Structural Evolution and Uniaxial Negative Thermal Expansion in $RbNdTa_2O_7$

P. N. Lekshmi[1], E. Lora da Silva[1], P. Rocha-Rodrigues[1], J. S. O. Evans[2], J. H. Belo[1], P. Silva de Sousa[1], A. M. Manjón-Sanz[3], A. M. dos Santos[3], A. M. L. Lopes[1], J. P. Araújo[1]

1 IFIMUP, Institute of Physics for Advanced Materials, Nanotechnology and Photonics, Department of Physics and Astronomy, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 687, 4169-007 Porto, Portugal

2 Department of Chemistry, University Science Site, Durham University, South Road, Durham, DH1 3LE, U.K.

3 Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

neenulekshmi@fc.up.pt

Layered perovskite derivatives exhibit symmetry breaking arising from the combined effects of layering and cooperative octahedral tilting, giving rise to hybrid improper ferroelectricity (HIF).[1, 2] HIF in layered perovskites, particularly in Ruddlesden–Popper ($A_{n+1}B_nO_{3n+1}$) and Dion–Jacobson ($A'A_{n-1}B_nO_{3n+1}$) phases, provides an important platform for subtle structural analysis. Here, we investigate the structural phase transitions and thermal expansion behaviour of the n=2 Dion–Jacobson oxide $RbNdTa_2O_7$ using variable-temperature X-ray and neutron powder diffraction, complemented by Raman spectroscopy and DFT calculations. The previously reported sequential phase transitions [3], *I2cm → Cmce → I4/mcm → P4/mmm* were analysed to understand the origin of the uniaxial negative thermal expansion (NTE) observed across the first-order I2cm → Cmce transition. Unlike the corkscrew mechanism commonly reported for Ruddlesden–Popper phases [4], the uniaxial NTE observed is dominated by compression of the $NdTa_2O_6$ layers, coupled with changes in Ta-off-centering and Nd-ion displacements, with minimal impact from octahedral bilayer tilts and limited to the temperature range where the first-order structural transition occurs (Figure 1). This phase transition driven uniaxial NTE, is associated with the high flexibility of the NdTa2O6 intralayer bonds, highlighting the intricate interplay of the presence of second order Jahn-Teller Ta^{5+} ion, Nd-ion displacement, Nd/Ta-ion coordination and polyhedral regularisation [5]. Our temperature-dependent Raman studies further confirm the first-order structural phase transition and support the observed NTE to the contraction of the $NdTa_2O_6$ layer.

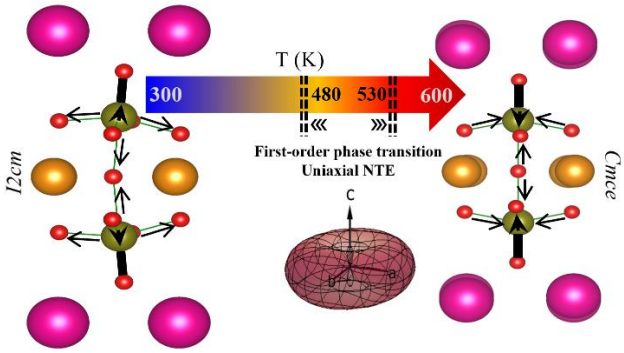


Figure 1. *Representation of high flexibility of the $NdTa_2O_6$ intralayer bonds, and the Ta-off centering with neighbouring apical oxygen, across the first-order transition along with the thermal expansion indicatrix obtained from PASCal webtool. [Pink, orange, green, and red spheres represent Rb, Nd, Ta, and O ions, respectively; the thick black line and arrow indicate the stiff Ta–O(apical) bond and its paired displacement]*

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