Experimental report

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Proposal:	**5-15-610**	**Council:**	4/2016
Title:	The ferroelectric-paraelectric transition in the hybrid improper ferroelectric material Ca3Ti2O7		
Research area:	Physics		

This proposal is a new proposal

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Samples: Ca3Ti2O7

Instrument	Requested days	Allocated days	From	To
D2B	3	3	13/06/2016	16/06/2016
D9	14	10	06/07/2016	16/07/2016

Abstract:

It is rather rare to find a new ferroelectric (FE) material, let alone predicted theoretically in the first place and then later confirmed by experiments. However, it was recently shown that (Ca,Sr)3Ti2O7 bulk single crystals become hybrid improper ferroelectrics just as theoretically predicted [1]. It is remarkable how two types of octahedron rotation can be coupled trilinearly to produce the FE state at room temperature. Despite the experimental report [3], it is still largely unknown how the FE state transforms into a paraelectric (PE) phase at high temperatures. In this proposal, we suggest to investigate the FE-PE transition at high temperatures and provide the detailed description of the theoretically proposed trilinear coupling of the two octahedron rotations.

Experimental report – experiment 5-15-610: The ferroelectric-paraelectric transition in the hybrid improper ferroelectric material $Ca_3Ti_2O_7$.

In "proper" ferroelectrics, the ferroelectric (FE) and magnetic orders are associated with different ions resulting in a weak coupling between both phenomena [1]. On the other hand, in "improper" ferroelectrics, polarization appears as part of a more complex lattice distortion or as an accidental byproduct of some other ordering.

Recently, these FE phenomena were reported on bulk single crystals of $(Ca,Sr)_3Ti_2O_7$ where a first-order FE-PE (paraelectric) transition was observed at ~1100 K in the pure $Ca_3Ti_2O_7$ compound according to the DSC measurement [2]. The layered perovskite structure of $Ca_3Ti_2O_7$ and low Ca-Sr substitutions is orthorhombic with the $A2_1am$ space group. The structure consists of two layers of TiO_6 octahedra with body-centered Ca/Sr ions (perovskite block) alternating with the rock-salt block. The TiO_6 octahedra tilt and rotate simultaneously leading to Ca/Sr displacements and to non-zero electric polarization along [100]. Such situation corresponds to the scenario of hybrid improper ferroelectricity which was demonstrated by measuring electric polarization vs. electric field hysteresis loops [3].

Despite the successful experimental demonstration of the FE phase in the $Ca_{3-x}Sr_xTi_2O_7$ single crystals, it is still largely unknown how the FE transition actually occurs on the atomic scale. In this proposal, we suggest to investigate the FE-PE transition at high temperatures (HT) and provide the detailed description of the theoretically proposed trilinear coupling of the two octahedron rotations. Neutron diffraction is an ideal tool for answering such a question. In particular, D9 diffractometer with high energy neutrons and 2D detector has proven to be very powerful for such studies as was demonstrated on the investigation of a similar HT phase transition of $BiFeO_3$ [4].

Although we succeeded in growing several $Ca_{3-x}Sr_xTi_2O_7$ ($x = 0 - 0.9$) single crystals, we focused entirely on one composition with $x = 0.85$ which provided single crystals of the best quality. As the atomic displacements were expected to be rather small, we needed to collect data relatively far in Q for an accurate mapping of the atomic positions. Moreover, to evidence these small changes it was necessary to measure at several temperatures from the room temperature (RT) up to the highest possible $T = 900$ K provided by the four-cycle furnace. For this, we obtained a total beam time of 10 days at D9. Prior to the single-crystal measurement we measured the powder sample of the same composition for 3 days on the high-resolution powder diffractometer D2B to follow the evolution of the Debye-Waller factors and to monitor the FE-PE transition.

We have measured approx. 3 g of $Ca_{2.15}Sr_{0.85}TiO_7$ powder using $\lambda = 1.59$ Å at room temperature, 470 K, and at 13 temperatures from 670 K up to 1200 K in 30-50 K steps. In contrast to the rough expectations of the transition temperature value from the DSC measurements of $Ca_3Ti_2O_7$, no abrupt changes in the structure parameters or emergence/suppression of any Bragg intensities were observed at around 1100 K or at even higher temperatures. The lattice parameters increase linearly within the error bar with the increasing temperature.

We have measured single crystal of the same Sr concentration ($Ca_{2.15}Sr_{0.85}TiO_7$) on the D9 instrument using $\lambda = 0.84$ Å. We have also tested several other single crystals of various Sr concentrations ($x = 0, 0.5, 0.85$) using the CYCLOPS instrument and selected the substituted sample ($x = 0.85$) of the mass of 16.7 mg.

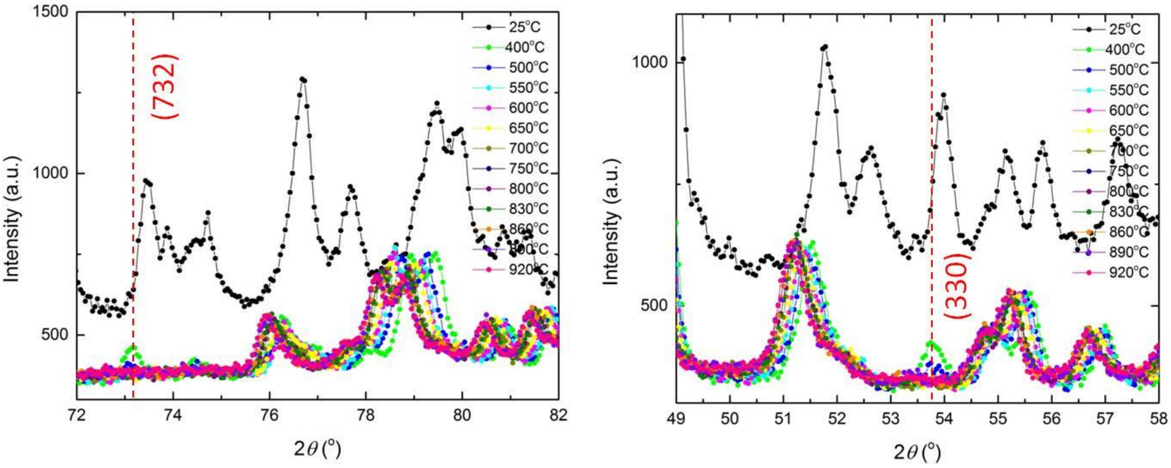

Fig. 1: The temperature evolution of the powder diffraction patterns of $Ca_{2.15}Sr_{0.85}TiO_7$. The left figure shows the detail of the suppression of the (732) reflection at ~ 770 K. The right figure shows a similar temperature dependence of the intensity of the (330) reflection.

The sample at D9 was first measured at room temperature and then upon increasing temperature in 50 K steps up to 900 K. We have focused on the (330) reflection which disappeared in the case of the powder sample measured on D2B at ~ 770 K. In the single crystal, the (330) reflection disappeared at 850 K which is probably caused by a slight difference in the Sr concentrations in the powder and single crystal. We have continued scanning the Q-space and the reflections from newly generated UB matrix for the *P1* and $Cmc2_1$ space group (#36) symmetry (expected from the literature [3]) at 900 K. From the measured reflections during the remaining experimental time we have found 23 non-equivalent reflections in total (including (330) obtained from the D2B measurement) which are observed at the room temperature but disappear at high temperature, 34 non-equivalent reflections which are observed both in the RT and HT phase, and 26 non-equivalent reflections observed at HT and not measured at RT.

Detailed analysis of measured data consisted in (i) applying the reflection conditions of all monoclinic and orthorhombic space groups on measured reflection at D9, (ii) fitting the powder diffraction patterns from D2B to possible model structures and (iii) searching the atomic positions employing the simulated annealing procedure. We excluded the structure with expected space group #36 [3] and also all other orthorhombic space groups to describe the RT phase. Instead, several monoclinic space groups remained as a possible solution. Analogically, only few orthorhombic candidates are consistent with measured HT phase data. The results of analysis are summarized in Table 1.

RT	HT
13	68
7*	68*
3*	68*
13	54
7*	54*
4*	54*
6	40
7	39
6	38

Table 1: Space groups to describe the RT and HT phases of $Ca_{2.15}Sr_{0.85}TiO_7$ based on the D2B and D9 data analysis. The table rows represent relations *t*-subgroup < group for structure below and above structural phase transition.

The red color marks the polar space groups and the green color marks the centrosymmetric space groups. The most probable scenario is that the structural transition is connected to the observed FE-PE transition (i.e. the transition from the polar to the centrosymmetric structure), i.e. the number of possible solutions is reduced to space groups marked by a star in Table 1. With respect to the sample quality we have not been able to determine the structure properties more closely (specify the space group and estimate the atomic coordinates). Fitting the measured powder diffraction patterns by models with space groups listed in Table 1 did not lead to reasonable agreement. To solve the crystal structure in both phase is still in progress and further experiments are underway.

References:

[1] Cheong, S-W., Mostovoy, M., Nat. Mat. 6, 13-20 (2007).

[2] Liu, X. Q., Wu, J. W., Shi, X. X., Zhao, H. J., Zhou, H. Y., Qiu, R. H., Zhang, W. Q., Chen, X. M., Appl. Phys. Lett. 106, 202903 (2015).

[3] Oh, Y. S., Luo, X., Huang, F-T., Wang, Y., Cheong, S-W., Nat. Mat. 14, 407–413 (2015).

[4] Lee, S., Fernandez-Diaz, M. T., Kimura, H., Noda, Y., Adroja, D. T., Lee, S., Park, J., Kiryukhin, V., Cheong, S.-W., Mostovoy, M., Park, J-G., Phys. Rev. B 88, 060103(R) (2013).