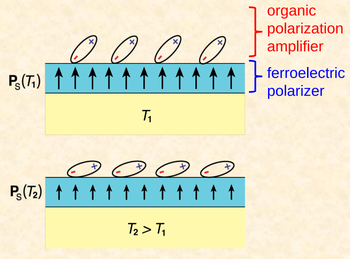
Thin $BaTiO_3$ films were studied under UHV using STM, PFM, electron diffraction and photoemission. The films are atomically flat terminated with TiO polarizable with PFM

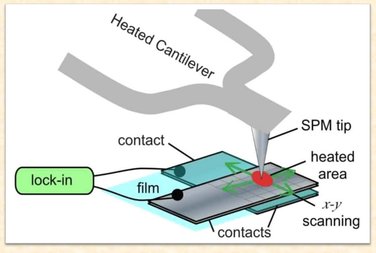
Chen, Enders, et al. *New J. Physics*, 2011, 13, 083037.

Engineering the Interface Polarization with Dipolar Molecules

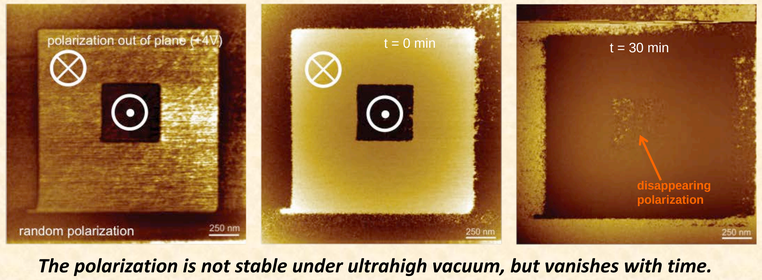
Key idea: modify the surfaces of pyroelectric samples with dipolar adsorbates to amplify temperature dependent changes in surface polarization

Approach: The tip of an atomic force microscope is used as an electrode to detect and manipulate the polarization of pyroelectric thin films



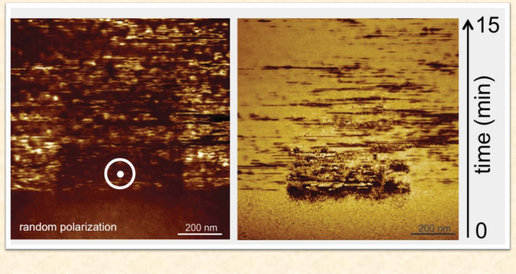


UHV studies of Dipolar Molecules-BTO interface



The polarization is not stable under ultrahigh vacuum, but vanishes with time.

Piezo Response Force Microscopy study of a $BaTiO_3$ thin film covered with benzoquinonemonoimine zwitterions. Left: Amplitude, Right: Phase



Discovery: Strongly dipolar molecules enhance the surface polarization but reduce the polarization stability.