A new formula and crystal structure for nickelskutterudite, (Ni,Co,Fe)As₃, and occupancy of the icosahedral cation site in the skutterudite group

BENJAMIN N. SCHUMER¹,*, MARCELO B. ANDRADE², STANLEY H. EVANS¹, AND ROBERT T. DOWNS¹

¹Department of Geosciences, University of Arizona, 1040 E. 4th Street, Tucson, Arizona 85721-0077, U.S.A.
²São Carlos Institute of Physics, University of São Paulo, Caixa Postal 369, 13560-970, São Carlos, São Paulo, Brazil

ABSTRACT

We propose a new formula for the mineral nickelskutterudite, based on our observation that either (or both) Co or Fe³⁺ are essential structure constituents. The crystal structure of nickelskutterudite, (Ni,Co,Fe)As₃, cubic, Im³, Z = 8: a = 8.2653(6) Å, V = 564.65(7) Å³, has been refined to Rᵢ = 1.4% for 225 unique reflections I > 2σ(I) collected on a Bruker X8 four-circle diffractometer equipped with fine-focus, sealed tube MoKα 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 BAS₆ octahedra is likely a consequence of the As-As bonding. The nickelskutterudite structure differs from the ideal perovskite structure (A₄B₆X₁₂) in that As₈ 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 (AB₆X₁₂).

Electron microprobe analyses of nickelskutterudite gave an empirical chemical formula of (Ni₀.₆₂Co₀.₃₆Fe₀.₀₂)₃As₆S₀₁₆Sb₀₃₀₀. Normalized to three anions. Pure NiAs₃ 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 Co³⁺ and Fe²⁺, consistent with previous models since Ni³⁺ cannot spin-pair its seven non-bonded electrons, Co³⁺ and Fe²⁺, 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 NiAs₁₋₄ by the IMA) should be considered (Ni,Co,Fe)As₃.

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

INTRODUCTION

The skutterudite mineral group consists of minerals that exhibit cubic space group symmetry Im³ with ideal formula BX₆ or B₆X₁₂, where B is Co, Ni, or Fe, and X is As or Sb. Skutterudite group minerals adopt a distorted perovskite structure with unoccupied A sites, constructed from a framework of tilted, corner-linked BX₆ octahedra, bringing together four anions in three-quarters of the otherwise vacant icosahedral cages, where they form rectangular four-member rings (Aleksandrov and Beznosikov 2007). Numerous synthetic compounds exist, which are isomorphous with skutterudite group minerals, and these materials fall into two categories: (1) filled, which follow the general formula AB₆X₁₂, in which A is a large cation partially to completely occupying the remaining quarter of the icosahedral cages, B is generally a transition metal cation, and X is a P, As, or Sb anion; and (2) unfilled with the general formula BX₆. Synthetic filled skutterudite materials, such as Th₂Co₂Sb₂ and Nd₀₅Sb₂, have been widely studied due to their particular thermoelectric properties including high Seebeck coefficients, high electrical conductivity, and low thermal conductivity (Aleksandrov and Beznosikov 2007; Chakoumakos and Sales 2006; Fukuoka and Yamanaka 2009; Navrátil et al. 2010). We suspect that the structures of natural skutterudites can accommodate cations within the icosahedral site.

The skutterudite mineral group currently consists of four members (with current IMA formula): skutterudite (CoAs₃), nickelskutterudite (NiAs₃), ferroskutterudite [(Fe,Co)As₃], and kieffite (CoSb₃). The IMA nomenclature commission currently defines the chemical formula for skutterudite and nickelskutterudite as anion deficient, BX₅₋₄, after the work of Palache et al. (1944). Pauling (1978) suggested that the ideal formula of skutterudite be written Co₄(As₃), emphasizing the four member As rings.

The study of the skutterudite group has a long history, with skutterudite sensu stricto first reported by Breithaupt (1827) and its chemical composition reported as CoAs₃ by Haidinger (1845). Over the course of the next century, a series of mineral species were described to account for the diversity of chemical compositions and physical properties exhibited by minerals related to skutterudite (Vollhardt 1888). In particular a nickel-dominant phase was described by Waller and Moses (1893) from the Bullard’s Peak Mining District, Grant County, New Mexico, and more recently an iron-dominant phase was described by Spiridonov et al. (2007). The 7th edition of Dana’s System by Palache et al. (1944), included a summary of the skutterudite minerals, defining them as consisting of cubic R₅As₅ minerals where R = Fe, Co, or Ni. The IMA adopted...