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Received 11 May 2007
Accepted 22 June 2007
Online 26 July 2007

Tyrellite, a naturally occurring Co–Ni–Cu selenide, has been studied by single-crystal X-ray diffraction. It possesses the normal spinel-type structure, with Cu occupying the tetrahedral site and (Co+Ni) the octahedral site. The average Cu–Se distance of 2.3688 (2) Å is close to that of 2.3703 (8) Å in CuCr_2Se_4, whereas the average (Co+Ni)–Se distance of 2.3840 (1) Å appears to be slightly shorter than most octahedral Co–Se or Ni–Se distances (~2.40–2.50 Å) in other selenides. The refined structure provides a basis for a redefinition of the ideal chemical formula of tyrellite, which should be Cu(Co,Ni)_2Se_4, rather than the previously suggested (Cu,Co,Ni)_2Se_4.

Comment

Selenide materials with the spinel-type structure, AB_2Se_4, where A and B are tetrahedrally and octahedrally coordinated sites, respectively, have been the subject of numerous studies because of their magnetic and semiconducting properties (see, for example, Justczyn & Gogolowicz, 1991; Kim et al., 2006; Skrzypek et al., 2006; Noh et al., 2007). Of particular interest is the distribution of various cations between the A and B sites, as such structural variations could significantly alter many physical properties of these materials (see, for example, Hazen & Yang, 1999; Œkoński-Kozłowska et al., 2001). Tyrellite, a Co–Ni–Cu selenide, was first described by Robinson & Brooker (1952) to have a face-centered cubic lattice (Fm3m), with a = 10.005–10.042 Å and a chemical formula Co_{3.0}Ni_{0.75}Cu_{3.5}Se_{3.5}. However, Machatschki & Stradner (1952) pointed out that the X-ray powder pattern of tyrellite resembled that of spinel minerals and the calculated intensities, assuming a spinel-type structure, agree well with the probable formula of (Co,Cu,Ni)_2Se_4. Harris (1970) used a single-crystal X-ray diffractometer to examine the original tyrellite material separated by Robinson & Brooker (1952) and found that all the fragments gave split reflections and were unsuitable for structure determination. No further structural investigation has been reported since then. This study presents the first structure refinement of tyrellite based on single-crystal X-ray diffraction data and provides a basis for a redefinition of its ideal chemical formula.

Tyrellite is isostuctural with spinel, with Cu and (Co+Ni), respectively, occupying the tetrahedral A and octahedral B sites in the cubic close-packed array of Se atoms (Fig. 1). The preference of Cu for the tetrahedral site has been observed for other spinel-type selenides and sulfides, such as CuCr_2Se_4 (Őkoński-Kozłowska et al., 1993), Cu_{1−x}Co_xCr_2Se_4 (Őkoński-Kozłowska et al., 2001), Cu_{1−x}Ni_xCr_2Se_4 and Cu_{2−x}Ni_xSe_4 (Jendrzejewska, 2000), CuCo_2Se_4 (Williamson & Grimes, 1974), and Cu(Ni_{0.7}Sn_{0.3})_2S_4 (Garg et al., 2001). The Cu—Se distance of 2.3688 (2) Å in tyrellite is comparable with the range of 2.3664–2.3740 Å in spinel-type CuCr_2Se_4 (Őkoński-Kozłowska et al., 1993; Payer et al., 1993; Rodic et al., 1998), whereas the average (Co+Ni)—Se distance of 2.3840 (1) Å appears to be shorter than most Cu—Se or Ni—Se distances (~2.40–2.50 Å) for six-coordinated Co or Ni in other selenides (see, for example, Furuseth et al., 1969; Kamat Dalal et al., 1971; Foecker & Jeitschko, 2001; García-García et al., 2004).

Unlike oxide spinels, the valence of ions in selenide spinels has been a matter of discussion. For example, three models of electronic structure have been proposed for CuCr_2Se_4: Cu^{+}Cr^{2+}Se^{2−} (Goodenough, 1967), Cu^{+}[Cr^{3+}Cr^{4+}]Se^{2−} (Lotgering, 1964), and Cu^{2+}[Cr^{2+}Se^{2−}] (Lotgering & Van Stapele, 1967). Although there is still some disagreement regarding the valence of Cr and Se, experimental results from X-ray photoelectron spectroscopy and neutron diffraction have demonstrated the presence of Cu^{+}, rather than Cu^{2+}, in CuCr_2Se_4 (Hollander et al., 1974; Yamashita et al., 1979; Payer et al., 1990; Rodic et al., 1998). Since the Cu—Se bond length in

Figure 1

A polyhedral view of the crystal structure of tyrellite.
inorganic compounds

tyrellite agrees very well with that in CuCr$_2$Se$_4$, presumably Cu in tyrellite is also monovalent. Noteworthy, nevertheless, is the appreciably short (Co+Ni)—Se bond distance in tyrellite compared with the Cr—Se distances (2.508—2.512 Å) in CuCr$_2$Se$_4$ (Okońska-Kozłowska et al., 1993; Payer et al., 1993; Rodic et al., 1998). If we assume that the chemical bond between Se and the octahedrally coordinated cation is predominately ionic (Juszczysz & Gogolowicz, 1991; Rodic et al., 1998), the calculation of the bond-valence sum using the parameters given by Brese & O’Keefe (1991) yields a value of 3.77 valence units for (Co+Ni), suggesting that some Co/or/and Ni in tyrellite might exist in a formal charge greater than 3+.

Experimental

The tyrellite specimen used in this study is from the type locality Eagle Claims, Beaverlodge Lake area, Saskatchewan, Canada, and is in the collection of the RRUFF project (deposition No. R060481; http://rruff.info). The specimen was described by Robinson & Brooker (1952) and Harris (1970). The average chemical composition (15 point analyses), Cu$_{0.94}$Co$_{0.05}$Ni$_{0.01}$Se$_4$, was determined with a CAMECA SX50 electron microprobe.

Crystal data

Co$_{0.93}$Cu$_{0.06}$Ni$_{0.01}$Se$_4$
M. = 497.06
Cubic, Fd$ar{3}$m
a = 9.9885 (1) Å
V = 996.55 (2) Å$^3$
Z = 8
Mo Kα radiation
μ = 40.12 mm$^{-1}$
T = 293 (2) K
0.07 × 0.07 × 0.06 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS: Sheldrick, 2005)
T$_{min}$ = 0.123, T$_{max}$ = 0.142 (expected range = 0.078-0.900)

Refinement

R[F$^2$ > 2σ(F$^2$)] = 0.014
wR(F$^2$) = 0.028
S = 1.12
227 reflections

The A site was assumed to be fully occupied by Cu during the refinement. The Co Ni ratio in the B site was allowed to vary and yielded occupancies of 0.68 (6) for Co and 0.32 (6) for Ni.

Data collection: APEX2 (Bruker, 2003); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELX97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: X-Draw (Downs & Hall-Wallace, 2003); software used to prepare material for publication: SHELXTL (Bruker, 1997).

The authors gratefully acknowledge the support of this study from the RRUFF project and the National Science Foundation (grant No. EAR-0609906). The sample was donated to the project by Michael Scott.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3052). Services for accessing these data are described at the back of the journal.

References