High-pressure study of ferroelectric SbSI: from long-range order to local probes

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Abstract

Ferroelectric materials with intrinsic spontaneous polarization are of broad interest due to their rich fundamental physics and their potential for applications in advanced sensors, memory devices, energy conversion, and photovoltaics [1]. In these systems, the coupling between crystal structure and electronic properties is often correlated with lone-pair formation. Due to their stereochemical activity, lone pairs promote structural distortions that can drive ferroic behavior. Among the most promising classes of materials, van der Waals antimony-based chalcohalides have recently attracted attention as potential solar absorbers [2]. In particular, antimony sulfoiodide (SbSI) exhibits a spontaneous polarization below the transition temperature close to room temperature, arising from a displacive structural transition from the orthorhombic Pnam to $Pna2_1$ space group, together with a suitable band gap for photovoltaic applications [3]. However, the underlying physics of this material is not yet fully understood. For instance, at low temperature a negative thermal expansion is observed along the crystallographic c-axis, which can be associated with a larger Sb displacement along z position and plays a key role in the emergence of spontaneous polarization.

Applying external pressure provides an additional powerful and clean way to modify local structure and atomic coordination, offering direct insight into the mechanisms that govern ferroelectricity and phase stability [4].

In this work, we investigate the high-pressure behavior of SbSI using a combination of complementary synchrotron techniques, including X-ray Diffraction, X-ray Absorption Spectroscopy (XAS), and Nuclear Forward Scattering (NFS) on ^{121}Sb. Under compression, SbSI exhibits very subtle structural modifications, consistent with those observed as a function of temperature [5]. While diffraction probes the average crystal structure, XAS and NFS provide direct access to the local environment of Sb, which is believed to play a central role in driving the ferroelectric state through its lone-pair activity. Focusing on the local response of antimony reveals signatures of distortions and electronic rearrangements that cannot be unambiguously identified using a single technique. This multi-scale approach is essential for disentangling the complex coupling between structure and ferroelectricity in SbSI.

Based on these results, we propose a pressure-temperature (P-T) phase diagram of SbSI, highlighting the presence of a low-temperature high-pressure phase, characterized by a structural transition from the orthorhombic to a monoclinic crystal structure. Particular emphasis is placed on the unique sensitivity of ^{121}Sb NFS, technique available at the ID14 Nuclear Resonance beamline of the ESRF, to the local electronic and structural environment of antimony. This local probe approach is further supported by complementary studies on elemental Sb under high pressure, illustrating the broader applicability of NFS to Sb-based systems and its ability to reveal subtle changes which are difficult to access with other techniques.

[1] J. F. Scott, Science 315, 954–959 (2007)

[2] J. He et al., Adv. Funct. Mater., 33, 2306075 (2023)

[3] G. Cuono et al., Phys. Rev. Materials 9, 064412 (2025)

[4] C. R. dela Cruz et al., Phys. Rev. B 76, 174106 (2007)

[5] T. Liu et al., Materials 15, 3845 (2022)