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14. ABSTRACT
We have discovered a new metal organic framework piezoelectric material which has not been reported in the literature, nicknamed “red”
until we can publish our results. We have identified several other strong candidates, which we are synthesizing and characterizing.
Organic ferroelectric research is receiving a great deal of interest in the scientific community. With the help of this grant, CSUSB is at the

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Timothy Usher
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Report Title

Final Report: Materials Research of Novel Organic Piezoelectric/Ferroelectric compounds at a H.S.I.

ABSTRACT

We have discovered a new metal organic framework piezoelectric material which has not been reported in the literature, nicknamed “red” until we can publish our results. We have identified several other strong candidates, which we are synthesizing and characterizing.
Organic ferroelectric research is receiving a great deal of interest in the scientific community. With the help of this grant, CSUSB is at the forefront of this endeavor.
The results from this research provided the foundation for a successful National Science Foundation – Centers of Research Excellence in Science and Technology (NSF-CREST) grant awarded to CSUSB ($5,000,000.00 for five years). The grant is renewable, and has several supplements specifically associated with it. We have already applied for one supplement.
ARO funds from this grant provided stipends to directly support several students, most from unrepresented groups. In addition, numerous students received financial support from other sources; however, they too benefited from this grant in terms of faculty mentors supported by the grant and the use of scientific equipment.
Details of the research progress are described in the scientific progress section.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
08/27/2014	2.00	Donna A. Kunkel, James Hooper, Scott Simpson, Sumit Beniwal, Katie L. Morrow, Douglas C. Smith, Kimberley Cousins, Stephen Ducharme, Eva Zurek, Axel Enders. Rhodizonic Acid on Noble Metals: Surface Reactivity and Coordination Chemistry, The Journal of Physical Chemistry Letters, (10 2013): 0. doi: 10.1021/jz4016124
08/28/2013	1.00	Donna A. Kunkel, James Hooper, Scott Simpson, Geoffrey A. Rojas, Stephen Ducharme, Timothy Usher, Eva Zurek, Axel Enders. Proton transfer in surface-stabilized chiral motifs of croconic acid, Physical Review B, (01 2013): 41402. doi: 10.1103/PhysRevB.87.041402
TOTAL:	**2**	

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received		Paper
TOTAL:		

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Kimberley R. Cousins, Douglas C. Smith, Timothy Usher, Investigating functional organic single crystals at the CSUSB Center for Advanced Functional Materials, invited speakers for the San Gorgonio Section of the ACS meeting, May 2014

Timothy Usher, Kimberley Cousins, Douglas Smith; Materials Research of Novel Organic Piezoelectric/Ferroelectric compounds; Organic Materials Chemistry portfolio Review, October 27?31, 2014, Arlington, VA

Number of Presentations: 2.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

NSF-CREST grant Award # 1345163 http://www.nsf.gov/awardsearch/showAward?AWD_ID=1345163

Cousins applied for and was awarded an NSF-funded XSEDE start up account (50,000 SU's)

Graduate Students

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Post Doctorates

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Timothy Usher	0.24	
Kimberly Cousins	0.16	
Douglas Smith	0.16	
FTE Equivalent:	**0.56**	
Total Number:	**3**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 12.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 12.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 9.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 3.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 1.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 3.00

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

The results from this research provided the foundation for a successful National Science Foundation – Centers of Research Excellence in Science and Technology (NSF-CREST) grant awarded to CSUSB ($5,000,000.00 for five years). The grant is renewable, and has several supplements specifically associated with it. We have already been awarded one of these supplements. With this NSF funding we are able to extend the research far beyond the original scope of the AFRL award.

Details of the research conducted over the three year period can be described in terms of Modeling (Cousins), Synthesis (Smith) and Experimental (Usher).
Computer Modeling (Cousins)

A variety of computational and data mining efforts have been conducted in order to better understand existing organic ferroelectric compounds, and discover new candidates. Many of these efforts have required using the research computers purchased with this grant's funds; A 12 CPU workstation with 32 GB ram, and 3 TB hard disk, as well as two workstations (one Desktop station and one laptop, each running MedeA), and additional software purchased with funds from this grant. The software includes updating our Vienna ab initio structure package (VASP)[ref 1] license to version 5.3.3 for greater capabilities; updating our Cambridge Structure Database System (CCDC)[ref 2] license to six workstations; and purchasing a MedeA [ref 3] "front end" to VASP with transition state locator software. We continued to use a variety of grant-funded and free/publicly licensed software, including Spartan 10 [ref 4], MOPAC 12 [ref 5], GAMESS [ref 6], Avogadro [ref 7], and VESTA [ref 8]. In addition, Cousins applied for and was awarded an NSF-funded XSEDE start up account (50,000 SU's) [ref 9] to perform larger and more sophisticated VASP 5.3.3 and other calculations that are possible using local workstations. The XSEDE calculations are performed on TACC-STAMPEDE, one of the fastest supercomputers in the world.[ref 10] We are also exploring using both VASP 5.3.3 and Quantum Espresso [ref 11] (public domain) plane wave code on new campus-based GPUs.

One project is our study of the aromaticity of the oxocarbons and their mono- and dianions. This project grew from the assertion that the ferroelectric transition for croconic acid arose in part due to the "aromatic transition state" of the process. We are finalizing and preparing for publication results from our study of the oxocarbons, using newly devised isodesmic reactions, and a novel NIC-scan-difference method for predicting ring current due to aromaticity. Our results (Scheme 1) show subtle differences in modeled aromatic behavior from that predicted previously, and the NIC-scan difference method appears to better account for ring size effects than previous methods using calculated NMR chemical shifts. Our results indicate that of the fully conjugated oxocarbon species (C, F and H), only neutral deltic acid (C, n=0), and the deltate dianion (H, n=0) possess significant aromatic character, and that the rhodizonate dianion (H, n=3) has, if fact, some antiaromatic character. (Figure 1)

Figure 1: NICs difference values for the potentially aromatic species in

Scheme 1. The more negative the y-axis values, the more shielded a position is relative to a reference cyclic structure of the same ring size and charge. (see attachments)

We utilized a data mining approach to systematically seek yet-undiscovered organoferroelectric "green" compounds from among crystal structures archived in the CSD database. [ref 13] Based on the observed strong ferroelectric response for one polymorph of diisopropyl ammonium bromide [ref 14], and a weaker response for the corresponding chloride, [ref 15] we identified a number of other small organic salts of halide ions with promise for ferroelectric behavior. Of the ten potential ferroelectric compounds identified during this initial screening, three had been previously reported as weakly ferroelectric. Several others were eliminated after carefully examining the steric requirements for inversion. Two of the remaining candidates are currently being studied computationally using VASP (aminoacetonitrile hydrochloride and melamine hydrochloride in Table 1), including predicting ferroelectric properties using the Berry Phase method [ref 16] and developing models for the necessary transition states for conversion from one polar phase to another. In particular, our candidates are predicted to have similar or lower energies needed to reach transitions state as the diisopropyl ammononium systems [ref 13 and 14] and thus should be active with experimentally achievable coercive fields. The aminoacetonitrile salt might be expected to have a somewhat lower polarization change than the reported diisopropyl ammonium salts, while the melamine hydrochloride may have significantly larger polarization change than the known salts.

Table 1. Preliminary results from calculations performed using VASP 4.6 or 5.3.3 using the PAW-PBE pseudopotentials. (see attachments)

This database searching approach has been repeated with new initial search criteria to include only compounds that contain carboxylate and ammonium ions, leading in discovery of nearly 30 small peptide-like potential ferroelectric candidates. These thirty structures have polar space group symmetry, a close pseudosymmetric structure, and a dipole nearly perpendicular to the pseudosymmetric plane. We are examining these structures more closely in order to uncover additional compounds for study using plane wave density functional theory (VASP calculation) prior to suggesting them for synthesis and testing by the

experimental members of the team. We believe, based on small molecule calculations that the necessary inversion of the chirality center next to the carboxylic acid group could be accomplished through an enolic-like transition state. As was seen for our previous halide ion search, several of these crystals or co-crystals based on amino acid-like compounds have been reported to have ferronic properties, [ref 17] validating our search. These materials, which are expected to be biodegradable, have potential utility for biocompatible functional materials for medical implants.
CCDC and related software has also been used to support our experimental team in other ways including: (1) providing morphology images to assist in determining crystal axes for experimental study of properties such as potential ferroelectricity and piezoelectricity. (see Figure 1); (2) providing simulated x-ray diffraction patterns for different polymorphs of crystals. to match to experimental powder x-ray spectra, and thus identify active polymorphs; (3) providing structures and simulated patterns for other potential "new" materials, for example, to rule out possible know polymorphs or co-crystals from consideration.
Learning to use VASP effectively has proven a formidable task. Recently the MedeA software package, a commercial product integrated with VASP has been purchased. Both Cousins and students Luke Vinson and Carlos Mora are learning to use MedeA to simplify the process of creating input files and interpreting output. Student Carlos Mora spent the summer performing VASP calculations in the Zurek group at University of Buffalo.

Several important results have been obtained thus far from VASP calculations at CSUSB:

(1) To better understand the piezoelectric response observed in the Usher group, on a crystal sample nicknamed "Red", extensive computational study of this compound has ensued. Neither manual manipulation and molecular dynamics simulation of the input files has uncovered a ground state polar form for Red. This is consistent with there being no room temperature or ferroelectric domains observed in the material, and no phase change observed at reduced temperatures (see Usher). Additional calculations have predicted a moderate piezoelectric response for Red, when a current is applied along the "a axis." (Figure 2). Red is a somewhat unusual example of a metal-organic framework with alkali metal cations (Cesium and Sodium) that is predicted to be semi-conducting. Unlike many other metal-organic frameworks, there are no molecular-sized gaps in the structure; that is, the high density of the materials give both a high degree of association between the metal cations and the organic anions, and very little void space.

Figure 2: Cross section of molecular model of "Red". The horizontal axis (a) is the one predicted to have the largest piezoelectric force, but there are smaller predicted effects along the b and c axes. Superimposed on the structure is the predicted morphology. (see attachments)

(2) To better understand the mode of transition for the reported ferroelectric behavior for diisopropylammonium bromide13 and diisopropylammonium chloride,14 two different transition state models were built for the transformation for the chloride. The model with least molecular motion (but which resulting in cleaving the formal molecular bonds, Figure 3) was predicted to be almost twice as edergonic as the more sterically-demanding formal bond rotation (Figure 4). Full transition state calculations for this system are ongoing, as are analogous calculations for the proposed fluoride and iodide salts for diisopropylammonium (Figure 5). As these latter two compounds have not yet been shown to crystalize in a polymorph with the same symmetry as the chloride and bromide salt do, the computations will be used to determine if there is an energy minimum that might lead to crystallization and experimental study. Our collaborators in Nebraska have crystalized a polymorph of the iodide with an above-room-temperature solid phase transition that supports the existence of such a polymorph (unpublished results).

Figure 3: Models showing the orientation of a single unit of diispropylammonium chloride in the optimized structure based on the reported crystal structure (3c) and the inverted reported structure (3a). Structure 3b was the originally proposed non-polar intermediate (higher energy); structure 3d is lower by nearly 400 kJ/mol. (see attachments)

Figure 4. Predicted, but yet unreported polar analogs DIAF (diisopropylammonium fluoride, left) and DIAI (diisopropylammonium iodide, right). (see attachments)

(3) Energies for transition and Berry Phase predicted changes in polarizations have are being calculated for potential ferroelectric compounds uncovered by our database searching. Results to date are summarized in Table 1.

2012-2015 Students (Cousins)

Margarita Cuadras (Magy, Hispanic/Native American) worked for more than two years developing NIC-difference method for evaluating aromaticity. She presented a posters describing the project at the Southern California Conferences on Undergraduate Research in both November 2012, and November 2013. She completed her BS-Chemistry (biochemistry option) at the end of summer 2014, and is preparing to apply to graduate programs in chemistry.

Maressah Ynfante-Coral (Hispanic Female and BS-ACS Chemistry major) has been continuing Magy's work by correlating the

calculated NICs-difference values with other measures of aromaticity.

Luke Vinson is a senior chemistry major (BS-ACS Certified option, mathematics minor) graduating in Summer, 2014. Luke worked with Dr. Cousins for more than a year to find potential new ferroelectric candidates from structures in the Cambridge Crystallographic database, and evaluate the hits as potential ferroelectric candidates. He developed the database searching protocol we use. Luke is seeking employment in Chemistry after graduation.

Carlos Mora (Hispanic) is a chemistry major (BS-ACS Certified option) who worked with Dr. Cousins during W/S 2014, and performed summer research on solid state modeling at the University Buffalo. He returned in August to assist with solid state modeling at CSUSB, working to uncover a transition state for the aminoacetonitrile hydrochloride ferroelectric candidate. He has secured a research position in materials after graduating in Spring, 2015.

Alejandra Quezada (Hispanic female) is a Chemistry major (BS-Biochemistry option) who has been working with Dr. Cousins since April 2014. She performed the database search to uncover 33 potential ferroelectric amino-acid-like compounds, presented her work at SCCUR in November, 2014, and is continuing modeling possible ferroelectric transition states for one of the molecules she uncovered.

Cruz Jacques (Hispanic) is a chemistry major (BA) and mathematic minor student who worked with Dr. Cousins for one quarter. He learned to use Spartan software and completed several energy calculations to contribute to the aromaticity project.

Natalie Quintaro (Hispanic female) is an Upward Bound student (rising High School Senior) who spent six weeks in Dr. Cousins' lab this summer. She is assisting in completing the aromaticity calculations using Spartan.

Gisele Osuna (mixed race/Hispanic) was a student from College of the Desert (local Community College), now at University of California, Riverside, who spent four weeks working the Dr. Cousins this summer. She is also assisting in completing the aromaticity calculations using Spartan, and presented her results at SCCUR in Fall, 2014.

Jason Zhang is a high school student (rising senior) helped Dr. Cousins' group initial solid state modeling using the Quantum Espresso software.
Outcomes from the Computational Group (publications and presentations)

Presentations and posters

1. Quezada, Alejandra; Cousins, Kimberley. "Predicting Organic Amino-acid-like and Potentially Ferroelectric Compounds," Southern California Conference on Undergraduate Research, CSU Fullerton, November 22, 2014.
2. Osuna, Gisele; Cousins, Kimberley Farmer, Carl. "Investigative Analysis on the Aromaticity of Croconic Acid and its Anions," Southern California Conference on Undergraduate Research, CSU Fullerton, November 22, 2014.
3. Margarita Cuadras, Kimberley Cousins, "Nucleus independent chemical shifts (NICS) scan method analysis for cyclic oxocarbons," Southern California Conference on Undergraduate Research, November 23, 2013, Whittier College; also at CSUSB Student Research Symposium, May 27, 2014.
4. Luke Vinson, Kimberley Cousins, "Identification of Possible Organoferroelectric Crystals", Southern California Conference on Undergraduate Research, November 23, 2013, Whittier College
5. Cuadras, Margarita, Cousins, Kimberley, "Reevaluating the Aromaticity of Oxocarbon Molecules," Southern California Conference on Undergraduate Research, CSU Channel Islands, November 17, 2012.

6. Cousins, Kimberley, "Possible mechanisms for interconversion of polar forms for the ferroelectric diisopropylammonim halides," (COMP Poster Session and SciMix), 249th ACS National Meeting, Denver, Colorado, March 22-26, 2015.
7. Kimberley R. Cousins, Douglas C. Smith, Timothy Usher, Investigating functional organic single crystals at the CSUSB Center for Advanced Functional Materials, invited speakers for the San Gorgonio Section of the ACS meeting, May 2014.

Publications:
8. Donna A. Kunkel, James Hooper, Scott Simpson, Sumit Beniwal1, Katie L. Morrow, Douglas C. Smith, Kimberley Cousins, Stephen Ducharme, Eva Zurek, Axel Enders, "Rhodizonic Acid on Noble Metals: Surface Reactivity and Coordination Chemistry" J. Phys. Chem. Lett., 2013, 4 (20), pp 3413–3419.

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14. (a) Da-Wei Fu, Hong-Ling Cai, Yuanming Liu, Qiong Ye, Wen Zhang, Yi Zhang, Xue-Yuan Chen, Gianluca Giovannetti, Massimo Capone, Jiangyu Li, and Ren-Gen Xiong. “Diisopropylammonium Bromide Is a High-Temperature Molecular Ferroelectric Crystal”, Science 2013 339 (6118), 425- 428.; (b)Piecha, Anna and Gagor, Anna and Jakubas, Ryszard and Szklarz, Przemyslaw,"Room- temperature ferroelectricity in diisopropylammonium bromide",Cryst. Eng. Comm, 2013, 940-944
15. Da-Wei Fu, Wen Zhang*, Hong-Ling Cai, Jia-Zhen Ge, Yi Zhang, Ren-Gen Xiong. “Diisopropylammonium Chloride: A Ferroelectric Organic Salt with a High Phase Transition Da- Temperature and Practical Utilization Level of Spontaneous Polarization,” Advanced Materials, 2011, 23, 5658–5662.
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17. (a) Dmitry Isakov, Daria Petukhova, Semen Vasilev, Alla Nuraeva, Timur Khazamov, Ensieh Seyedhosseini, Pavel Zelenovskiy, Vladimir Ya. Shur, and Andrei L. KholkinIn Situ Observation of the Humidity Controlled Polymorphic Phase Transformation in Glycine Microcrystals, Crystal Growth & Design 2014 14 (8), 4138-4142; (b) Ensieh Seyedhosseini, Maxim Ivanov, Vladimir Bystrov, Igor Bdikin, Pavel Zelenovskiy, Vladimir Ya. Shur, Andrei Kudryavtsev, Elena D. Mishina, Alexander S. Sigov, and Andrei L. Kholkin Growth and Nonlinear Optical Properties of ß-Glycine Crystals Grown on Pt Substrates, Crystal Growth & Design 2014 14 (6), 2831-2837; (c) A.S. Haja Hameed, G. Ravi, C.W. Lan, Studies on amino acids admixtured triglycine sulphophosphate crystals, Journal of Crystal Growth, 2005, 275, e1461- e1465; (d) C.M. Raghavan, R. Sankar, R. Mohan Kumar, R. Jayavel, Effect of amino acid doping on the growth and ferroelectric properties of triglycine sulphate single crystals, Materials Research Bulletin, 2008, 43, 305-311; (e) Batra, A.K.; Mathur, S.C. Electric conductivity of doped triglycine sulphate crystals; Journal of Materials Science Letters, 1985, 4, 679-680; (f) V.V. Lemanov, S.N. Popov, G.A. Pankova, Phase Transitions in Crystals of Protein Amino Acids, 2011, Physics of the Solid State, 53, 1603–1607; (g) G. Arunmozhi, R. Jayavel, C. Subramanian, Ferroelectric studies on amino acids mixed TGSP single crystals, Materials Letters, 1998, 33, 251-254; (h) S. Aravazhi, R. Jayavel, C. Subramanian, Growth and characterization of L-alanine and L-valine doped triglycine sulphate crystals, Materials Research Bulletin, 1997, 32, 1503-1513; (i) J. Novotný, J. Zelinka, F. Moravec, Broadband infrared detectors on the basis of PATGS/Pt(IV) single crystals, Sensors and Actuators A: Physical, 2005, 119, 300-304.

Synthesis and Crystal Growth (Smith)

To date, the Smith lab has produced multi-gram quantities of croconic acid, rhodizonic acid and several derivatives of croconic acid. Recently, efforts have concentrated on the production of a compound we refer to as “Red”, a croconic acid derivative that has demonstrated piezoelectric behavior (see Usher later). Additionally, we have been recently prepared a new derivative of croconic acid, a compound closely related to “Red” which we refer to as “Amber”, in hopes that it might display similar properties to its analogue, “Red”. The procedures of Fatiadi1 and Geoffroy2 are being adapted to produce these materials. Efforts also continue in preparing deltic acid. Currently, we are duplicating the procedures of Serratosa3 for this synthesis. This synthesis requires the use of compounds such as chlorine gas and ammonia gas. These considerations seriously restrict when this material can be prepared (limited to summer months only). , and student collaborators have not been permitted to assist with this effort..

We continue to work with Rhodizonic acid and efforts to continue to convert the dihydrate form (prepared from synthesis) to its anhydrous form. This has been a difficult process and may require the use of a diffusion vacuum pump (ultra-high vacuum) in order to accomplish this dehydration.

In addition to these considerations, we continue to supply Dr. Usher’s lab with quantities of diisopropylammonium bromide, melamine hydrochloride, and samples of both “Red” and “Amber”. We are also attempting to grow other crystals identified by Dr. Cousins as mentioned above in Dr. Cousins’ section of this document.

Several undergraduates have worked with Dr. Smith during the duration of this grant.

Margarita (Magy) Cuadras is an underrepresented minority student that majored in chemistry (BS) with a concentration in

biochemistry. Additionally, she has been part of the Math and Science Scholars Program (MASS) here at CSUSB. Magy worked with Smith for three quarters preparing synthetic intermediates and growing crystals. Magy graduated in the Spring of 2014. She is considering graduate studies in chemistry.

Amylee Martin is an undergraduate student majoring in Chemistry (BA, biochemistry concentration). She is entering into her senior year. Amy began working (synthesis/crystal growth) with Smith in Spring 2014 and she worked part time over the summer (2014) supported by this grant. She is presently considering a career in the health related fields. She recently presented her research via a poster presentation at the Meeting of the Minds student research symposium here at CSUSB in Spring 2015.

Elizabeth Martinez is underrepresented minority student that majored in chemistry (BA). She worked in Smith's lab for six quarters performing synthetic work. Additionally, Elizabeth was part of the MASS program here at CSUSB. She presented her research via a poster presentation at the Meeting of the Minds student research symposium here at CSUSB in Spring 2014. Elizabeth graduated in Spring 2014 and she is pursuing a Masters degree in chemistry at Cal Poly Pomona.

Steven Merrill is an undergraduate student majoring in chemistry (BS) with a biochemistry concentration. Steven has been part of the Pro-active Recruitment in Introductory Science and Mathematics (PRISM) program here at CSUSB. Steven joined Smith' s group in Spring 2014 and he worked (synthetic/crystal growth) on this project over the summer, 2014. This year, Steven will enter his senior year. Upon graduating, Steven plans to attend graduate school in a STEM field, or pursue a career in the health professions.

Katie Morrow is a recent graduate (Winter 2015) that is majored in chemistry (BS) with a concentration in biochemistry. Katie joined Smith's group in the spring of 2012 and she has worked (synthesis/crystal growth)) consistently throughout this period, including full time summer 2013 and part time summer, 2014, supported by this grant. She has one publication to her credit on this grant and she also presented her research (along with Elizabeth Martinez) via a poster presentation at the Meeting of the Minds student research symposium here at CSUSB Spring 2014. Katie is now employed in a STEM related field however she is considering pursuing a career in the health related fields.

Carlos Navarro is underrepresented minority student majoring in chemistry (BS) with a concentration in biochemistry. Carlos has been part of the PRISM program here at CSUSB. Carlos joined Smith's group Spring 2014 (synthetic/crystal growth) and he participated in an REU Summer, 2014 and he is participating in an REU Summer 2015. This year, Carlos will enter his senior year. Upon graduating, Carlos plans to attend graduate school in a STEM field. He recently presented her research via a poster presentation at the Meeting of the Minds student research symposium here at CSUSB in Spring 2015.

Geovanni Rangel is underrepresented minority student majoring in chemistry (BS) with an ACS accredited option. Geovanni has been part of the PRISM program here at CSUSB. Geovanni joined Smith's group in Spring 2014 and he performed research on this project here at CSUSB during the Summer 2014 (synthesis/crystal growth). This summer (2015) he will participate in a REU. This year, Geovanni will enter his senior year. Upon graduating, Geo plans to attend graduate school in a STEM field.

Brandon Hallaway is a recent graduate (Spring 2013) that is majored in chemistry (BS) with a concentration in biochemistry. Brandon joined Smith's group in the fall of 2011 and he has worked (synthesis) consistently throughout this period, including full time summer 2012, supported by this grant. Brandon will be pursuing a MS degree in biomedical sciences at Philadelphia College of Osteopathic Medicine in Georgia.

Outcomes from the Synthesis Group (publications and presentations)

Presentations and posters (students underlined)

1. Martinez, Elizabeth; Morrow, Katie; Smith, Douglas. "The Preparation of Croconic and Rhodizonic Acid," Meeting of the Minds 3rd Annual Student Research Symposium, CSU San Bernardino, May 27, 2014.

2. Merrill, Steven; Rangel, Geovanni; Martin, Amylee; Navarro, Carlos; Morrow, Katie; Smith, Douglas "The Synthesis of Croconic and Rhodizonic Acid," ACS Southern California Undergraduate Research Conference, UC San Diego, March 14, 2015.

3. Martin, Amylee; Navarro, Carlos; Merrill, Steven; Morrow, Katie; Rangel, Geovanni; Smith, Douglas. "Preparation of Croconic and Rhodizoinc Acid," Meeting of the Minds 4th Annual Student Research Symposium, CSU San Bernardino, May 21, 2015.

Publications:

Donna A. Kunkel, James Hooper, Scott Simpson, Sumit Beniwal1, Katie L. Morrow, Douglas C. Smith, Kimberley Cousins, Stephen Ducharme, Eva Zurek, Axel Enders, “Rhodizonic Acid on Noble Metals: Surface Reactivity and Coordination Chemistry” J. Phys. Chem. Lett., 2013, 4 (20), pp 3413–3419

Experimental (Usher)

The theoretically predicted and subsequently synthesized compounds were characterized by a range of techniques.

We were able to obtain saturated hysteresis loops on single crystal croconic acid. See figure.
Figure 4: Hysteresis loop of single crystal croconic acid. (see attachments)
The compound code named “Red” is a variation of croconic acid. It does not appear to be ferroelectric. However, it is piezoelectric. When placed in a petri dish of mineral oil (to prevent electrical arcing) ripples in the mineral oil are clearly visible when a voltage is applied to the sample. We quantified the piezoelectric response. See figure of Piezo Response for “red”.

Figure 5: Piezo Response for “red”. (see attachments)

We also have piezoforce microscopy results on red. See Figures.

Figure 6: piezoforce microscopy results on red (30V@100kHz). (see attachments)

We have produced iron doped croconic acid as well as Manganese doped croconic acid. These samples were analyzed in our epr spectrometer as a function of angle to map out the g- tensor.

Figure 7 : Epr spectra of ironed doped Croconic acid showing anisotropic g-factor. (see attachments)

After concluding that “red” was not ferroelectric at room temperature, we looked for a paraelectric – ferroelectric transition over a temperature range of 80K to 523K by measuring the capacitance as a function of temperature. The results show that red is not ferroelectric over this range.
Since this grant was originally awarded, new room temperature organic ferroelectrics have been reported by others. One of these is diisopropylammonium bromide, abbreviated, DIAP. Smith has grown single crystals of DIAP and Usher’s group has been able to reproduce the phase transition evident in the dielectric constant vs temperature data.

Students (Usher group)

Victor Jimenez is an underrepresented minority undergraduate, majoring in physics. He has won several awards and honors. He was awarded a Smart Scholarship, from the Department of Education (Title V) for underrepresented minorities in STEM majors with high GPAs. He was also awarded a McNair Scholarship, also funded by the Department of Education. In addition he was a LSAMP scholar, funded by NSF. He graduated in Spring of 2013. He is taking a year off before going to graduate school.

Abraham Garcia is an underrepresented minority undergraduate, majoring in physics. He has also won several awards and honors. He was awarded a Smart Scholarship, from the Department
of Education (Title V) for underrepresented minorities in STEM majors with high GPAs. He was also awarded a McNair Scholarship, also funded by the Department of Education, He in Spring of 2013. He is now employed at a local aerospace company, Kelly Space and Technology.

Earl Smith is an underrepresented minority undergraduate, majoring in physics. He has also won several awards and honors. He was also awarded a McNair Scholarship. He took a break from this research project in the summer of 2014 to be a NASA intern. He graduated in Spring of 2013. He is currently employed as a counselor in the CSUSB Upward Bound program. He is planning on going to graduate school next year.

Kevin Collins is an undergraduate physics major. He spent the summer of 2014 as a research student at the Materials Research Center, University of Lincoln Nebraska. This summer 2015 he as been awarded a NASA internship.
Melissa Hannan is a female physics major. After participating in research under this grant she was awarded an REU at Arecibo National lab in the summer of 2014. For the summer of 2015 she was awarded an REU at SETI institute.

Two High School Students were supported through a supplement to this main grant, Joseph Vasquez and Salina Gomez. Joseph and Salina are both of Hispanic heritages. In addition, Salina is female. Joseph and Salina conducted research over the summer with our group. Earl Smith (African American heritage) and Melissa Hannan were their undergraduate mentors. We partnered with the CSUSB Upward Bound (UB) STEM program, Department of Education grant P047A120164. This worked out very well. The UB program already had well established procedures and protocols for hosting High School students on the

CSUSB campus. For example, fingerprinting mentors and making sure legal documentation is in place. In addition, the UB program provided housing in college dorms, lunch, social activities, and college counseling, Joseph and Salina each gave a poster presentation at the end of the summer. They also presented a poster at the Southern California Conference on Undergraduate Education in November 2013.

Outcomes from Experimental Group

Joseph Vasquez (Rialto High School), Mentors: Earl Smith and Timothy Usher, “How is the Powder X-Ray Diffraction machine cool?” CSUSB Upward Bound final presentation July 25, 2013.

Selena Gomez (Eisenhower High School) Mentors: Melissa Hannan and Timothy Usher “The Significance of Ferroelectrics” CSUSB Upward Bound final presentation July 25, 2013.

Earl Smith (Mentor: Timothy Usher, Associate: Victor Jimenez), “First EPR Results on Croconic Acid Single Crystals: G-tensor Quantification”, (Talk), NASA-Dryden, 2012.

Victor Jimenez and Earl Smith “Experimental Investigations of Croconic Acid Single Crystals and Thin Films” McNair Symposium, University of Maryland, March 16, 2012.

Victor Jimenez, “Polarization Properties of croconic acid Single crystals and thin films” McNair Symposium CSUSB July 31, 2012.

Timothy D. Usher, Kenneth R. Ulibarri, Jr. and Gilberto S. Camargo, “Piezoelectric Microfiber Composite Actuators for Morphing Wings.” ISRN Materials Science, Article ID 189659, Undergraduate underrepresented minority authors, 2013.

Technology Transfer

Tesla motors (the manufactures of electric vehicles) contacted Dr. Usher. Due to a non-disclosure agreement (NDA), the details cannot be made available. The interaction was relevant to the funded research.

The results from this research provided the foundation for a successful National Science Foundation – Centers of Research Excellence in Science and Technology (NSF-CREST) grant awarded to CSUSB ($5,000,000.00 for five years). The grant is renewable, and has several supplements specifically associated with it. We have already been awarded one of these supplements. With this NSF funding we are able to extend the research far beyond the original scope of the AFRL award.

Details of the research conducted over the three year period can be described in terms of Modeling (Cousins), Synthesis (Smith) and Experimental (Usher).

Computer Modeling (Cousins)

A variety of computational and data mining efforts have been conducted in order to better understand existing organic ferroelectric compounds, and discover new candidates. Many of these efforts have required using the research computers purchased with this grant's funds; A 12 CPU workstation with 32 GB ram, and 3 TB hard disk, as well as two workstations (one Desktop station and one laptop, each running MedeA), and additional software purchased with funds from this grant. The software includes updating our *Vienna ab initio structure package* (VASP)[1] license to version 5.3.3 for greater capabilities; updating our Cambridge Structure Database System (CCDC)[2] license to six workstations; and purchasing a MedeA[3] "front end" to VASP with transition state locator software. We continued to use a variety of grant-funded and free/publicly licensed software, including Spartan 10,[4] MOPAC 12,[5] GAMESS,[6] Avogadro,[7] and VESTA.[8] In addition, Cousins applied for and was awarded an NSF-funded XSEDE start up account (50,000 SU's)[9] to perform larger and more sophisticated VASP 5.3.3 and other calculations that are possible using local workstations. The XSEDE calculations are performed on TACC-STAMPEDE, one of the fastest supercomputers in the world.[10] We are also exploring using both VASP 5.3.3 and Quantum Espresso[11] (public domain) plane wave code on new campus-based GPUs.

One project is our study of the aromaticity of the oxocarbons and their mono- and dianions. This project grew from the assertion that the ferroelectric transition for croconic acid arose in part due to the "aromatic transition state" of the process. We are finalizing and preparing for publication results from our study of the oxocarbons, using newly devised isodesmic reactions, and a novel NIC-scan-difference method for predicting ring

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[1] https://www.vasp.at

[2] http://www.ccdc.cam.ac.uk/Solutions/CSDSystem/pages/CSDSystem.aspx

[3] http://www.materialsdesign.com/medea/modeling-analysis

[4] http://wavefun.com

[5] MOPAC2012, James J. P. Stewart, Stewart Computational Chemistry, Colorado Springs, CO, USA, HTTP://OpenMOPAC.net (2012).

[6] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, together with M. Dupuis, J.A.Montgomery, *J. Comput. Chem.* 14, 1347-1363(1993).

[7] M.D. Hanwell, D.E. Curtis, D.C. Lonie, T. Vandermeersch, E. Zurek and G.R. Hutchison; *Journal of Cheminformatics*, 4:17, (2012).

[8] K. Momma and F. Izumi (2011): VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data *J. Appl. Crystallogr.*, 44, 1272-1276.

[9] TG-DMR140027 at xsede.org

[10] https://www.tacc.utexas.edu/stampede/

[11] http://www.quantum-espresso.org

current due to aromaticity. Our results (Scheme 1) show subtle differences in modeled aromatic behavior from that predicted previously,[12] and the NIC-scan difference method appears to better account for ring size effects than previous methods using calculated NMR chemical shifts. Our results indicate that of the fully conjugated oxocarbon species (**C**, **F** and **H**), only neutral deltic acid (**C**, n=0), and the deltate dianion (**H**, n=0) possess significant aromatic character, and that the rhodizonate dianion (**H,** n=3) has, if fact, some antiaromatic character. (Figure 1)

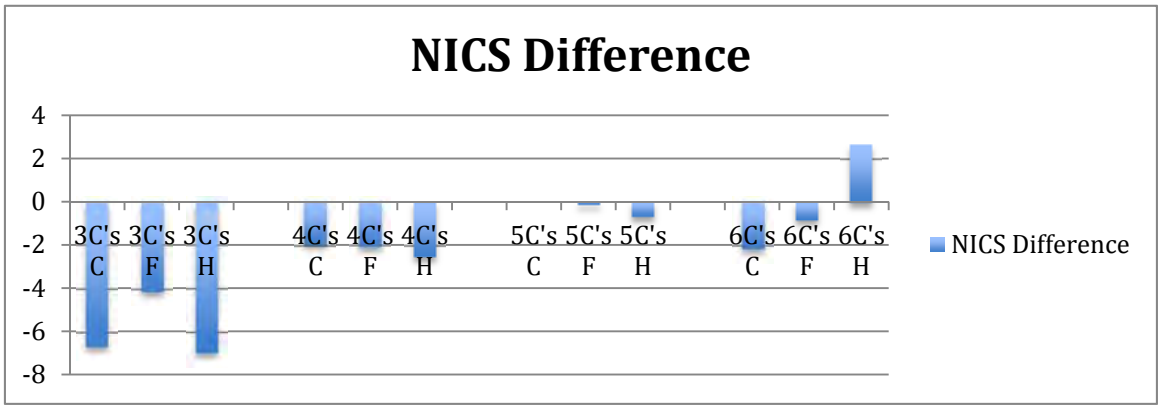
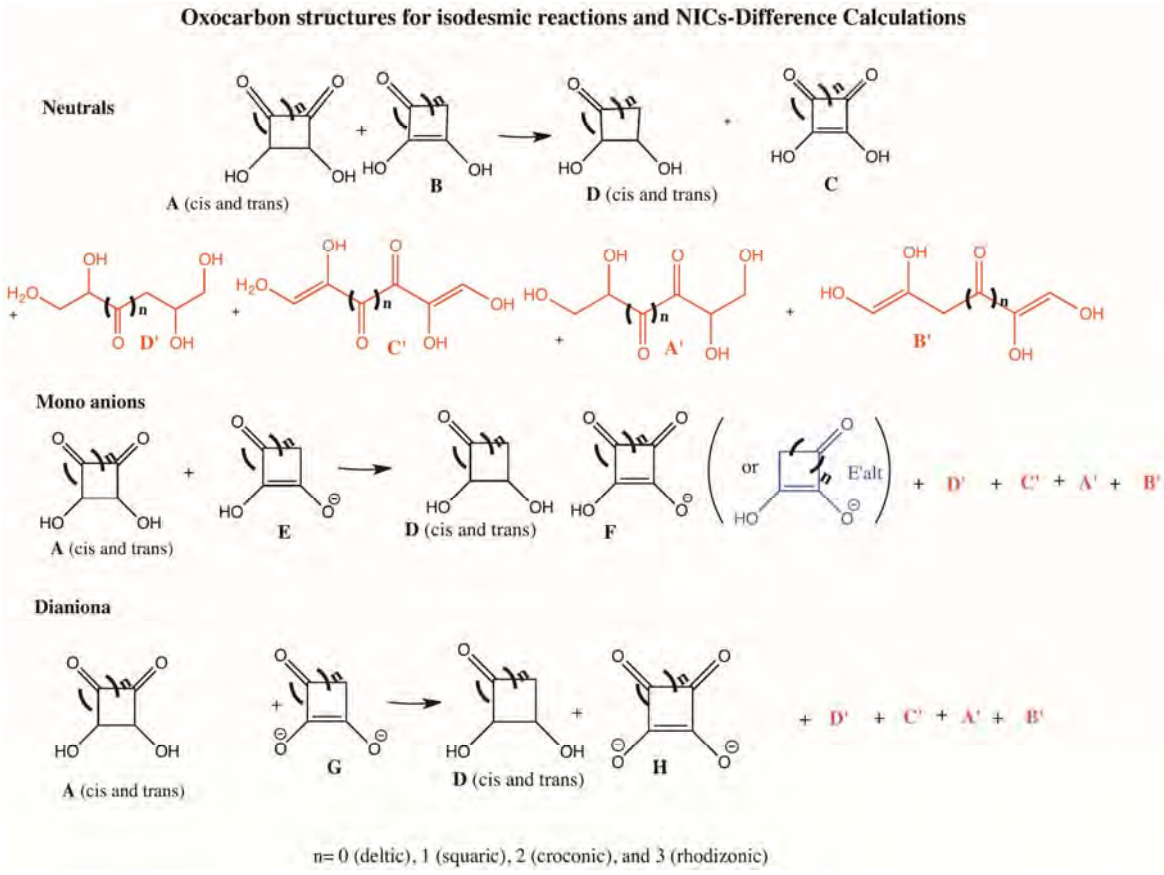


Figure 1: NICs difference values for the potentially aromatic species in Scheme 1. The more negative the y-axis values, the more shielded a position is relative to a reference cyclic structure of the same ring size and charge.

Scheme 1:



[12] P. Schleyer, K. Najafian, B. Kiran, and H. Jiao, *J. Org. Chem*. 2000, **65**, 426-431, and references therein).

We utilized a data mining approach to systematically seek yet-undiscovered organoferroelectric "green" compounds from among crystal structures archived in the CSD database.[13] Based on the observed strong ferroelectric response for one polymorph of diisopropyl ammonium bromide,[14] and a weaker response for the corresponding chloride,[15] we identified a number of other small organic salts of halide ions with promise for ferroelectric behavior. Of the ten potential ferroelectric compounds identified during this initial screening, three had been previously reported as weakly ferroelectric. Several others were eliminated after carefully examining the steric requirements for inversion. Two of the remaining candidates are currently being studied computationally using VASP (aminoacetonitrile hydrochloride and melamine hydrochloride in Table 1), including predicting ferroelectric properties using the Berry Phase method[16] and developing models for the necessary transition states for conversion from one polar phase to another. In particular, our candidates are predicted to have similar or lower energies needed to reach transitions state as the diisopropyl ammononium systems[13, 14] and thus should be active with experimentally achievable coercive fields. The aminoacetonitrile salt might be expected to have a somewhat lower polarization change than the reported diisopropyl ammonium salts, while the melamine hydrochloride may have significantly larger polarization change than the known salts.

Table 1. Preliminary results from calculations performed using VASP 4.6 or 5.3.3 using the PAW-PBE pseudopotentials.

Known or potential ferroelectric crystal identity	Polar space group	Energy calculated necessary to achieve pseudosymmetric intermediate/transition state	Polarization predicted by Berry Phase method $\mu C/cm^2$	Experimental polarization $\mu C/cm^2$
Diisopropylammonium chloride (known)	P21	383 kJ/mol	83**	8.9[14]
Diisopropylammonium bromide (known)	P21	306 kJ/mol	37	23,[13a] 15[13b]
aminoacetonitrile hydrochloride (potential)	P21	190.44 kJ/mol	22	Not yet reported
melamine hydrochloride monohydrate	Cmc21	314 kJ/mol	>100**	Not yet reported

** This crystal likely distorts significantly in the real system due to crowding, lowering the experimental polarization.

[13] F. H. Allen, Acta Cryst., B58, 380-388, 2002 "The Cambridge Structural Database: a quarter of a million crystal structures and rising" [DOI: 10.1107/S0108768102003890]

[14] (a) Da-Wei Fu, Hong-Ling Cai, Yuanming Liu, Qiong Ye, Wen Zhang, Yi Zhang, Xue-Yuan Chen, Gianluca Giovannetti, Massimo Capone, Jiangyu Li, and Ren-Gen Xiong. "Diisopropylammonium Bromide Is a High-Temperature Molecular Ferroelectric Crystal", *Science* **2013** *339* (6118), 425-428.; (b)Piecha, Anna and Gagor, Anna and Jakubas, Ryszard and Szklarz, Przemyslaw,"Room-temperature ferroelectricity in diisopropylammonium bromide",*Cryst. Eng. Comm*, **2013**, 940-944

[15] Da-Wei Fu, Wen Zhang*, Hong-Ling Cai, Jia-Zhen Ge, Yi Zhang, Ren-Gen Xiong. "Diisopropylammonium Chloride: A Ferroelectric Organic Salt with a High Phase Transition *Da*-Temperature and Practical Utilization Level of Spontaneous Polarization," *Advanced Materials*, **2011**, *23*, 5658–5662.

[16] (a) Berry, M.V. ; "Quantal phase factors accompanying adiabatic changes." *Proc. R. Soc. London*, Ser. A 392, 45, (1984); (b) Berry, M.V., *Geometric Phases in Physics*, edited by A. Shapere and F. Wilczek (World Scientific, Singapore), p.7, (1989).

This database searching approach has been repeated with new initial search criteria to include only compounds that contain carboxylate and ammonium ions, leading in discovery of nearly 30 small peptide-like potential ferroelectric candidates. These thirty structures have polar space group symmetry, a close pseudosymmetric structure, and a dipole nearly perpendicular to the pseudosymmetric plane. We are examining these structures more closely in order to uncover additional compounds for study using plane wave density functional theory (VASP calculation) prior to suggesting them for synthesis and testing by the experimental members of the team. We believe, based on small molecule calculations that the necessary inversion of the chirality center next to the carboxylic acid group could be accomplished through an enolic-like transition state. As was seen for our previous halide ion search, several of these crystals or co-crystals based on amino acid-like compounds have been reported to have ferronic properties,[17] validating our search. These materials, which are expected to be biodegradable, have potential utility for biocompatible functional materials for medical implants.

CCDC and related software has also been used to support our experimental team in other ways including: (1) providing morphology images to assist in determining crystal axes for experimental study of properties such as potential ferroelectricity and piezoelectricity. (see Figure 1); (2) providing simulated x-ray diffraction patterns for different polymorphs of crystals. to match to experimental powder x-ray spectra, and thus identify active polymorphs; (3) providing structures and simulated patterns for other potential "new" materials, for example, to rule out possible know polymorphs or co-crystals from consideration.

Learning to use VASP effectively has proven a formidable task. Recently the MedeA software package, a commercial product integrated with VASP has been purchased. Both Cousins and students Luke Vinson and Carlos Mora are learning to use MedeA to simplify the process of creating input files and interpreting output. Student Carlos Mora spent the summer performing VASP calculations in the Zurek group at University of Buffalo.

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[17] (a) Dmitry Isakov, Daria Petukhova, Semen Vasilev, Alla Nuraeva, Timur Khazamov, Ensieh Seyedhosseini, Pavel Zelenovskiy, Vladimir Ya. Shur, and Andrei L. KholkinIn Situ Observation of the Humidity Controlled Polymorphic Phase Transformation in Glycine Microcrystals, *Crystal Growth & Design* **2014** *14* (8), 4138-4142; (b) Ensieh Seyedhosseini, Maxim Ivanov, Vladimir Bystrov, Igor Bdikin, Pavel Zelenovskiy, Vladimir Ya. Shur, Andrei Kudryavtsev, Elena D. Mishina, Alexander S. Sigov, and Andrei L. Kholkin Growth and Nonlinear Optical Properties of β-Glycine Crystals Grown on Pt Substrates, *Crystal Growth & Design* **2014** *14* (6), 2831-2837; (c) A.S. Haja Hameed, G. Ravi, C.W. Lan, Studies on amino acids admixtured triglycine sulphophosphate crystals, *Journal of Crystal Growth*, 2005, 275, e1461- e1465; (d) C.M. Raghavan, R. Sankar, R. Mohan Kumar, R. Jayavel, Effect of amino acid doping on the growth and ferroelectric properties of triglycine sulphate single crystals, *Materials Research Bulletin*, 2008, *43*, 305-311; (e) Batra, A.K.; Mathur, S.C. Electric conductivity of doped triglycine sulphate crystals; *Journal of Materials Science Letters*, **1985**, *4*, 679-680; (f) V.V. Lemanov, S.N. Popov, G.A. Pankova, Phase Transitions in Crystals of Protein Amino Acids, **2011,** *Physics of the Solid State*, *53,* 1603–1607; (g) G. Arunmozhi, R. Jayavel, C. Subramanian, Ferroelectric studies on amino acids mixed TGSP single crystals, *Materials Letters*, **1998**, *33*, 251-254; (h) S. Aravazhi, R. Jayavel, C. Subramanian, Growth and characterization of L-alanine and L-valine doped triglycine sulphate crystals, *Materials Research Bulletin*, **1997**, *32*, 1503-1513; (i) J. Novotný, J. Zelinka, F. Moravec, Broadband infrared detectors on the basis of PATGS/Pt(IV) single crystals, *Sensors and Actuators A: Physical*, **2005**, *119*, 300-304.

Several important results have been obtained thus far from VASP calculations at CSUSB:

(1) To better understand the piezoelectric response observed in the Usher group, on a crystal sample nicknamed “Red”, extensive computational study of this compound has ensued. Neither manual manipulation and molecular dynamics simulation of the input files has uncovered a ground state polar form for Red. This is consistent with there being no room temperature or ferroelectric domains observed in the material, and no phase change observed at reduced temperatures (see Usher). Additional calculations have predicted a moderate piezoelectric response for Red, when a current is applied along the “a axis.” (Figure 2). Red is a somewhat unusual example of a metal-organic framework with alkali metal cations (Cesium and Sodium) that is predicted to be semi-conducting. Unlike many other metal-organic frameworks, there are no molecular-sized gaps in the structure; that is, the high density of the materials give both a high degree of association between the metal cations and the organic anions, and very little void space.

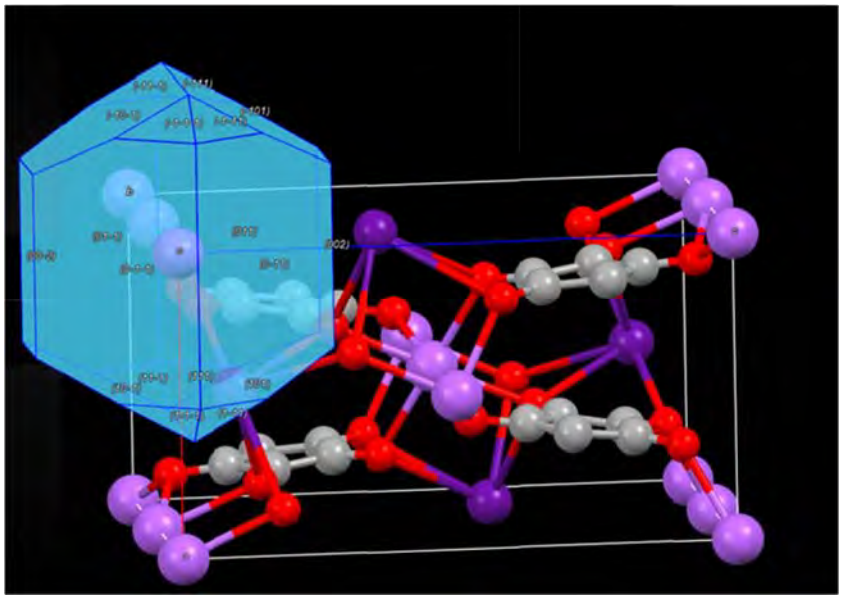

Figure 2: Cross section of molecular model of “Red”. The horizontal axis (a) is the one predicted to have the largest piezoelectric force, but there are smaller predicted effects along the b and c axes. Superimposed on the structure is the predicted morphology.

(2) To better understand the mode of transition for the reported ferroelectric behavior for diisopropylammonium bromide13 and diisopropylammonium chloride,[14] two different transition state models were built for the transformation for the chloride. The model with least molecular motion (but which resulting in cleaving the formal molecular bonds, Figure 3) was predicted to be almost twice as edergonic as the more sterically-demanding formal bond rotation (Figure 4). Full transition state calculations for this system are ongoing, as are analogous calculations for the proposed fluoride and iodide salts for diisopropylammonium (Figure 5). As these latter two compounds have not yet been shown to crystalize in a polymorph with the same symmetry as the chloride and bromide salt do, the computations will be used to determine if there is an energy minimum that might lead to crystallization and experimental study. Our collaborators in Nebraska have crystalized a polymorph of the iodide with an above-room-temperature solid phase transition that supports the existence of such a polymorph (unpublished results).

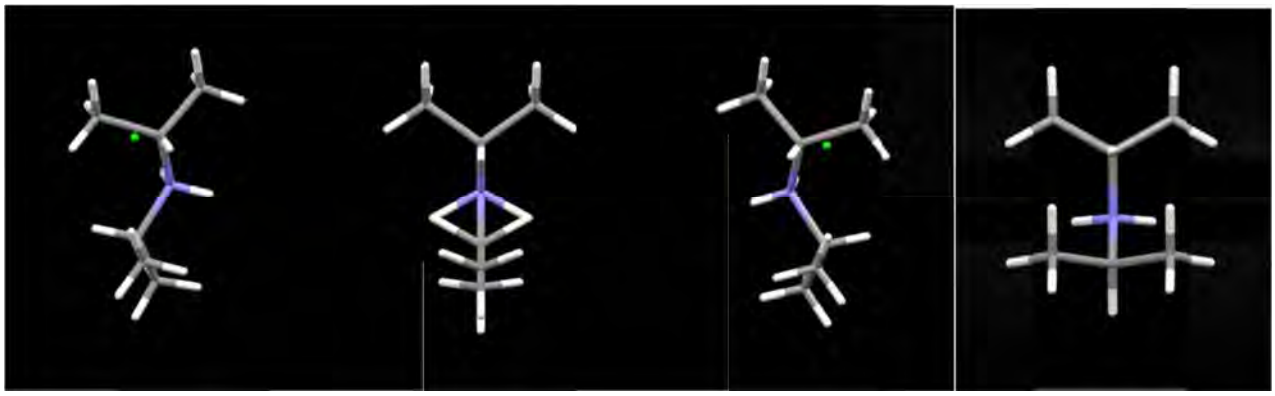

Figure 3 a b c d
Models showing the orientation of a single unit of diispropylammonium chloride in the optimized structure based on the reported crystal structure (3c) and the inverted reported structure (3a). Structure 3b was the originally proposed non-polar intermediate (higher energy); structure 3d is lower by nearly 400 kJ/mol.

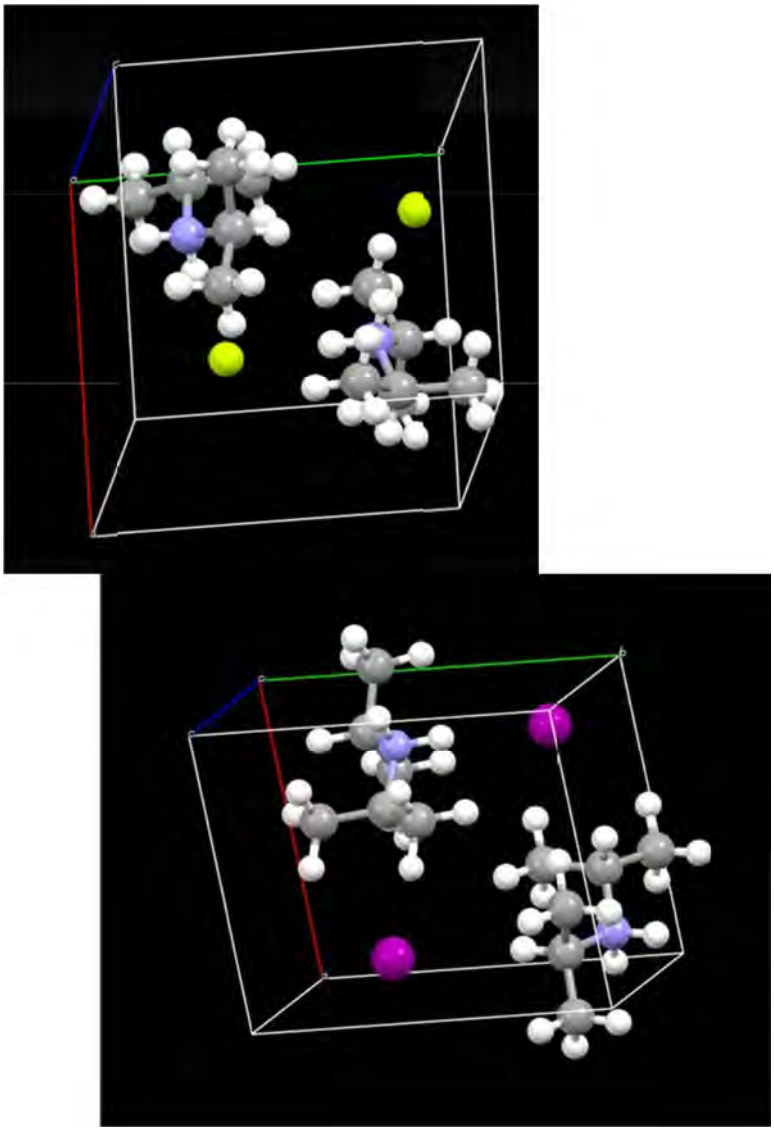

Figure 4. Predicted, but yet unreported polar analogs DIAF (diisopropylammonium fluoride, left) and DIAI (diisopropylammonium iodide, right).

(3) Energies for transition and Berry Phase predicted changes in polarizations have

are being calculated for potential ferroelectric compounds uncovered by our database searching. Results to date are summarized in Table 1.

2012-2015 Students (Cousins)

Margarita Cuadras (Magy, Hispanic/Native American) worked for more than two years developing NIC-difference method for evaluating aromaticity. She presented a posters describing the project at the Southern California Conferences on Undergraduate Research in both November 2012, and November 2013. She completed her BS-Chemistry (biochemistry option) at the end of summer 2014, and is preparing to apply to graduate programs in chemistry.

Maressah Ynfante-Coral (Hispanic Female and BS-ACS Chemistry major) has been continuing Magy's work by correlating the calculated NICs-difference values with other measures of aromaticity Luke Vinson is a senior chemistry major (BS-ACS Certified option, mathematics minor) graduating in Summer, 2014. Luke worked with Dr. Cousins for more than a year to find potential new ferroelectric candidates from structures in the Cambridge Crystallographic database, and evaluate the hits as potential ferroelectric candidates. He developed the database searching protocol we use. Luke is seeking employment in Chemistry after graduation.

Carlos Mora (Hispanic) is a chemistry major (BS-ACS Certified option) who worked with Dr. Cousins during W/S 2014, and performed summer research on solid state modeling at the University Buffalo. He returned in August to assist with solid state modeling at CSUSB, working to uncover a transition state for the aminoacetonitrile hydrochloride ferroelectric candidate. He has secured a research position in materials after graduating in Spring, 2015.

Alejandra Quezada (Hispanic female) is a Chemistry major (BS-Biochemistry option) who has been working with Dr. Cousins since April 2014. She performed the database search to uncover 33 potential ferroelectric amino-acid-like compounds, presented her work at SCCUR in November, 2014, and is continuing modeling possible ferroelectric transition states for one of the molecules she uncovered.

Cruz Jacques (Hispanic) is a chemistry major (BA) and mathematic minor student who worked with Dr. Cousins for one quarter. He learned to use Spartan software and completed several energy calculations to contribute to the aromaticity project.

Natalie Quintaro (Hispanic female) is an Upward Bound student (rising High School Senior) who spent six weeks in Dr. Cousins' lab this summer. She is assisting in completing the aromaticity calculations using Spartan.

Gisele Osuna (mixed race/Hispanic) was a student from College of the Desert (local Community College), now at University of California, Riverside, who spent four weeks working the Dr. Cousins this summer. She is also assisting in completing the aromaticity calculations using Spartan, and presented her results at SCCUR in Fall, 2014.

Jason Zhang is a high school student (rising senior) helped Dr. Cousins' group initial solid

state modeling using the Quantum Espresso software.

Outcomes from the Computational Group (publications and presentations)

Presentations and posters (students underlined)

1. Quezada, Alejandra; Cousins, Kimberley. "Predicting Organic Amino-acid-like and Potentially Ferroelectric Compounds," Southern California Conference on Undergraduate Research, CSU Fullerton, November 22, 2014.
2. Osuna, Gisele; Cousins, Kimberley Farmer, Carl. "Investigative Analysis on the Aromaticity of Croconic Acid and its Anions," Southern California Conference on Undergraduate Research, CSU Fullerton, November 22, 2014.
3. Margarita Cuadras, Kimberley Cousins, "Nucleus independent chemical shifts (NICS) scan method analysis for cyclic oxocarbons," Southern California Conference on Undergraduate Research, November 23, 2013, Whittier College; also at CSUSB Student Research Symposium, May 27, 2014.
4. Luke Vinson, Kimberley Cousins, "Identification of Possible Organoferroelectric Crystals", Southern California Conference on Undergraduate Research, November 23, 2013, Whittier College
5. Cuadras, Margarita, Cousins, Kimberley, "Reevaluating the Aromaticity of Oxocarbon Molecules," Southern California Conference on Undergraduate Research, CSU Channel Islands, November 17, 2012.
6. Cousins, Kimberley, "Possible mechanisms for interconversion of polar forms for the ferroelectric diisopropylammonim halides," (COMP Poster Session and SciMix), 249th ACS National Meeting, Denver, Colorado, March 22-26, 2015.
7. Kimberley R. Cousins, Douglas C. Smith, Timothy Usher, Investigating functional organic single crystals at the CSUSB Center for Advanced Functional Materials, invited speakers for the San Gorgonio Section of the ACS meeting, May 2014.

Publications:

8. Donna A. Kunkel, James Hooper, Scott Simpson, Sumit Beniwal1, Katie L. Morrow, Douglas C. Smith, Kimberley Cousins, Stephen Ducharme, Eva Zurek, Axel Enders, "Rhodizonic Acid on Noble Metals: Surface Reactivity and Coordination Chemistry" *J. Phys. Chem. Lett.*, **2013**, *4* (20), pp 3413–3419.

Synthesis and Crystal Growth (Smith)

To date, the Smith lab has produced multi-gram quantities of croconic acid, rhodizonic acid and several derivatives of croconic acid. Recently, efforts have concentrated on the production of a compound we refer to as "Red", a croconic acid derivative that has demonstrated piezoelectric behavior (see Usher later). Additionally, we have been recently prepared a new derivative of croconic acid, a compound closely related to "Red" which we refer to as "Amber", in hopes that it might display similar properties to its analogue, "Red". The procedures of Fatiadi[1] and Geoffroy[2] are being adapted to produce these materials. Efforts also continue in preparing deltic acid. Currently, we are duplicating the procedures of Serratosa[3] for this synthesis. This synthesis requires the use of compounds such as chlorine gas and ammonia gas. These considerations seriously restrict when this material can be prepared (limited to summer months only). , and student collaborators have not been permitted to assist with this effort..

We continue to work with Rhodizonic acid and efforts to continue to convert the dihydrate form (prepared from synthesis) to its anhydrous form. This has been a difficult process

and may require the use of a diffusion vacuum pump (ultra-high vacuum) in order to accomplish this dehydration.

In addition to these considerations, we continue to supply Dr. Usher's lab with quantities of diisopropylammonium bromide, melamine hydrochloride, and samples of both "Red" and "Amber". We are also attempting to grow other crystals identified by Dr. Cousins as mentioned above in Dr. Cousins' section of this document.

Several undergraduates have worked with Dr. Smith during the duration of this grant.

Margarita (Magy) Cuadras is an underrepresented minority student that majored in chemistry (BS) with a concentration in biochemistry. Additionally, she has been part of the Math and Science Scholars Program (MASS) here at CSUSB. Magy worked with Smith for three quarters preparing synthetic intermediates and growing crystals. Magy graduated in the Spring of 2014. She is considering graduate studies in chemistry.

Amylee Martin is an undergraduate student majoring in Chemistry (BA, biochemistry concentration). She is entering into her senior year. Amy began working (synthesis/crystal growth) with Smith in Spring 2014 and she worked part time over the summer (2014) supported by this grant. She is presently considering a career in the health related fields. She recently presented her research via a poster presentation at the Meeting of the Minds student research symposium here at CSUSB in Spring 2015.

Elizabeth Martinez is underrepresented minority student that majored in chemistry (BA). She worked in Smith's lab for six quarters performing synthetic work. Additionally, Elizabeth was part of the MASS program here at CSUSB. She presented her research via a poster presentation at the Meeting of the Minds student research symposium here at CSUSB in Spring 2014. Elizabeth graduated in Spring 2014 and she is pursuing a Masters degree in chemistry at Cal Poly Pomona.

Steven Merrill is an undergraduate student majoring in chemistry (BS) with a biochemistry concentration. Steven has been part of the Pro-active Recruitment in Introductory Science and Mathematics (PRISM) program here at CSUSB. Steven joined Smith's group in Spring 2014 and he worked (synthetic/crystal growth) on this project over the summer, 2014. This year, Steven will enter his senior year. Upon graduating, Steven plans to attend graduate school in a STEM field, or pursue a career in the health professions.

Katie Morrow is a recent graduate (Winter 2015) that is majored in chemistry (BS) with a concentration in biochemistry. Katie joined Smith's group in the spring of 2012 and she has worked (synthesis/crystal growth)) consistently throughout this period, including full time summer 2013 and part time summer, 2014, supported by this grant. She has one publication to her credit on this grant and she also presented her research (along with Elizabeth Martinez) via a poster presentation at the Meeting of the Minds student research symposium here at CSUSB Spring 2014. Katie is now employed in a STEM related field however she is considering pursuing a career in the health related fields.

Carlos Navarro is underrepresented minority student majoring in chemistry (BS) with a concentration in biochemistry. Carlos has been part of the PRISM program here at CSUSB. Carlos joined Smith's group Spring 2014 (synthetic/crystal growth) and he participated in an REU Summer, 2014 and he is participating in an REU Summer 2015. This year, Carlos will enter his senior year. Upon graduating, Carlos plans to attend

graduate school in a STEM field. He recently presented her research via a poster presentation at the Meeting of the Minds student research symposium here at CSUSB in Spring 2015.

Geovanni Rangel is underrepresented minority student majoring in chemistry (BS) with an ACS accredited option. Geovanni has been part of the PRISM program here at CSUSB. Geovanni joined Smith's group in Spring 2014 and he performed research on this project here at CSUSB during the Summer 2014 (synthesis/crystal growth). This summer (2015) he will participate in a REU. This year, Geovanni will enter his senior year. Upon graduating, Geo plans to attend graduate school in a STEM field.

Outcomes from the Synthesis Group (publications and presentations)

Presentations and posters (students underlined)

1. Martinez, Elizabeth; Morrow, Katie; Smith, Douglas. "The Preparation of Croconic and Rhodizonic Acid," Meeting of the Minds 3rd Annual Student Research Symposium, CSU San Bernardino, May 27, 2014.

2. Merrill, Steven; Rangel, Geovanni; Martin, Amylee; Navarro, Carlos; Morrow, Katie; Smith, Douglas "The Synthesis of Croconic and Rhodizonic Acid," ACS Southern California Undergraduate Research Conference, UC San Diego, March 14, 2015.

3. Martin, Amylee; Navarro, Carlos; Merrill, Steven; Morrow, Katie; Rangel, Geovanni; Smith, Douglas. "Preparation of Croconic and Rhodizoinc Acid," Meeting of the Minds 4th Annual Student Research Symposium, CSU San Bernardino, May 21, 2015.

Publications:

Donna A. Kunkel, James Hooper, Scott Simpson, Sumit Beniwal1, Katie L. Morrow, Douglas C. Smith, Kimberley Cousins, Stephen Ducharme, Eva Zurek, Axel Enders, "Rhodizonic Acid on Noble Metals: Surface Reactivity and Coordination Chemistry" *J. Phys. Chem. Lett.*, **2013**, *4* (20), pp 3413–3419

Experimental (Usher)

The theoretically predicted and subsequently synthesized compounds were characterized by a range of techniques.

We were able to obtain saturated hysteresis loops on single crystal croconic acid. See figure.

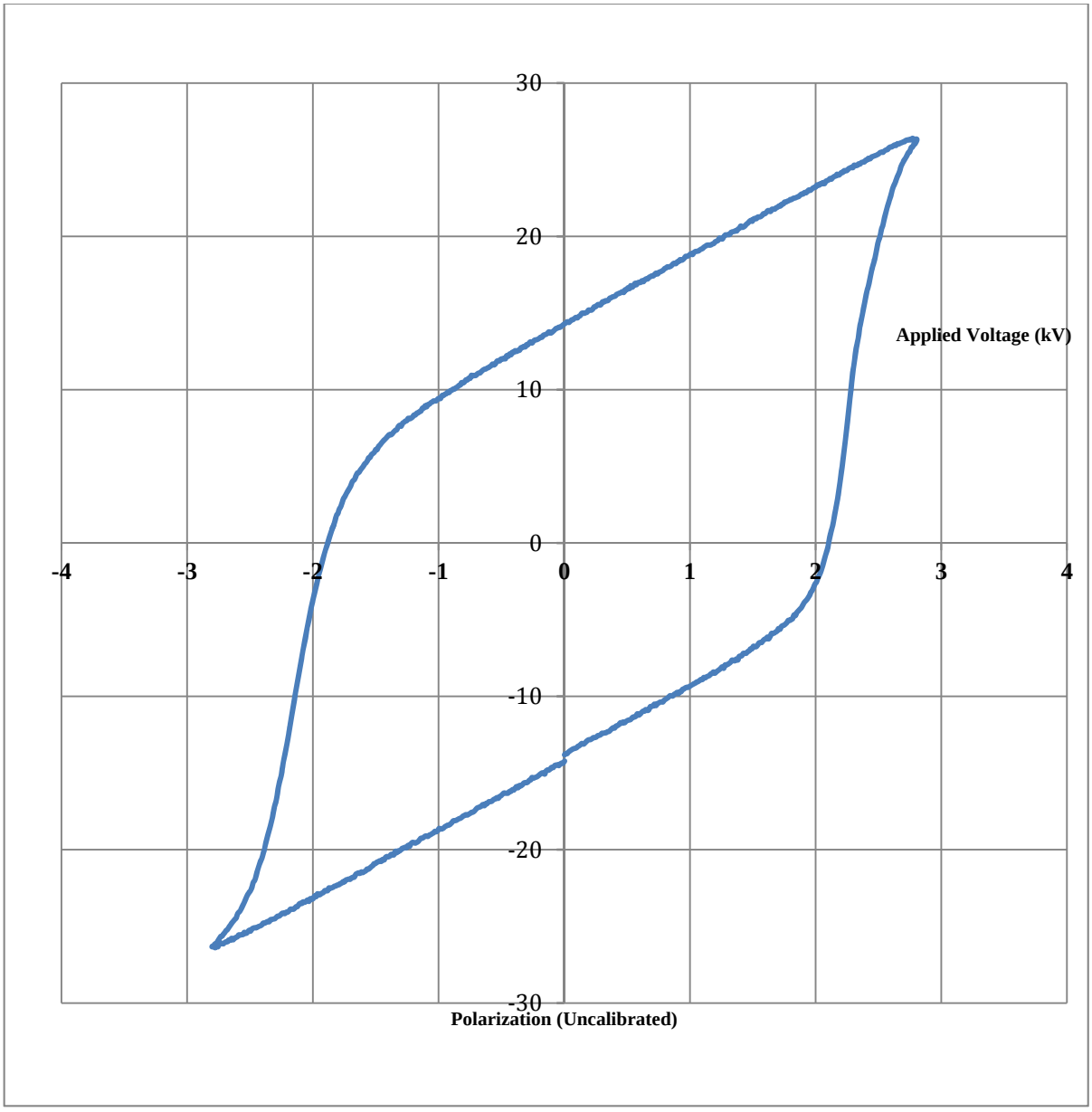

Figure 4: Hysteresis loop of single crystal croconic acid

The compound code named “Red” is a variation of croconic acid. It does not appear to be ferroelectric. However, it is piezoelectric. When placed in a petri dish of mineral oil (to prevent electrical arcing) ripples in the mineral oil are clearly visible when a voltage is applied to the sample. We quantified the piezoelectric response. See figure of Piezo Response for “red”.

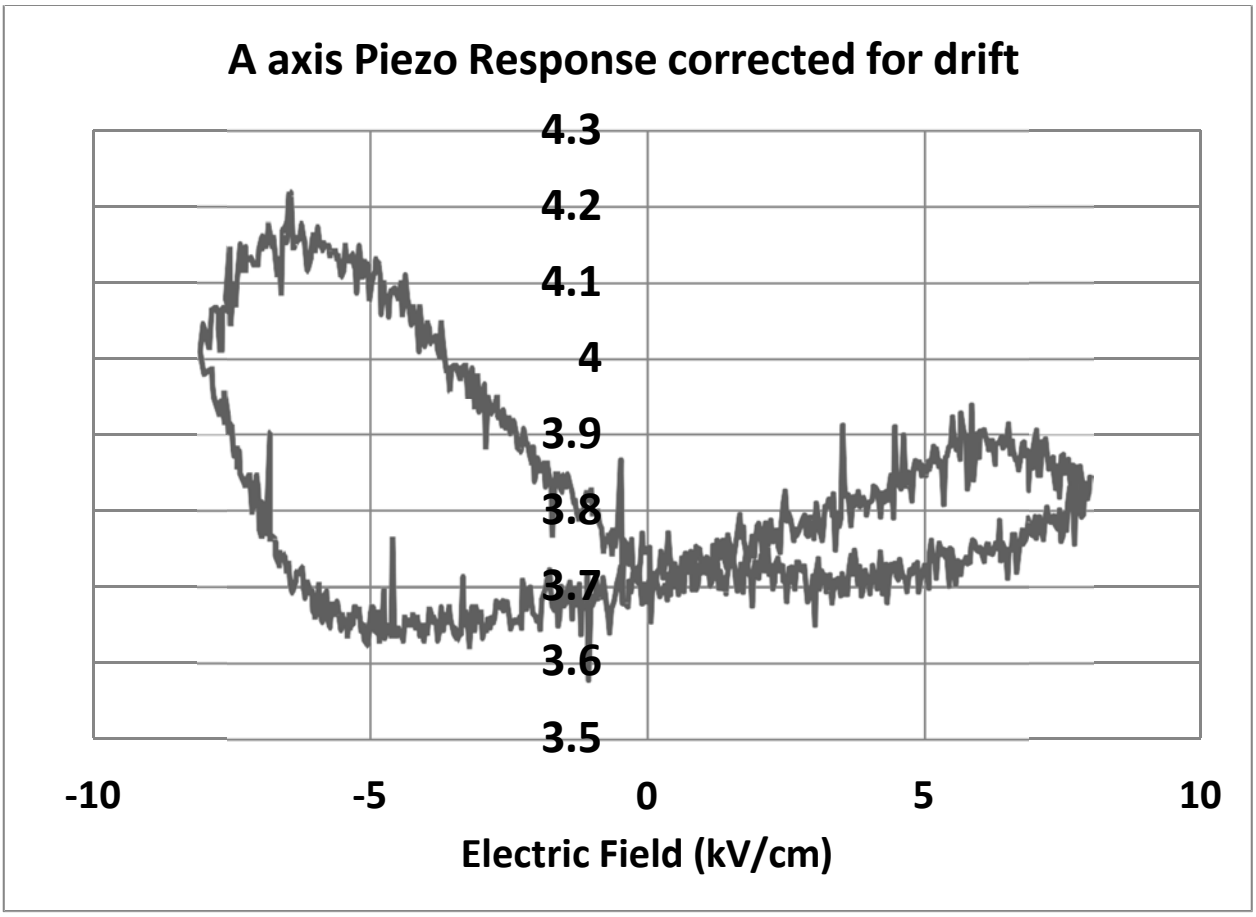

Figure 5: Piezo Response for "red".

We also have piezoforce microscopy results on red. See Figures.

Red 30V@100kHz

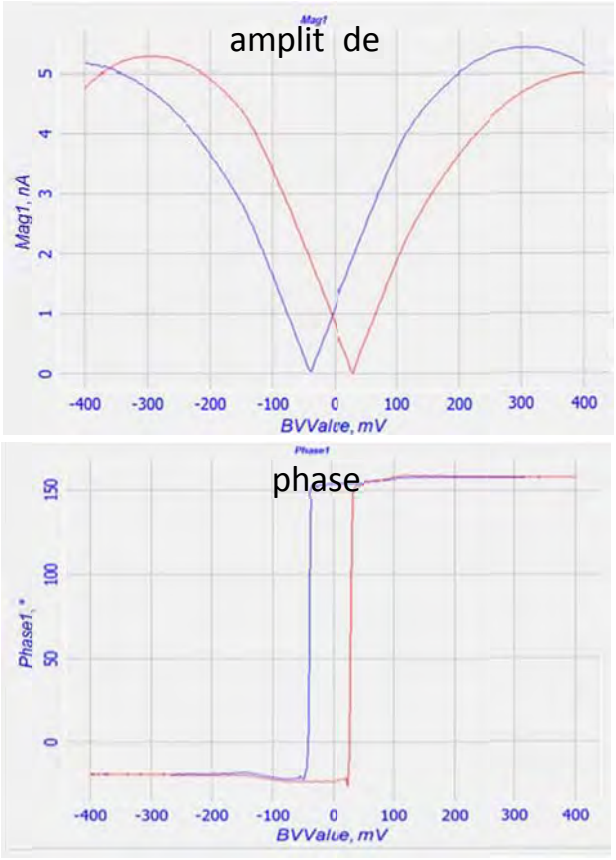

Figure 6: piezoforce microscopy results on red (30V@100kHz).

We have produced iron doped croconic acid as well as Manganese doped croconic acid. These samples were analyzed in our epr spectrometer as a function of angle to map out the g- tensor.

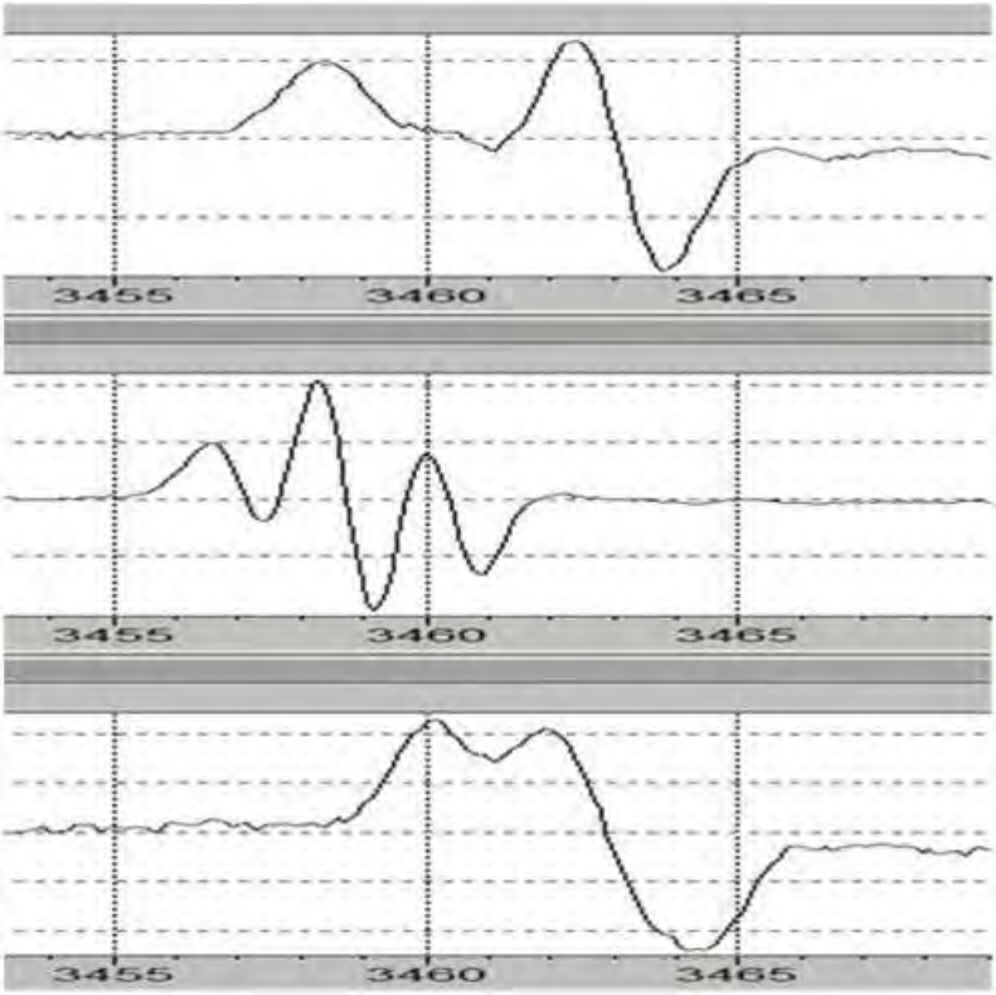

Figure 7 : Epr spectra of ironed doped Croconic acid showing anisotropic g-factor.

After concluding that “red” was not ferroelectric at room temperature, we looked for a paraelectric – ferroelectric transition over a temperature range of 80K to 523K by measuring the capacitance as a function of temperature. The results show that red is not ferroelectric over this range.

Since this grant was originally awarded, new room temperature organic ferroelectrics have been reported by others. One of these is diisopropylammonium bromide, abbreviated, DIAP. Smith has grown single crystals of DIAP and Usher’s group has been able to reproduce the phase transition evident in the dielectric constant vs temperature data.

Four students were directly supported on this grant.

Victor Jimenez is an underrepresented minority undergraduate, majoring in physics. He has won several awards and honors. He was awarded a Smart Scholarship, from the Department of Education (Title V) for underrepresented minorities in STEM majors with high GPAs. He was

also awarded a McNair Scholarship, also funded by the Department of Education. In addition he was a LSAMP scholar, funded by NSF. He graduated in Spring of 2013. He is taking a year off before going to graduate school.

Abraham Garcia is an underrepresented minority undergraduate, majoring in physics. He has also won several awards and honors. He was awarded a Smart Scholarship, from the Department of Education (Title V) for underrepresented minorities in STEM majors with high GPAs. He was also awarded a McNair Scholarship, also funded by the Department of Education, He in Spring of 2013. He is now employed at a local aerospace company, Kelly Space and Technology.

Earl Smith is an underrepresented minority undergraduate, majoring in physics. He has also won several awards and honors. He was also awarded a McNair Scholarship. He took a break from this research project in the summer of 2014 to be a NASA intern. He graduated in Spring of 2013. He is currently employed as a counselor in the CSUSB Upward Bound program. He is planning on going to graduate school next year.

Kevin Collins is an undergraduate physics major. He spent the summer of 2014 as a research student at the Materials Research Center, University of Lincoln Nebraska. This summer 2015 he as been awarded a NASA internship.

Melissa Hannan is a female physics major. After participating in research under this grant she was awarded an REU at Arecibo National lab in the summer of 2014. For the summer of 2015 she was awarded an REU at SETI institute.

Two High School Students were supported through a supplement to this main grant, Joseph Vasquez and Salina Gomez. Joseph and Salina are both of Hispanic heritages. In addition, Salina is female. Joseph and Salina conducted research over the summer with our group. Earl Smith (African American heritage) and Melissa Hannan were their undergraduate mentors. We partnered with the CSUSB Upward Bound (UB) STEM program, Department of Education grant P047A120164. This worked out very well. The UB program already had well established procedures and protocols for hosting High School students on the CSUSB campus. For example, fingerprinting mentors and making sure legal documentation is in place. In addition, the UB program provided housing in college dorms, lunch, social activities, and college counseling, Joseph and Salina each gave a poster presentation at the end of the summer. They also presented a poster at the Southern California Conference on Undergraduate Education in November 2013.

Outcomes from Experimental Group

Joseph Vasquez (Rialto High School), Mentors: Earl Smith and Timothy Usher, "How is the Powder X-Ray Diffraction machine cool?" CSUSB Upward Bound final presentation July 25, 2013.

Selena Gomez (Eisenhower High School) Mentors: Melissa Hannan and Timothy Usher "The Significance of Ferroelectrics" CSUSB Upward Bound final presentation July 25, 2013.

Earl Smith (Mentor: Timothy Usher, Associate: Victor Jimenez), "First EPR Results on Croconic Acid Single Crystals: G-tensor Quantification", (Talk), NASA-Dryden, 2012.

Victor Jimenez and Earl Smith "Experimental Investigations of Croconic Acid Single Crystals and Thin Films**"** McNair Symposium, University of Maryland, March 16, 2012.

Victor Jimenez, "Polarization Properties of croconic acid Single crystals and thin films" McNair Symposium CSUSB July 31, 2012.

Timothy D. Usher, Kenneth R. Ulibarri, Jr. and Gilberto S. Camargo, "Piezoelectric Microfiber Composite Actuators for Morphing Wings." ISRN Materials Science, Article ID 189659, Undergraduate underrepresented minority authors, 2013.