

Exploration of Phase Transition Behaviours and Magnetic Structures in Some Polar Sulphides Containing Diatomic Anions

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Ferroelectric materials are employed in numerous technological applications, such as non-volatile memories and capacitors. The conventional strategy to stabilise ferroelectric structures involves second-order Jahn-Teller (SOJT) cations with either d^0 or ns^2 electronic configurations. However, SOJT cations do not inherently guarantee ferroelectric structures, and their diamagnetic character precludes the magnetic properties necessary for multiferroic behaviour and spintronic applications. Consequently, there is a significant demand for identifying new mechanisms capable of breaking inversion symmetry.

Within this context, heteronuclear diatomic ions present an excellent alternative for designing ferroelectric structures. These ions are intrinsically polar and can collectively order to induce bulk electric polarisation. At elevated temperatures, an order-disorder (static-dynamic) transition can also occur, introducing an additional order parameter susceptible to manipulation by external stimuli.

In this study, we synthesised a series of materials containing a small heteronuclear diatomic hydrosulphide anion (SH^-), with the general composition $\text{A}_x\text{B}_y(\text{SH})_z$. The ordering of SH^- can lead to polar symmetry, thus accurately determining the hydrogen position becomes crucial. Although synchrotron X-ray diffraction can effectively locate the positions of atoms A, B, and S, it cannot precisely determine the hydrogen position. Therefore, we performed neutron powder diffraction (NPD) experiments using the HERMES instrument at JRR-3 to accurately identify the hydrogen position and the precise crystal symmetry of the material.

The NPD data obtained from our samples are of exceptionally high quality. Figure 1 illustrates the fitting of room-temperature data from one sample, which can be effectively modelled using

a polar structure with the space group $P2_1ab$. This result aligns with our optical measurements showing positive second-harmonic generation, a technique widely utilised for rapid determination of non-centrosymmetry. Detailed analysis of the refined structure also supports the conclusion that SH^- anion ordering is responsible for the observed polar symmetry.

Supplementary H-NMR data reveal two distinct transitions at elevated temperatures, suggesting two structural phase transitions likely associated with the order-disorder transition of SH^- anions. Analysis of high-temperature diffraction data is ongoing to clarify the exact symmetry changes.

Overall, this neutron powder diffraction study has been highly successful, and we anticipate publishing these findings shortly. We hope our work will encourage future exploration of ferroelectric materials based on heteronuclear diatomic ions.

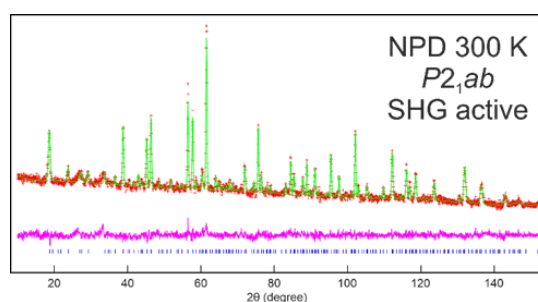


Fig. 1. Refinement against room-temperature neutron powder diffraction data using a polar structural model.