Ferroelectricity in underdoped La-214 cuprates

Z. Viskadourakis[1,2], S. S. Sunku[3], S. Mukherjee[4], B. M. Andersen[4], T. Ito[5], T. Sasagawa[6] and C. Panagopoulos[3,1,7]

1. CCQCN, University of Crete, Heraklion 71003, Greece
2. IESL-FORTH, Vassilika Vouton, Heraklion 71110, Greece
3. Nanyang Technological University, 637371 Singapore
4. Niels Bohr Institute, University of Copenhagen, Copenhagen DK-2100, Denmark
5. National Institute of Advanced Industrial Science and Technology, Japan
6. Materials and Structures Laboratory, Tokyo Institute of Technology, Japan
7. Department of Physics, University of Crete, Heraklion 71003, Greece

Introduction

In the current study we report on the ferroelectricity (FE) and magnetoelectricity (ME) in underdoped Sr and Li doped La_2CuO_4 single crystals. The main purpose of the study is:

1. ***to clarify whether ferroelectricity is present in La_2CuO_4 when different dopant ions (other than interstitial excess oxygen ions [1]) are introduced into the lattice.***
2. ***to shed further light on the nature of ferroelectricity and magnetoelectricity, and to reveal if these are generic ground state properties of the underdoped La-214 cuprates.***

Experimental details

- High quality twinned $La_{1.999}Sr_{0.001}CuO_4$ (LSCO) and $La_2Li_xCu_{1-x}O_4$ (LLCO), (x=0.01 and x=0.04) single crystals used in this study [2, 3].

Experiments performed in this study:

1. Dielectric permittivity measurements [1]:
   - temperature range: 2 K – 100 K
   - frequency range: 21 Hz – 1 MHz
   - AC Voltage range: 1mV – 1V

2. Electrical Polarization measurements (Pyroelectric current method):
   - temperature range: 2 K – 20 K
   - applied electrical field: up to 8 KV cm^{-1}
   - applied magnetic field: up to 10 T

Dielectric permittivity of LSCO

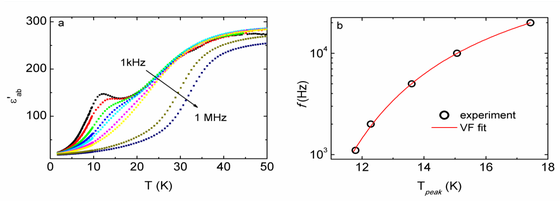


Figure 1: a. *ε'_{ab} as vs. temperature for LSCO at various frequencies.* ***b.*** *Experimental data for frequency f vs. peak temperature T_{peak} as extracted from fig. 1a (black open circles). The red solid line corresponds to the Vogel-Fulcher fit.*

- A dielectric peak develops below ~15K, which shifts to higher T and suppressed with increasing f (fig. 1a).
- Experimental tests reveal the intrinsic character of the low – T dielectric peaks [4].
- Such relaxation process can be described by the Vogel-Fulcher (VF) relation:

$$f = f_o \exp\left[\frac{-E_a}{k_B\left(T - T_{fr}\right)}\right]$$

where T_{fr} is the charge cluster freezing temperature, ***below which FE behavior can be observed*** **[5].**

For LSCO: ***In-plane: $T_{fr\text{-}ab}$ = (7.3 ± 0.3) K (fig. 1b)***
Out of plane: $T_{fr\text{-}c}$ = (8.6 ± 0.5) K

✓ ***The observed behavior is due to a FE relaxor behavior, characterized by a diffused phase transition and the freezing of short-range cluster-like order.***

✓ ***Anisotropic behavior in the charge dynamics in agreement with an earlier report*** **[6].**

Electric Polarization of LSCO

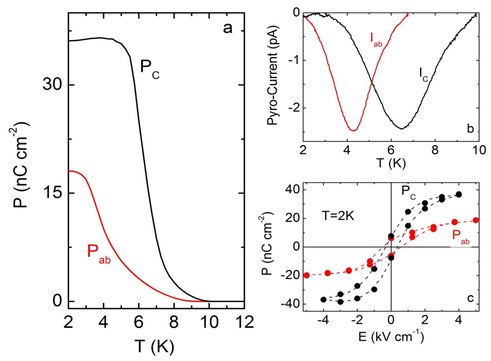


Figure 2: a. *P_{ab} (red line) and P_c (black line) as a function of temperature for LSCO.* ***b.*** *The corresponding pyroelectric current curves are shown.* ***c.*** *Electric polarization vs. applied electric field (P-E hysteresis loops) for both P_{ab} (red solid circles) and P_c (black solid circles) at 2K. Broken lines are a guide to the eye.*

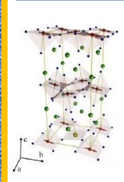
- Both P_c and P_{ab} increase with decreasing temperature, below ~10 K (fig. 2a).
- P_c and P_{ab} exhibit distinct temperature dependences.
- Corresponding pyroelectric local minima (fig. 2b) occur at different temperatures: **$I_{ab\text{-}min}$ = 4 K** and **$I_{c\text{-}min}$ = 6.5 K**
- P - E hysteresis loops for both P_c and P_{ab} (fig. 2c), similar to those obtained for La_2CuO_{4+x} single crystals [1] ("Sawyer-Tower" measurement).
- Anisotropic electric polarization:

  P_{ab} = 18 nC cm^{-2} , P_c = 36 nC cm^{-2}
- Anisotropy has also been confirmed for La_2CuO_{4+x} samples (T_N = 312 K) with similar T_N as the LSCO (T_N = 313 K)
- Similar anisotropy has been observed in the spin-glass temperature [7].

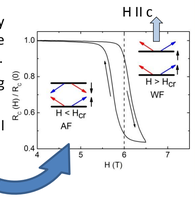
✓ ***FE occurs due to the presence of Sr dopants, similarly to La_2CuO_{4+x}.***

✓ ***Anisotropy between in-plane and out-of-plane electric polarization, attributed to the charge carrier doping.***

Magnetoelectric coupling in LSCO



- Spins in the AF phase of LSCO are weakly canted out-of-plane due to the presence of Dzyaloshinskii-Moriya (DM) interaction.
- Weak ferromagnetic (WF) moment along the c-axis in each CuO_2 plane.
- WF moments are aligned above a critical magnetic field H_{cr} → ***onset of WF state***



LSCO: H_{cr} = 6T

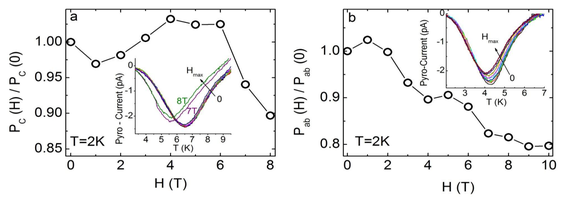


Figure 3: a. *P_c vs. H at for LSCO (T =2K, E || c and H || c).* ***Inset.*** *Pyro - current vs. temperature for various H.* ***b.*** *P_{ab} vs. H (T=2K, E || ab, H || ab).* ***Inset.*** *Pyro - current vs. temperature for various H.*

- P_c decreases abruptly above H_{cr} = 6 T (WF state) (fig. 3a)
- Pyro - current minimum (inset in fig. 3a) shifts to lower temperatures above H_{cr} = 6 T
- P_{ab} and the pyro – current (E||ab and H||ab) decrease smoothly with increasing H (fig. 3b).

✓ ***Weak magnetoelectric coupling***

✓ ***DM interaction influences the electrical polarization in a manner similar to La_2CuO_{4+x}*** **[1, 9, 10].**

Electric Polarization of LLCO

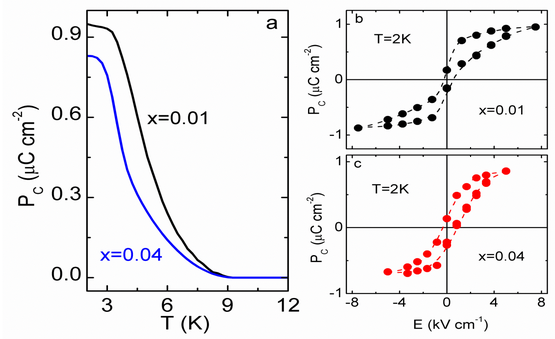


Figure 4: a. *P_C vs. temperature for LLCO with x = 0.01 (black solid line) and x = 0.04 (blue solid line). Polarization vs. applied electric field (P-E) hysteresis loops for* ***b.*** *x = 0.01 and* ***c.*** *x = 0.04 at 2K are also shown. Broken lines are a guide to the eye.*

- P_c increases with decreasing temperature, below ~9 K for both samples.
- Slope change in the electric polarization at **5 K (x = 0.01)** and **3.5 K (x = 0.04)**, respectively.
- Remarkably large P_C values observed (T = 2K): **900 nC cm^{-2} (x = 0.01)** and **800 nC cm^{-2} (x = 0.04).**
- No pyroelectric signal is observed along the in-plane direction

Similar FE behavior to both LSCO and La_2CuO_{4+x}

Magnetoelectric coupling in LLCO

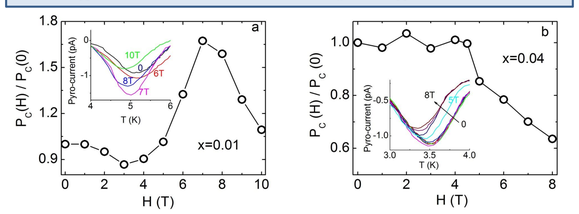


Figure 5: a. *P_C vs. H for LLCO x=0.01. The corresponding pyroelectric current is shown in the inset of the graph, for selected magnetic fields.* ***b.*** *P_C vs. H for LLCO x=0.04. The corresponding pyroelectric signal is shown in the inset. In both cases T =2K and E || c and H || c.*

For x = 0.01:

- P_c is enhanced below H_{cr} = 6.5 T (WF transition), due to a DM induced magnetoelectric coupling [9, 10].
- P_c and corresponding pyro-current peak temperature are suppressed above H_{cr} .

For x = 0.04:

- P_c is roughly constant up to H_{cr} = 4 T (WF transition).
- It decreases when the WF state sets in.

✓ ***DM interaction enables the tuning of the ME coupling.***

✓ ***Similar ME behavior to LSCO and La_2CuO_{4+x}.***

References

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Discussion

Experimental facts:

1. Low temperature FE for LSCO, LLCO and La_2CuO_{4+x}.
2. FE anisotropy
3. Magnetoelectric coupling: DM interaction affects the electric polarization in a similar manner to all samples.

✓ ***Ubiquitous FE ground state for underdoped La-214 cuprates.***

✓ ***FE emerges as the first charge carriers are introduced in to the parent insulating compound.***

Proposed mechanism

LSCO and LLCO: Presence of dopant atoms → ***Local CuO_6 octahedral distortions*** (*The presence of local octahedral distortions and their correlation to charge inhomogeneities has already been proven* [11-14]).

may cause

Spatial inversion symmetry breaking resulting to the ***formation of electric dipoles.*** (*Non-centrosymmetric monoclinic distortions have been discussed for LSCO and La_2CuO_{4+x}* [11] .)

Electric dipoles are ***localized around the dopants*** creating fluctuating ***polar clusters***. → *Decreasing Temperature* → ***FE observed***

Summary -Conclusions

✓ Evidence for the presence of FE and ME coupling in underdoped La-214 cuprates, are shown.

✓ For LSCO distinct electric polarization behavior along in-plane and out-of-plane crystallographic directions, is observed.

✓ For LLCO very high electric polarization values are obtained.

✓ In all cases the electric polarization is strongly influenced by DM interaction.

1. ***FE phase is generic to underdoped La-214 cuprates and is prompted by charge carrier doping.***
2. ***FE may originate from the CuO_6 octahedral distortions, occurring around the dopant ions and/or due to the formation of charge clustering, resulting to a local-scale spatial symmetry breaking symmetry.***

Acknowledgements

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