Invited Lecture

$Ba_{1-p}Cr_2Se_{4-p}$: Thermoelectric material at the frontier of order and disorder

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Several transition metal chalcogenides, boasting diverse structural types like rutile, perovskite, and rocksalt, have exhibited promising thermoelectric properties [1]. Thus, $Ba_{1-p}Cr_2Se_{4-p}$ selenides [2] have garnered significant attention. Within this family of materials, the crystal structure manifests as an intergrowth of three distinct structural units, sharing a common hexagonal basal plane but with three different c axes. The modular block within channels resembles a hexagonal perovskite, while the threefold framework mirrors a rutile network. Combining these structures offers an appealing prospect due to their inherent structural and functional flexibility. Moreover, alongside the typically rigid rutile framework, trigonal and hexagonal channels further enhance structural complexity (Fig.1).

The coexistence of these modular blocks fosters disorder. Past studies utilizing electron diffraction have unveiled diffuse scattering lines [3], indicating directional order. Our preliminary investigations also uncovered low-intensity reflections (Fig.1) characteristic of incommensurable structural modulations. The presence of such aperiodicities, coupled with disorders, complicates fine structural analysis, necessitating dedicated crystallographic formalisms (e.g., superspaces) and a complementarity of techniques for comprehensive insight at various scales.

Single-crystal X-ray diffraction has proven instrumental in unravelling atomic order, revealing the incommensurable modulations inherent in the coexistence of different structural types. These measurements further elucidated the nature of previously observed diffusions (Fig.1), highlighting the presence of strong correlated disorders within hexagonal tunnels. Augmenting our study, high-resolution image-mode electron microscopy coupled with highly accurate EDX mapping revealed notable variations in local composition within the channels. These findings are pivotal for comprehending the observed thermal conductivity and magnetic properties in this material.

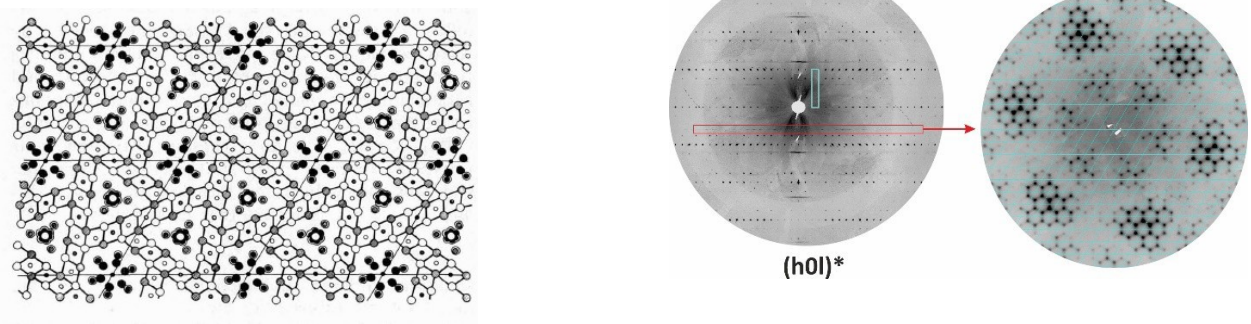

Figure 1. Structural model and diffraction patterns of $Ba_{1-p}Cr_2Se_{4-p}$ exhibiting both satellite reflections related to incommensurate modulation and diffuse scattering related to correlated disorder.

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[3] H. Fukuoka, M. Onoda, T. Saito (1995). Journal of Solid State Chemistry **115**, pp. 7-12.