Experimental report

09/09/2022

Proposal: **7-02-205**

Council: 4/2020

Title: Characterising the soft modes in NTE material Ca2Mn1-yTiyO4

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Mark SENN**

Experimental team: Quentin BERROD

Local contacts: Jean-Marc ZANOTTI

Samples: Ca2Mn0.3Ti0.7O4
Ca2Mn0.4Ti0.6O4

Instrument	Requested days	Allocated days	From	To
IN6-SHARP	3	3		
SHARP	3	3	20/09/2021	23/09/2021

Abstract:

Ruddlesden-Popper (RP) layered perovskites, play host to remarkable properties such as superconductivity, ferroelectricity and fast anion conductivity. These properties are invariably coincident with symmetry breaking distortions driven by soft phonon modes whose character is that of BO6 octahedral tilts or rotations. We have recently added negative thermal expansion (NTE) to the list of remarkable properties that these RP compounds display. In this case, the property of interest seems to be driven by the proximity of the system to a phase transition whose driving soft modes have negative Grüneisen parameters. While we have made substantial progress in controlling the negative thermal expansion driven by these soft modes in these compounds over wide temperature ranges, we haven't yet managed to observe a direct experimental signature for their existence. Here we propose to study the temperature dependent evolution of these soft modes on IN6 between 300 and 1200 K.The results will complement our current theoretical studies in this area and will feed into a broader understanding of how soft mode phase transitions can be controlled in order to enhance functional properties.

Experimental Report

Characterising the soft modes in NTE material $Ca_2Mn_{1-y}Ti_yO_4$

Background

Ruddlesden-Popper (RP) layered perovskites, ($A_{n+1}B_nO_{3n+1}$) play host to remarkable properties such as superconductivity [1, 2], ferroelectricity [3, 4] and fast anion conductivity. These properties are invariably coincident with symmetry breaking distortions driven by soft phonon modes whose character is that of BO_6 octahedral tilts or rotations. We have recently added negative thermal expansion (NTE) to the list of remarkable properties that these RP compounds display [4]. In this case, the property of interest seems to be driven by the proximity of the system to a phase transition whose driving soft modes have negative Grüneisen parameters. While we have made substantial progress in controlling the negative thermal expansion driven by these soft modes in n = 1 and n = 2 RP compounds [5-8] over wide temperature ranges, we haven't managed to observe a direct experimental signature for their existence yet. Specifically, we would like to understand why these NTE driving modes don't condense out over a relatively small temperature range, such as is the case in unlayered perovskite, but instead appear to remain soft over a very large temperature range (2-1200 K).

Our most recent results in this area have enabled us to enhance the uniaxial negative thermal expansion in the RP compounds through the formation of the solid solution $Ca_{2-x}Sr_xMn_{1-y}Ti_yO_4$ [9]. The phase diagram derived by considering tolerance factor and temperature shows a rich variety in distortion symmetries. For x >1, y = 0, the aristotype *I*4/*mmm* is observed, while decreasing *x* drives the system to $I4_1/acd$, which we have shown is intrinsically linked to the unusual thermal expansion properties of these systems. Moving lower yet in tolerance factor by increasing *y* to 0.65, has led us to enhance NTE to a maximum value of 8.5 ppm K^{-1} (at 150 K) and discover a phase coexistence regime with a dramatic switch from NTE to pronounced PTE. The origin of this strong first order phase transition is evidently linked to the soft modes that drive the NTE.

Experimental setup

A variable temperature inelastic neutron scattering (VTINS) was performed on the SHARP BEAMLINE to ascertain the soft mode energy and its evolution in two polycrystalline samples in the CMTO series, where y= 0.6, 0.7 (both known henceforth as Ti06 and Ti07 respectively). A wavelength of 4.14 Å (approx. 4.8 meV) was used, which gave us the energy and momentum required to measure the excitation in the first Brillouin Zone (BZ, k_1 = (½ ½ 0), Q = 1.2 $Å^{-1}$). The range of the observed uniaxial NTE is large (from 2 – 1200 K), so 3 days of beamtime were used, where the samples were measured at various temperature points (300, 500, 700, 1000, 1150, 1200, 1300 K) on heating. Ti06 was also done a second time on cooling from 900-100 K where patterns were taken in 100 K steps.

Results

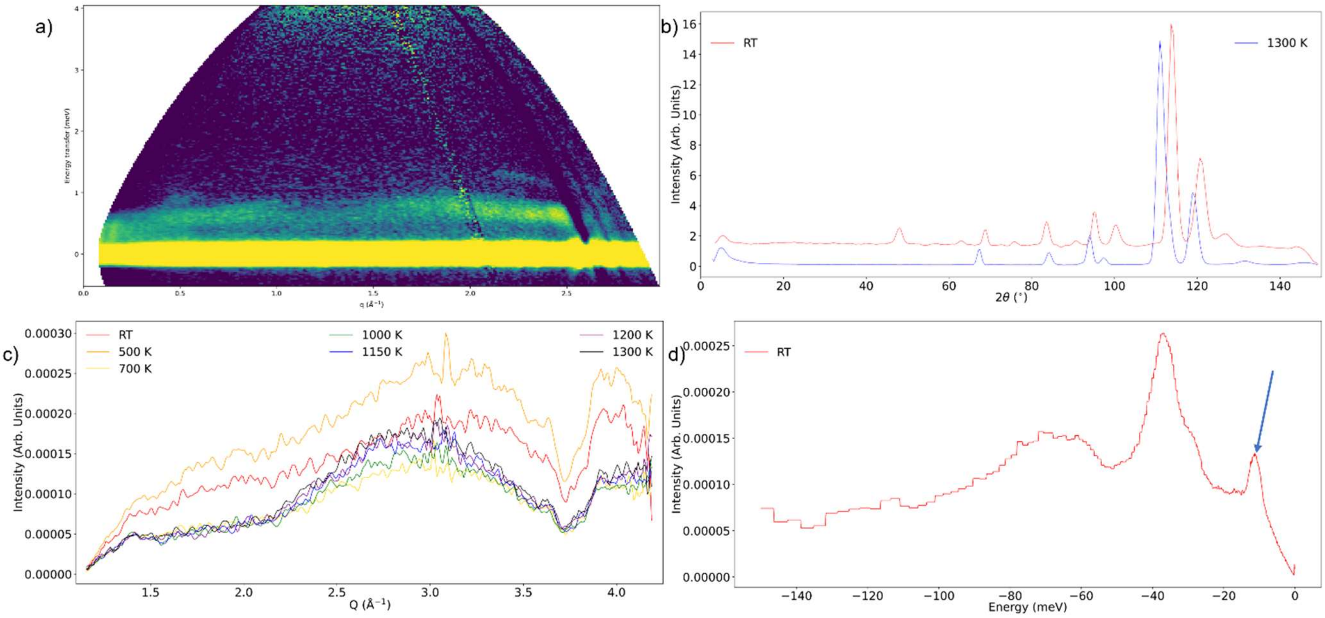

Figure 1: (a) 2D plot showing the relationship between the energy gain and Q for Ti06 between RT during the first heating cycle. The most intense blue line denotes the elastic line, and the cloudlike feature corresponds to the phonon dispersion observed at all temperatures in Ti06. (b) A comparison of the elastic line patterns taken at RT and at 1300 K, showing that Ti06 has undergone a phase transition from I4$_1$/acd to I4/mmm. (c) Cuts taken at each temperature point where E = -11 meV, the energy at which the soft mode was predicted to be observed (d) The General Density of States (GDOS) for Ti06 at RT showing the soft mode at an energy of -11 meV (the feature which the arrow is pointing to); other features are observed but are considered to be due to impurities in the sample.

Figure 1 shows the INS spectrum for Ti06 taken at RT. As can be seen from 1(a), the spectrum has 2 features in the energy gain side: the elastic line, which gives us structural information, and phonon dispersion, this cloudlike feature just above at approx. +0.6 meV. The phase transition from the low to high symmetry structure is observed in the elastic line (Figure 1(b)), evidenced by the lack of intensity of the (213) superstructure peak in the higher temperature pattern, confirmed by lattice parameter trends showing the switch from NTE to PTE behaviour on heating. The cuts shown in Figure 1(c) tentatively show the soft mode being experimentally observed, corroborated by the GDOS in figure 1(d) showing the feature believed to be the soft phonon mode corresponding to the dynamic tilting in these RP1 structures.

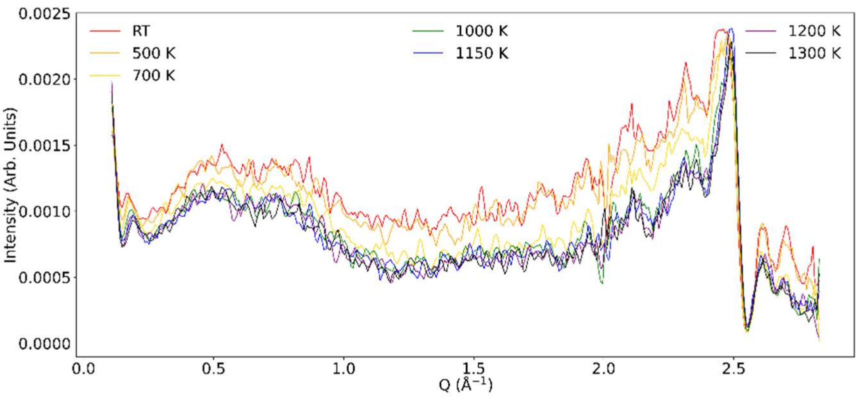

Figure 2: Plots showing the Q-dependant energy change (phonon dispersion) in Ti06 taken at different energy gains from the spectra shown above. The energy cuts shown are both from the energy gain side taken at +0.6 meV with a dE of 0.15 meV, encompassing the features either side

An unexpected feature observed in Ti06 is the phonon dispersion, the cloudlike feature shown in Figure 1(a) and emphasised through a slice taken through the data at +0.6 meV shown in Figure 2. Some analysis has been done to understand the dispersion; however, more understanding on the origin of the dispersion must be done to understand the effect this has on the properties exhibited by the CMTO series.

Summary and outlook

Samples in the *n*=1 $Ca_2Mn_{1-y}Ti_yO_4$ RP series (where y = 0.6, 0.7) were sent to the SHARP beamline to experimentally observe the soft modes and how they evolve with increasing temperature and Ti-substitution. In Ti06, the soft mode corresponding to this dynamic tilting of the octahedra has been observed at E=-11 meV across all values of T including through the phase transition from the low to high symmetry structures. An unexpected softer feature corresponding to phonon dispersion is also observed in both samples at +0.6 meV and work is currently in progress to understand the origin of this dispersion in Ti06 so that this rationale can be applied to Ti07. This data is also being supplemented with PDF and Neutron Powder diffraction, which will allow us to understand how the relationship between the structure and dynamics affect change in the NTE observed throughout the series. Follow-up experiments probing the dispersion further, as well as understanding the behaviour of the CMTO series on Ti-substitution and on cooling will give a much clearer picture as to the mechanisms that underpin the NTE in these structures.

References

[1] Keimer, B.; Kivelson, S. A.; Norman, M. R.; Uchida, S.; Zaanen, J, *Nature* **2015**, *518*, 179.

[2] Mackenzie, A. P.; Maeno, Y., *Rev. Mod. Phys.* **2003**, *75*, 657–712.

[3] Benedek, N. A.; Fennie, C. J., *Phys. Rev. Lett.* **2011**, *106*, 107204.

[4] Senn, M. S.; Bombardi, A.; Murray, C. A.; Vecchini, C.; Scherillo, A.; Lui, X.; Cheong, S. W., *Phys. Rev. Lett.* **2015**, *114*, 035701

[5] Senn, M. S.; Murray, C. A.; Luo, X.; Wang, L.; Huang, F.-T.; Cheong, S.-W.; Bombardi, A.; Ablitt, C.; Mostofi, A. A.; Bristowe, N. C. *J. Am. Chem. Soc.* **2016**, 138, 5479.

[6] Ablitt, C.; Craddock, S.; Senn, M. S.; Mostofi, A. A.; Bristowe, N. C. *npj Computational Materials* **2017**, 3, 44.

[7] Ablitt, C.; Mostofi, A. A.; Bristowe, N. C.; Senn, M. S. *Frontiers in Chemistry* **2018**, 6, 455.

[8] Chen, W.-T.; Ablitt, C.; Bristowe, N. C.; Mostofi, A. A.; Saito, T.; Shimakawa, Y.; Senn, M. S. *Chem. Commun.* **2019**, 55, 2984–2987.

[9] Tolerance Factor Control of Uniaxial Negative Thermal Expansion in a Layered Perovskite, Chris Ablitt, Harriet McCay, Sarah Craddock, Emily Reynolds, Arash A. Mostofi, Nicholas C. Bristowe, Claire A. Murray, Mark S. Senn. *Chem. Mater.* 2020, **32**, 605.