

Experimental report – D2AM - #02-02-835

Summary :

Our goal during this beamtime was unravel the origin, polar or chemical, of the various types of super-structures observed in lead scandium niobate single crystal using anomalous scattering and temperature-dependent XRD.

Our beamtime was very succesful as, even prior to any quantitative data treatment, we can already conclude to which SSR are of polar nature and which are of chemical nature. In addition, we also know now that the SSR of polar origin appears at the same temperature as the polarity appears in the rest of the sample, indicative a common transition mechanism.

The quantitative data treatment shall provide us with which atoms contribute majoritarily to the SSR of polar origin as well as whether there is a detectable contribution of oxygen octahedra rotations.

Introduction

We had previsouly observed four types of SSR :

1. $\{h/2 h/2 h/2\}$, hereafter labelled « CO ». These SSR are associated only with chemical order along the [111] direction of the pseudo-cubic perovskite cell.
2. $\{h/2 k/2 l/2\}$, hereafter labelled « CO+ ». These SSR are also associated with chemical order, but are also compatible with another cell multiplication mechanism : oxygen octahedra rotations. For symmetry reasons only antiphase rotations may contribute to the intensity of these SSR.
3. $\langle h/2 h/2 l \rangle$, labelled « M ». These SSR are associated neither with a chemical order along [111] nor with oxygen octahedra rotations.
4. $\{h/2 k/2 l\}$, labelled « M+ ». These SSR may have the same origin as the M superstructures and are also compatible with in-phase oxygen octahedra rotations.

CO+ SSR are therefore a subset of CO-type SSR, just like M+ SSR are a subset of M-type SSR.

The hypothesis we work under is that our sample is composed of chemically ordered and chemically disordered regions.

Temperature dependent XRD

Chemically disordered lead scandium niobate samples exhibit a $Pm-3m$ to $R3m$ phase transition at 420K. Partially ordered powder (high temperature space group : $Fm-3m$) exhibits the same phase transition but at lower temperature. The transition temperature for ordered crystals has not been reported yet.

We therefore followed several main (i.e. pseudo-cubic) Bragg peaks ($h00$), ($hh0$), and (hhh) in order to confirm the rhombohedral crystal system of our sample (see Fig. 1) as well as to determine its T_C . The only Bragg peaks that are split are the (hhh) one and we find $330 < T_C(K) < 340$ (see Fig.1).

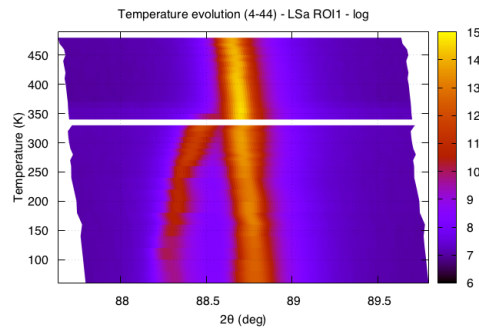


Fig 1 : Splitting of the (4-44)pc Bragg reflection signing the cubic to rhombohedral phase transition.

We then monitored the intensity of one M-type SSR and found the same transition temperature (see Fig. 2)

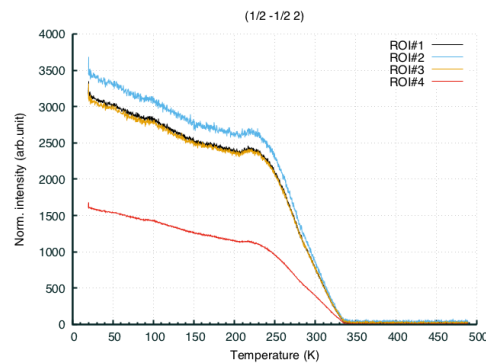


Fig 2: Intensity of the (1/2 -1/2 2) SSR (M-type) as a function of temperature for various ROI

This suggests a common transition mechanism for all polar phases in this material.

The comparison between the high- and low-temperatures (above T_C and 20K) scans along various directions of the reciprocal space enables to draw several conclusions :

- the « CO » SSR are of *chemical* nature rather than polar as they persist up to $T > T_C$ (see Figs.3 and 4). As expected these SSR are related to the B-site order along [111].
- the « M » (and therefore M+) SSR are *not of chemical nature* as they disappear at high temperature (see Figs.3 and 4). Such high temperature is much too low to enable ions to move within the structure.

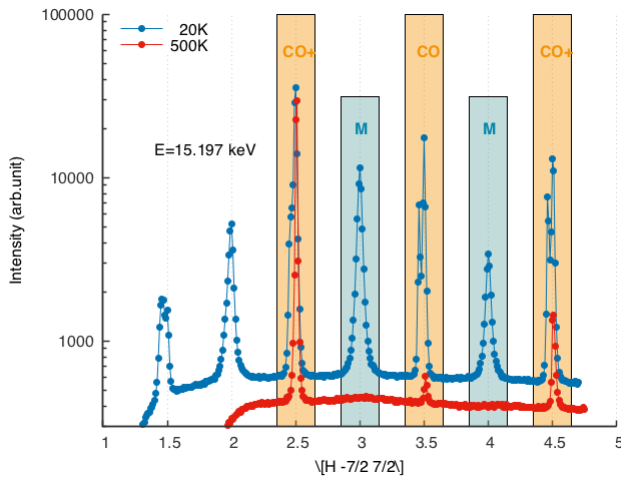


Fig 3: H-scan along the $[H - 7/2 \ 7/2]$ direction at 20 and 500K. The CO and CO+ SSR persist at high temperature, whereas the M superstructures disappear

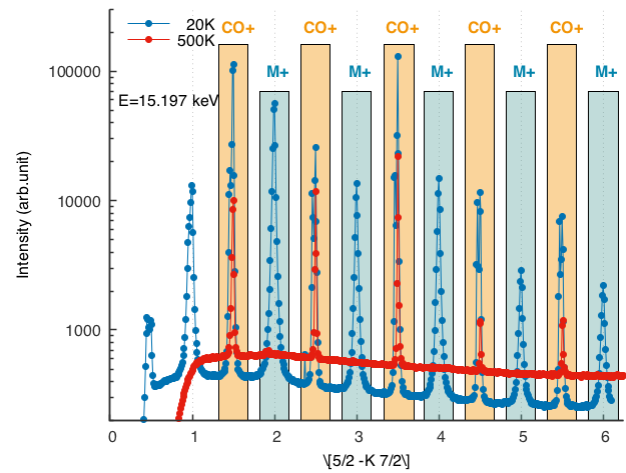


Fig 4: K-scan along the $[5/2 - K \ 7/2]$ direction at 20 and 500K. The CO+ SSR persist at high temperature whereas the M+ superstructures disappear

Having ruled out the chemical nature of the « M »-type SSR, a *polar* origin is our current work hypothesis.

The possible contribution of the oxygen octahedra rotations shall be investigated through a comparison between the evolution with temperature of the intensity of the « M » and « M+ » and « CO » and « CO+ » SSR. If oxygen octahedra rotations occur (in the M+ and/or CO+) then they shall contribute to the intensity of the « + » SSR and therefore plotting the intensity of the « + » SSR vs the one of the M and/or CO shall indicate whether such rotations occur or not. This analysis is under way.

Future work

In order to distinguish between the polar and chemical nature of our SSR, we have used the temperature as an external parameter.

Now that we know part of the SSR are of polar nature, applying an electric field should enable to unambiguously show that these polar SSR are related to antiferroelectricity whereas the rest of the material remains polar. As a consequence the transition temperatures of the two phases should exhibit opposite behavior under increasing electric-field : increase in T_C for the ferroelectric phase and decrease for the antiferroelectric phase.

This shall constitute the basis of our next proposal on D2AM.