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**Impact of Protein-Metal Ion Interactions on the Crystallization of Silk Fibroin Protein**<sup>1</sup> XIAO HU, QIANG LU, DAVID KAPLAN, PEGGY CEBE, Tufts University — Proteins can easily form bonds with a variety of metal ions, which provides many unique biological functions for the protein structures, and therefore controls the overall structural transformation of proteins. We use advanced thermal analysis methods such as temperature modulated differential scanning calorimetry and quasi-isothermal TMDSC, combined with Fourier transform infrared spectroscopy, and scanning electron microscopy, to investigate the protein-metallic ion interactions in *Bombyx mori* silk fibroin proteins. Silk samples were mixed with different metal ions ( $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ) with different mass ratios, and compared with the physical conditions in the silkworm gland. Results show that all metallic ions can directly affect the crystallization behavior and glass transition of silk fibroin. However, different ions tend to have different structural impact, including their role as plasticizer or anti-plasticizer. Detailed studies reveal important information allowing us better to understand the natural silk spinning and crystallization process.

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