Experimental report

02/11/2015

Proposal: **5-23-676** **Council:** 10/2014

Title: Enhancing barocaloric effects in molecular crystals by electric field

Research area: Physics

This proposal is a new proposal

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Samples: [C6H7N2]+BF4-

Instrument	Requested days	Allocated days	From	To
D1B	0	3	20/04/2015	23/04/2015
D20	3	0		

Abstract:

Cooling technologies based on caloric effects in solids driven by external fields are currently being proposed as environmentally friendly and efficient alternatives to gas compression refrigeration. Recent experiments carried out by our group of barocaloric effects driven by hydrostatic pressure have revealed that the molecular crystal [C6H7N2]+.BF4- (dabcoHBF4) possesses extraordinary barocaloric properties. The ferroelectric transition underlying these colossal barocaloric effects suggests that the application of electric field may also entail excellent electrocaloric performance. Neutron diffraction experiments can provide key information about the fascinating possibility to drive multicaloric effects in dabcoHBF4.

The aim of the performed experiment was to study the effect of the electric field on the structure of Lead Scandium Tantalate ($PbSc_{0.5}Ta_{0.5}O_3$, hereafter PST) close to its ferroelectric transition, occurring at room temperature, $T_t \sim 295$ K. Across the transition on cooling, the PST structure changes from a paraelectric cubic (Fm-3m) to a ferroelectric rombhoedral lattice (R3m). The strategy was to induce the phase transition by application of an external electric field.

The sample was a polycrystalline thick film of width d=450μm. For this purpose, a special sample holder (shown in figure 1) was designed to bring electrical voltage to the sample. In particular, the sample was allocated between two vanadium sheets. Pt electrodes were deposited in each face of the sample and the contact between Pt and V was ensured by means of Silver paint. The selected neutron wavelength was of λ = 1.28 Å and typical measurement times for each diffraction pattern was 120 to 150 min. During the smooth increase of the voltage between the selected voltage values, some eventual voltage drops were observed due to electric discharges through the sample. This is a signature that the voltage was successfully applied in the sample.

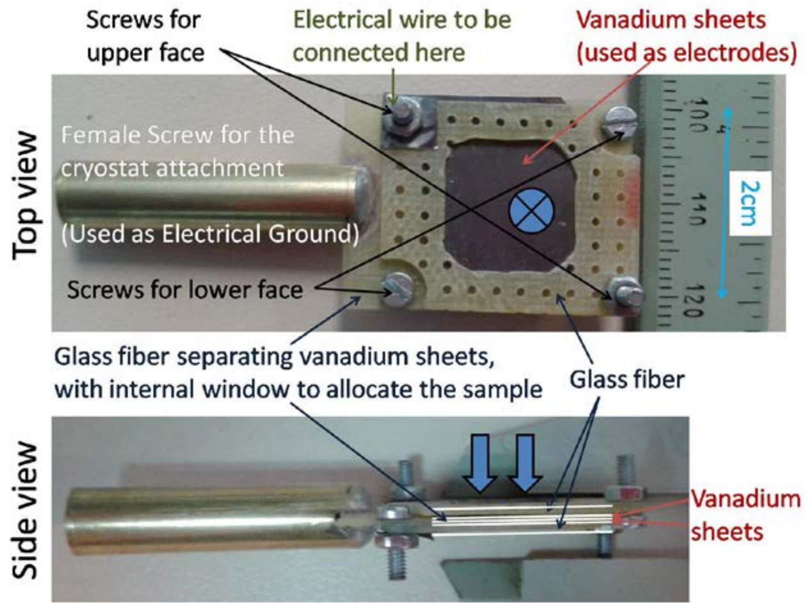

Fig. 1.- Home-made sample holder for application of external electric field. Thick blue arrows indicate the neutron beam.

First, two measurements of 3-4 hours weren taken in the absence of electric field, well below (204 K) and above (327 K) the transition temperature, which are shown in Fig. 2(a). Then, as shown in Fig. 2(b), measurements were taken at constant temperature of T=300K, just above the ferroelectric transition under different applied voltages: 0, 400, 800 and 1100V, rendering electric fields inside the sample of 0, 8.88, 17.78 and 24.44 kV/cm respectively. From previous calorimetry data under electric field we know that the electric field shifts the transition to higher temperatures. At the temperature of measurements (300K), the phase changes progressively when the field is increased, so that at 24.44kV the sample has undergone the full transition.

As it can be seen in the figure, all patterns appear to be very similar. This is explained because the differences between both phases in both the cell parameters and the angular distortion is so small that the splitting of the peaks could not be resolved with the resolution of D1B, at any value of the electric field and temperature.

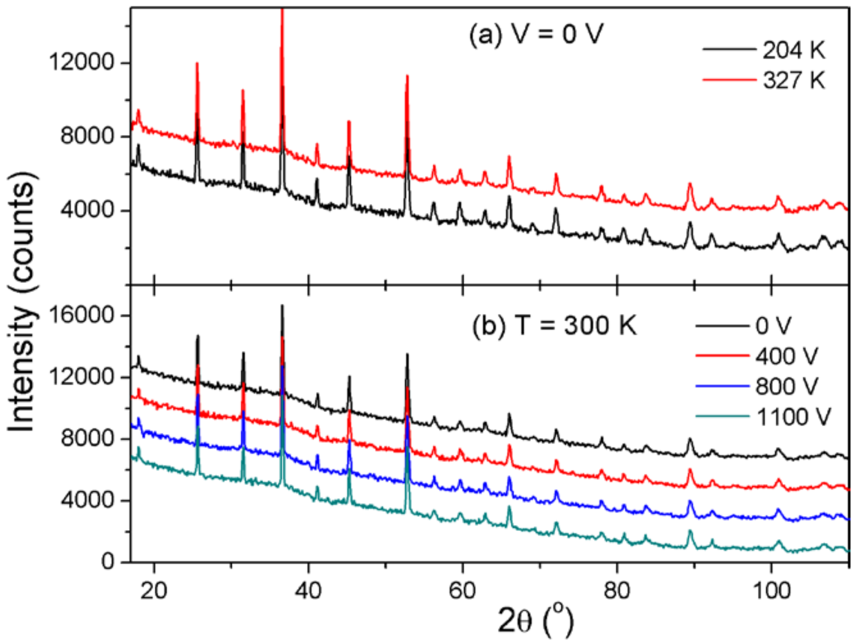

Fig2.- Diffraction patterns at (a) two different temperatures and null electric field and (b) constant temperature and different electric fields. Patterns have been vertically shifted for clarity.

Figure 3 shows two neutron powder diffraction patterns obtained at (a) 0V and (b) 1100kV, together with pattern matching results obtained from FullProf software. At 0V, the pattern is fitted according to the Fm-3m space group, rendering a cell parameter of a = 8.143 Å, and at 1100V the pattern is fitted according to the R3m space group, rendering values for the cell parameters in hexagonal axes of a = 11.512 Å and c = 14.152 Å, ($\alpha = \beta = 90^0, \gamma = 120^0$). Pattern matching has been carried out for all patterns (not shown). All the obtained values are consistent with previous own X-Ray data and literature X-Ray and neutron data. No traces of metals present in the beam path (Ag, Pt, V and Fe) were detected in the patterns, presumably due to very low quantity of material.

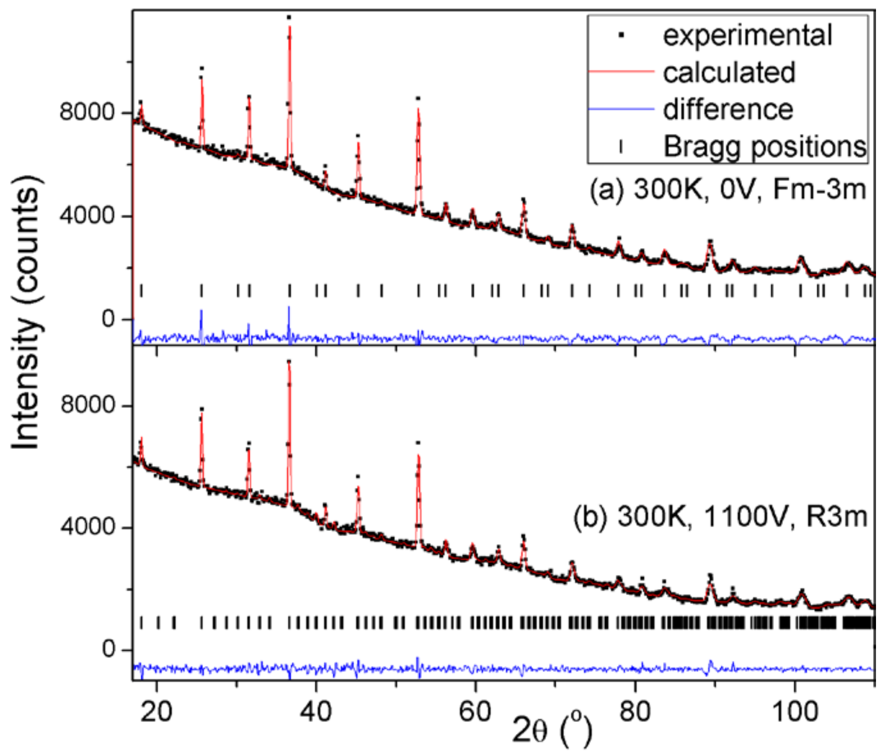

Fig. 3.- Pattern matching fits of measurements close to the pahse transition at (a) 0V and (b) 1100V.