$KCaEr_2CuS_5$: A Novel Pentanary Rare-earth Chalcogenide from Reactive Flux Synthesis

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Chemists have been paying much attention to the multiple-component rare-earth chalcogenides both for the fundamental interest of their varieties of structural features and in the search of potential candidates for luminescent materials, magneto-optical materials, infrared materials, and high-temperature superconducting materials[1-2]. It is widely realized that during the synthesis and crystal growth via flux methods, occasional inclusion of flux elements in the final product is inevitable and often leads to unexpected and interesting new structures. Serendipitously, in our effort to search analogues of superconducting rare-earth cuprates, a novel pentanary rare-earth sulfide, $KCaEr_2CuS_5$, was obtained by a two-step synthetic route. Precursors from the first-step solid state reaction were mixed with excess amount of the mixed KCl/KBr fluxes. The pressed pellet was then loaded into a sealed silica ampoule and thermally equilibrated at 800 °C for two weeks prior to slow cooling (~3 °C/h) to room temperature. Light yellow, transparent, and needle-like single crystals were isolated from the flux by washing the products with distilled water using a suction filtration technique. The title compound crystallizes in the orthorhombic *Cmcm* (No. 63) with $a = 3.933(1)$ Å, $b = 13.410(2)$ Å, $c = 17.042(2)$ Å, $V = 898.8(2)$ Å^3, $Z = 4$, $R = 0.069$, $R_w = 0.068$. $KCaEr_2CuS_5$ contains four types of building blocks in its structure: octahedral ErS_6 and CaS_6, tetrhedral CuS_4, and trigonal prismatic KS_6. The structure is characterized by infinite double-octahedral ErS_6 chains that each share opposite edges and are bridged together by across-sharing one side of octahedral edges in a zigzag manner. These double-octahedral chains are connected into a puckered layer via corner-sharing, with Cu atoms filling in the tetrhedral sites. In other words, the compound may be viewed as a layered structure composed of $[Er_2CuS_5]^{3-}$ slabs in which CuS_4 tetrahedra connect neighboring double-octahedral ErS_6 chains, or *vice versa*. The $[Er_2CuS_5]^{3-}$ slabs are stacked along the *b* direction with K^+ and Ca^{+2} cations located into different cavities between the layers. This compound illustrates a common feature in the rare-earth–transition-metal chalcogenides: although the basic building blocks are the same or similar, novel and different structure may occur due to different packing schemes of these MQ_n polyhedra. Since there are no S–S bonds in the structure, the formal oxidation states can be assigned as K^{+1}, Ca^{+2}, Ln^{+3}, Cu^{+1}, and S^{-2}. This, together with the transparent nature of the crystals, implies a semiconducting character for the phases with a bandgap around 2.5–2.7 eV estimated on the basis of the yellow color observed[3]. Further property characterizations on optical and electrical behavior are underway.

References

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