

PDF XRD analysis of the possibility of the spin singlet small bipolarons in Nb-doped BaTiO₃Taras Kolodiazhnyi¹⁾ Yoneda Yasuhiro²⁾, Mizuki Junichiro²⁾

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1. Purpose

The main goal of this project was to identify the changes in the local crystal symmetry associated with the formation of the small bipolarons in the Nb doped BaTiO₃.

2. Method

We performed a detailed PDF analysis of the BaTiO₃ doped with 10 % of Nb in the temperature interval of 25 -295 K at the X-ray energy of 60 keV and the 2θ range of 2.5 -52°. We anticipated that the formation of the immobile small bipolarons at low temperature in this compound should be associated with a small local lattice distortion around the Ti³⁺ - Ti³⁺ bipolaron center. In order to resolve this very small local lattice distortion by means of the PDF analysis, we needed to use the high-brilliance synchrotron radiation.

3. Results

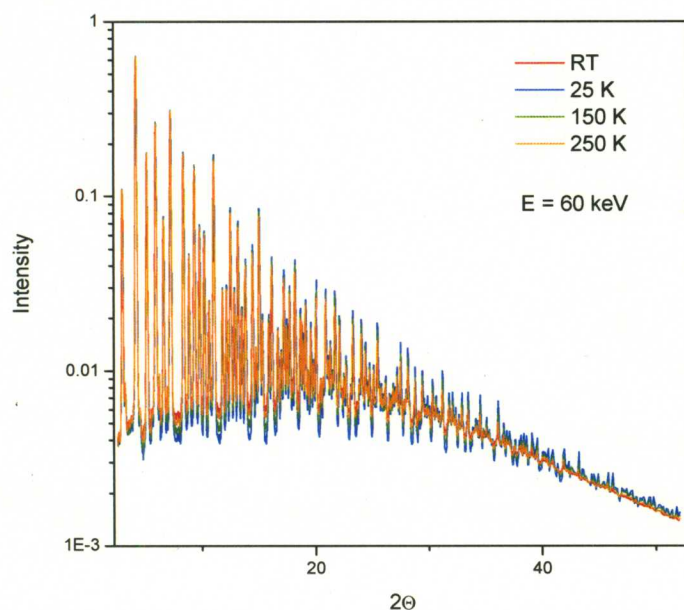


Figure 1

Figure 1 shows the background-corrected synchrotron X-ray diffraction patterns of the BaTiO₃: 10 % Nb obtained at 25, 150, 250 and 295 K.

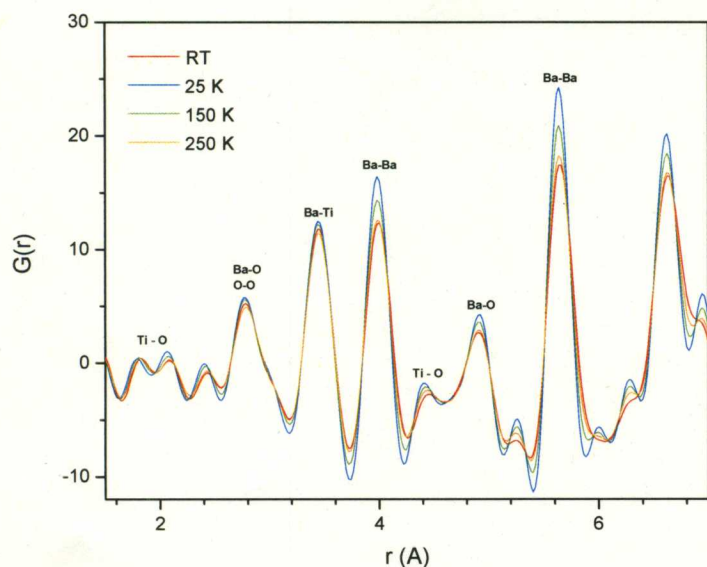


Figure 2

Figures 2 and 3 demonstrate the temperature evolution of the $G(r)$ function of the BaTiO_3 : 10 % Nb in the $r = 2 - 7$ Å and $r = 6 - 8.5$ Å interval, respectively.

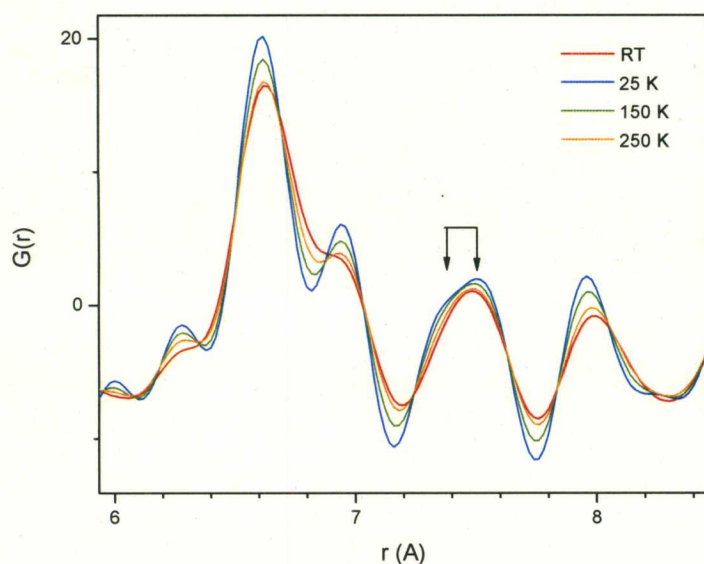


Figure 3

Upon decrease in temperature, a clear-cut splitting of the $r = 7.47$ Å peak into two peaks at $r = 7.38$ Å and 7.51 Å can be seen in Figure 3. This is a strong evidence of the local crystal distortion that might be caused by the 'freezing' out of the small radii bipolarons at low temperature.

4. Discussion and Conclusion

According to our intuitive model, formation of the small radii bipolarons (SBP) in barium titanate should be accompanied by a small attractive displacement of the two Ti^{3+} ions located at the neighbor lattice sites. An excess negative charge created by the SBP should be partially compensated by the outward displacement of the neighboring oxygen ions. Unlike first- or second-order phase transitions which are easily detectable by diffraction techniques, formation of the SBP is a statistical process and the concentration of the SBP changes gradually with temperature (see for example, equation 28 of Ref [3]). Hence, in order to detect any local lattice deformations associated with the SBP, one has to perform a PDF investigation in the widest possible temperature range.

According to earlier reports [4], BaTiO_3 is rather challenging compound for the PDF analysis due to the very different scattering cross section of Ti and Ba. Probably this is why the Ti-O correlation at around 2 Å in Figure 2 does not give rise to a $G(r)$ peak unless we observe a true two-site Ti-O and Nb-O correlation at 1.8 Å and 2.05 Å, respectively. Another interesting feature of the $G(r)$ function

is shown in Figure 3. Here we observe a splitting of the broad $G(r)$ peak at $r = 7.48$ Å into two peaks centered at $r = 7.38$ Å and 7.51 Å, respectively. This splitting may be an evidence of the local crystal distortion which develops at low temperature as the SBP freeze out. However, this is just a preliminary result and a more detailed analysis using a SBP crystal model has to follow up.

5. References

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