Experimental report

24/01/2024

Proposal: 5-24-715 **Council:** 4/2023

Title: Unraveling Structural Triggers forthe Anomalous Thermal Transport Behavior of Eu1¿xCaxTiO3¿d on the Long- and Short-range

Research area: Materials

This proposal is a new proposal

Main proposer: Marc WIDENMEYER

Experimental team: Marc WIDENMEYER
Ann-Katrin EMMERICH
Aasir RASHID
Marco SCAVINI
Federico BIANCONI
Andrea TRAPLETTI

Local contacts: Thomas HANSEN
Gabriel Julio CUELLO

Samples: Eu0.9Ca0.1TiO3
Eu0.6Ca0.4TiO3
Eu0.8Ca0.2TiO3
Eu0.7Ca0.3TiO3

Instrument	Requested days	Allocated days	From	To
D20	4	0		
D4	5	5	03/11/2023	08/11/2023

Abstract:

Anomalous thermal transport behavior below RT has been observed for several members of the solid solution Eu1-xCaxTiO3-d, e.g., glass-like thermal conductivity if x <0.3 (cubic phases) and 2 maxima of thermal conductivity for x>0.3 (orthorhombic phases). This implies that the crystal structure and in particular the local structure arrangements play a crucial role for the understanding of these phenomena. Additionally, all samples show a second order phase transition at ca. 290 K, while the origin is only understood for pristine EuTiO3 (tetragonal-cubic phase transition). For all other samples neutron diffraction and neutron PDF analysis are required to identify the role of the oxygen ions on this transition and thermal conductivity. The collected data will be combined with already measured complementary X-ray-based data providing information about the cations. The thermal transport data potentially imply a transition from a soft lattice (EuTiO3-like) via an intermediate state where soft and rigid sublattice are competing with each other to a rigid (CaTiO3-like) sublattice. The proposed experiments will enable to support (or disprove) this statement from a stuctural perspective.

Unraveling Structural Triggers for the Anomalous Thermal Transport Behavior of $Eu_{1-x}Ca_xTiO_{3-d}$ on the Long- and Short-range (5-24-715)

Marc Widenmeyer, Xingxing Xiao, Technische Universität Darmstadt, Germany
Marco Scavini, Federico Bianconi, University of Milano, Italy

D4 equipped with a cryofurnace at λ = 0.69746(5) Å was used to study the local structure of $Eu_{1-x}Ca_xTiO_{3-d}$ (x = 0.1, 0.2, 0.3) by pair distribution function (PDF) analysis method. For each composition measurements at four temperatures were carried out, namely 10 K (above T_N at 3–5 K), 100 K (fade out of unusual thermal transport behavior), 200 K (below the 2nd order transition in *Cp* measurement), and 400 K (above the transition). Initially, it was also planned to study x = 0.4, which had to be skipped due to multiple reasons: i) a longer than anticipated measurement time per temperature point (6 h instead of 4.5 h) was needed due to absorption of natural Eu in the Ca-poor compositions, ii) the latter also resulted in strong activation of the samples, requiring about 3 h waiting time for the sample change, and iii) we were facing some technical issues with the cold valve of the cryofurnace resulting in several hours of delay. The previously determined long-range structures and synchrotron-based PDF analysis results[1–3], respectively, were used as input models for the local structure analysis.

We have to admit that the level of data analysis is not as advanced as we wanted it to be. However, there is a good reason for it as we are currently facing some procedural issues with the new software package established at D4 for data reduction that were evidenced by our experiment performed at $\lambda \approx 0.7$ Å that allows better Q resolution than the usual setup at $\lambda \approx 0.5$ Å. We are observing variations in the Fourier-transformed data in dependency of the selected R_{max} value. It seems that it comes from the inverse transform routine used in order to be able to cut off spurious oscillations below the repulsion distance in correlation functions. Therefore, it is currently the question up to what R value we can go to obtain physically acceptable or at least stable results. Perhaps this is related to the coherence volume of the neutron wave packet, but further consideration is needed. We are working with our local

contact Gabriel Cuello on it to identify the origin and establish a physically meaningful workaround.

Despite this problem, skipping the inverse transform routine, we obtained "approximate" G(r) for a preliminary data analysis. We will focus in the further on the data collected on $Eu_{0.8}Ca_{0.2}TiO_{3-\delta}$ (the most important sample of the experiment) at 10 K, because at this temperature the thermal broadening of the G(r) peaks is minimized making it easier to identify any local distortion in respect to the average structure.

Figure 1 reports the experimental G(r) in the 1.5–8 Å range as black circles while the fits using different structural models are shown as red curves (see labels in each panel for details).

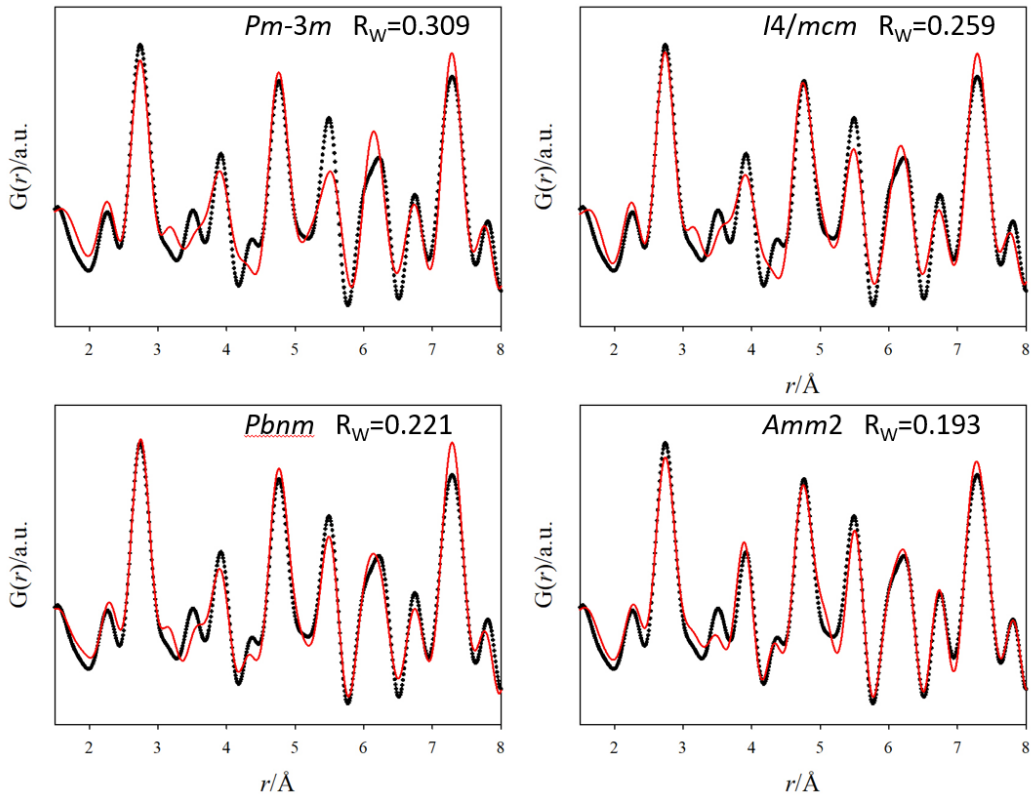

Figure 1. Experimental G(r) of $Eu_{0.8}Ca_{0.2}TiO_{3-\delta}$ (black circles) and fits (red curves) using different structural models. The labels in each panel report the space group adopted in the fit and the relative residual value R_W.

We tested the undistorted perovskite cubic $Pm\bar{3}m$ structure model, in accordance with the long-range structure of $Eu_{0.8}Ca_{0.2}TiO_{3-\delta}$ sample[3] first, obtaining a very high residual value (R_W = 0.309), especially for r < 6 Å, confirming that local structural distortion is present in this sample. Then, two models were tilting either

only along the *c*-axis (*I*4/*mcm*) or along all three axes (*Pbnm*) are present were tested, which correspond to the structures adopted by $EuTiO_3$[4] and $Eu_{0.6}Ca_{0.4}TiO_{3-\delta}$[3], respectively. As shown in Fig.1, the remaining high residual values (R_W = 0.259 and 0.221, respectively) and the well apparent mismatch between experiment and model strongly suggests that the local distortions cannot be mapped just by octahedra tilting. At last we tested the "polar" *Amm*2 space group, that is one of the ferroelctric phases of $BaTiO_3$, and supplied the best fit for X-ray PDF of $Eu_{0.8}Ca_{0.2}TiO_{3-\delta}$[3]. All the computed interatomic distances correspond to the maxima of the experimental G(*r*), confirming that the Ti ion shifts its position in respect to its octahedral oxygen cage. We note that the residuals are still high in respect to the ones obtained with X-ray PDF (R_W = 0.11) using the same *Amm*2 model. Since the X-ray PDF is mainly sensitive to interatomic distances involving the heavy cations, we suggest that further structural distortions involving oxygen ions should be present in the structure. This confirms the absolute need of neutron-PDF to map the complex disorder of the $Eu_{1-x}Ca_xTiO_{3-\delta}$ system and to understand its intriguing physical properties.

When, after fixing the inverse transform routine issue we will obtain the final PDFs a by far deeper analysis of all the G(*r*) functions, both, further lowering the symmetry in our "Real Space Rietveld analysis" and testing different approaches such as Reverse Montecarlo or flanking DFT calculations to the data analysis will be possible and tested against the collected experimental data.

References

[1] X. Xiao et al., *Mater. Phys. Today* **2018**, *7*, 96.
[2] M. Widenmeyer et al., Nanomaterials **2020**, *10*, 769.
[3] X. Xiao et al., *Mater. Phys. Today*, **2023**, *35*, 101132.
[4] M. Allieta et al, *Phys. Rev. B* **2012**, *85*, 184107.