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A new formula and crystal structure for nickelskutterudite, (Ni,Co,Fe)As_3, and occupancy of the icosahedral cation site in the skutterudite group

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Abstract

We propose a new formula for the mineral nickelskutterudite, based on our observation that either (or both) Co or Fe^{3+} are essential structure constituents. The crystal structure of nickelskutterudite, (Ni,Co,Fe)As_3, cubic, $Im\bar{3}$, $Z = 8$: $a = 8.2653(6)$ Å, $V = 564.65(7)$ Å^3, has been refined to $R_1 = 1.4\%$ for 225 unique reflections $I > 2\sigma(I)$ collected on a Bruker X8 four-circle diffractometer equipped with fine-focus, sealed tube Mo$K\alpha$ radiation and an APEX-II CCD detector. This is the first report of the crystal structure of nickelskutterudite. Nickelskutterudite, a member of the skutterudite group of isostructural minerals, adopts a distorted perovskite structure with notably tilted octahedra and an unoccupied to partially occupied icosahedral metal site. In the structure of nickelskutterudite, there is one metal (*B*) site occupied by Ni, Co, or Fe in octahedral coordination with six As atoms. Procrystal electron density analysis shows each As anion is bonded to two cations and two As anions, resulting in a four-membered ring of bonded As with edges 2.547 and 2.475 Å. The extreme tilting of *B*As_6 octahedra is likely a consequence of the As-As bonding. The nickelskutterudite structure differs from the ideal perovskite structure ($A_4B_4X_{12}$) in that As_4 anion rings occupy three of the four icosahedral cages centered on the *A* sites. There are reported synthetic phases isomorphous with skutterudite with the other *A* site completely occupied by a cation (AB_4X_{12}).

Electron microprobe analyses of nickelskutterudite gave an empirical chemical formula of $(Ni_{0.62}Co_{0.28}Fe_{0.12})_{\Sigma 1.02}(As_{2.95}S_{0.05})_{\Sigma 3.00}$ normalized to three anions. Pure $NiAs_3$ nickelskutterudite, natural or synthesized, has not been reported. In nature, nickelskutterudite is always observed with significant Co and Fe, reportedly because all non-bonded valence electrons must be spin-paired. This suggests that nickelskutterudite must contain Co^{3+} and Fe^{2+}, consistent with previous models since Ni^{4+} cannot spin-pair its seven non-bonded electrons, Co^{3+} and Fe^{2+}, which can spin-pair all non-bonded electrons, are required to stabilize the structure. No anion deficiencies were found in the course of this study so, including the structurally necessary Co and Fe, the chemical formula of nickelskutterudite (currently given as $NiAs_{3-x}$ by the IMA) should be considered (Ni,Co,Fe)As_3.

Keywords: Skutterudite, icosahedral metal site, cobalt, nickel, octahedral tilt