

Identification of kinetic factors that expedite solid state Fe₂SiS₄ crystal formation by *in situ* XRD

Understanding of the kinetic factors on complex crystal formation is beneficial to the efficient synthesis and discovery of inorganic materials. Here we utilized high-temperature *in situ* X-ray diffraction (XRD) to identify such kinetic factors in the formation of the model compound Fe₂SiS₄ during solid state reactions. It is observed from *in situ* XRD that the sulfidation kinetics differ drastically among the Fe and Si elements. The ability of this system to achieve thermodynamic equilibrium phase at low temperature is likely impeded by the slow sulfidation of Si. Here, from *in situ* XRD, we identified two factors that expedited the solid state reaction in forming Fe₂SiS₄ phase. The first factor is associated with the peritectic point of Fe-S system at 743 °C, which generated superheated S liquid and initiated fast Fe₂SiS₄ growth. The second factor involved the pre-bonding of Fe and Si to form intermetallics, whose subsequent sulfidation can generate Fe₂SiS₄ at temperatures as low as 550 °C. We expect the utilization of these two kinetic factors uncovered by *in situ* XRD can improve the synthesis of complex chalcogenides using solid state method, especially in those involving slowly-sulfidized elements.

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