Melting metal cyanidos with low-coordinate copper center

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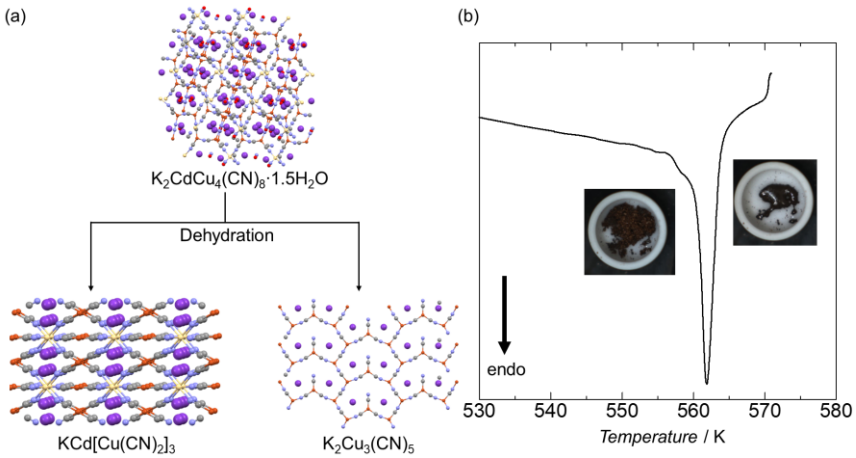
Metal cyanide is a kind of coordination polymer constructed from only metal ions and cyanide linkers. The representative example, Prussian blue, was first synthesized in 1704 and has long been studied since then, with reports of ferromagnetic transitions at room temperature[1] and adsorption of certain alkali metals[2]. However, despite more than a century of research, only three melting metal cyanidos have been obtained. They all consist of one-dimensional structures, and no melting two- (2D) or three-dimensional (3D) metal cyanides have ever been reported. Herein, we successfully synthesized a composite of melting 3D $KCd[Cu(CN)_2]_3$ and 2D $K_2Cu_3(CN)_5$.[3] These compounds melted at around 570 K and 565 K.

First, we synthesized a hydrated precursor $K_2CdCu_4(CN)_8 \cdot 1.5H_2O$.[4] Then, $KCd[Cu(CN)_2]_3$ and $K_2Cu_3(CN)_5$ were obtained as orange powder via structural transformation by simple dehydration. Uniquely, these compounds coexisted in the single particle. The crystal structure of these compounds were determined by micro-ED. DSC measurement and real-view system revealed $KCd[Cu(CN)_2]_3$ and $K_2Cu_3(CN)_5$ melted at around 567 K. Thus, variable temperature powder X-ray diffraction measurements demonstrated that diffraction peaks of $KCd[Cu(CN)_2]_3$ and $K_2Cu_3(CN)_5$ disappeared at 570 K and 565 K, respectively. Moreover, molecular-dynamics simulation clarified the cause of melting is geometrical flexibility of tow-coordinate Cu^I center. The coordination number and geometry of Cu^I varied at high temperature resulting in increase of ΔS and the reduction of melting point.



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