

Composite phases with translational disorder

Abstract

The MCr_2X_4 family ($\text{M} = \text{Pb}, \text{Sr}, \text{Ba}, \text{Eu}, \text{Sn}$; $\text{X} = \text{S}, \text{Se}$) comprises structurally complex compounds characterized by incommensurate channel-type frameworks [1]. Their structures are based on a hexagonal network of edge-sharing CrX_6 octahedra that defines two distinct types of channels: one hexagonal channel per unit cell, occupied by $\text{M}_6\text{Cr}_2\text{X}_6$ units, and two trigonal channels containing columns with an approximate M_3X composition. The periodicity of these guest columns may differ from that of the host framework, giving rise to structural incommensurability and, in some members of the family, significant translational disorder. Previous electron diffraction studies of BaCr_2Se_4 [2] and SnCr_2S_4 [3] have demonstrated different types of ordering and disorder within the channels. Such structural complexity is expected to influence charge and thermal transport, making these compounds of interest for thermoelectric applications [3].

In this work, PbCr_2S_4 was investigated as a model system, followed by partial substitution of Cr by V to form $\text{PbCr}_{2-x}\text{V}_x\text{S}_4$ ($x = 0.4, 0.6, 0.8$, and 1). The substitution strategy was motivated by the metallic conductivity previously reported for SrV_2S_4 by Omloo *et al.* [1], with the aim of exploring whether V incorporation could modify the electronic properties of PbCr_2S_4 . The compounds were synthesized by high-temperature solid-state reactions from stoichiometric amounts of high-purity elements sealed in evacuated silica tubes. For V-containing compositions, the silica tubes were carbonized to prevent reaction between V and the silica.

Pure PbCr_2S_4 was successfully obtained. Electron diffraction measurements reveal that coherence between the guest columns is maintained for specific values of l , indicating a degree of ordering within the channels. This behavior differs from that reported for BaCr_2Se_4 , where the guest columns exhibit a larger periodicity, and SnCr_2S_4 , where the columns are reported to be completely disordered. In the $\text{PbCr}_{2-x}\text{V}_x\text{S}_4$ series, compositions with $x = 0.4, 0.6$, and 0.8 were obtained with minor binary sulfide impurities, while the $x = 1$ composition contained significant amounts of PbS and Cr_2S_3 . Attempts to synthesize the fully substituted PbV_2S_4 phase were unsuccessful.

Powder X-ray diffraction reveals a systematic evolution of the lattice parameters with increasing V content, consistent with progressive V incorporation into the structure. TEM-EDX further confirms the presence of V, although its spatial resolution is insufficient to determine the specific crystallographic sites occupied by the substituting atoms.

References

- [1] Omloo, W. P. F. A. M.; Bommerson, J. C.; Heikens, H. H.; Risselada, H.; Vellinga, M. B.; van Bruggen, C. F.; Haas, C.; Jellinek, F. *Europium Chromium Sulfide (EuCr_2S_4) and Some Isotypic Compounds*. Phys. Status Solidi A **1971**, 6, 349.
- [2] Routledge, K. *Structurally and Magnetically Complex Materials: A Magnetocaloric, a Multiferroic Skyrmion Host and Related Systems*; PhD Thesis, University of Liverpool, **2023**.
- [3] Guiot, F. *Synthesis and Crystallographic Structure Analysis through Multiscale Characterization of Complex Sulfide Materials for Energy Conversion*; PhD Thesis, Université de Rennes, **2024**.