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Tyrrellite, Cu(Co$_{0.68}$Ni$_{0.32}$)$_2$Se$_4$, isostructural with spinel

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Tyrrellite, 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$_2$Se$_4$, 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 tyrrellite, which should be Cu(Co,Ni)$_2$Se$_4$, rather than the previously suggested (Cu,Co,Ni)$_3$Se$_4$.

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, Juszczyk & 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; Okońska-Kozlowska *et al.*, 2001). Tyrrellite, 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$_{2.0}$Cu$_{3.5}$Se$_{9.5}$. However, Machatschki & Stradner (1952) pointed out that the X-ray powder pattern of tyrrellite resembled that of spinel minerals and the calculated intensities, assuming a spinel-type structure, agree well with the probable formula of (Co,Cu,Ni)$_3$Se$_4$. Harris (1970) used a single-crystal X-ray diffractometer to examine the original tyrrellite 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 tyrrellite based on single-crystal X-ray diffraction data and provides a basis for a redefinition of its ideal chemical formula.

Tyrrellite is isostructural 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$_2$Se$_4$ (Okońska-Kozlowska *et al.*, 1993), Cu$_{1-x}$Co$_x$Cr$_2$Se$_4$ (Okońska-Kozlowska *et al.*, 2001), Cu$_{1-x}$Ni$_x$Cr$_2$Se$_4$ and CuCr$_{2-x}$Ni$_x$Se$_4$ (Jendrzejewska, 2000), CuCo$_2$S$_4$ (Williamson & Grimes, 1974), and Cu(Ni$_{0.25}$Sn$_{0.75}$)$_2$S$_4$ (Garg *et al.*, 2001). The Cu—Se distance of 2.3688 (2) Å in tyrrellite is comparable with the range of 2.3664–2.3740 Å in spinel-type CuCr$_2$Se$_4$ (Okońska-Kozlowska *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 Co—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; Garcia-Garcia *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$_2$Se$_4$: Cu^{2+}Cr$_2^{3+}$Se$_4^{2-}$ (Goodenough, 1967), Cu^{+}[Cr^{3+}Cr^{4+}]Se$_4^{2-}$ (Lotgering, 1964), and Cu^{+}Cr$_2^{3+}$[Se$_3^{2-}$Se^{-}] (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$_2$Se$_4$ (Hollander *et al.*, 1974; Yamashita *et al.*, 1979; Payer *et al.*, 1990; Rodic *et al.*, 1998). Since the Cu—Se bond length in

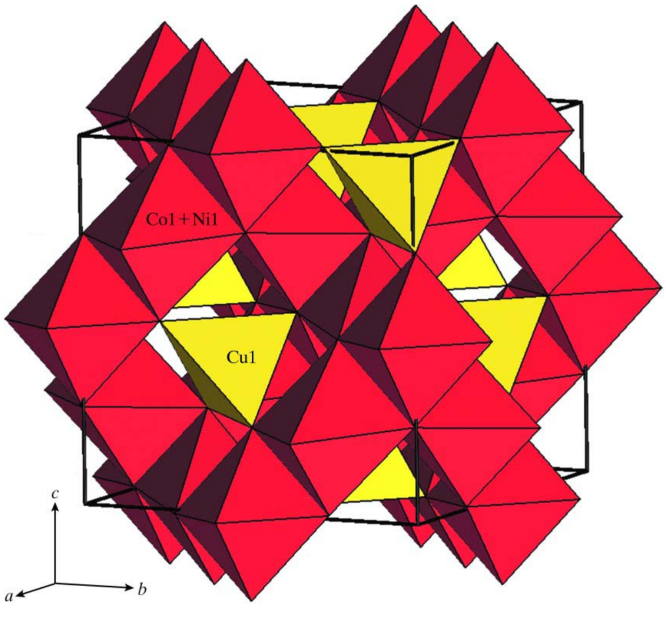

Figure 1
A polyhedral view of the crystal structure of tyrrellite.

tyrrellite agrees very well with that in $CuCr_2Se_4$, presumably Cu in tyrrellite is also monovalent. Noteworthy, nevertheless, is the appreciably short (Co+Ni)—Se bond distance in tyrrellite compared with the Cr—Se distances (2.508–2.512 Å) in $CuCr_2Se_4$ (Okońska-Kozlowska *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 (Juszczyk & Gogolowicz, 1991; Rodic *et al.*, 1998), the calculation of the bond-valence sum using the parameters given by Brese & O'Keeffe (1991) yields a value of 3.77 valence units for (Co+Ni), suggesting that some Co or/and Ni in tyrrellite might exist in a formal charge greater than 3+.

Experimental

The tyrrellite 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), $Cu_{0.99}(Co_{0.69}Ni_{0.31})_2Se_4$, was determined with a CAMECA SX50 electron microprobe.

Crystal data

$Co_{1.36}CuNi_{0.64}Se_4$
$M_r = 497.06$
Cubic, $Fd\bar{3}m$
$a = 9.9885$ (1) Å
$V = 996.55$ (2) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 40.12$ 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 = 0.078–0.090)
2566 measured reflections
227 independent reflections
206 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.014$
$wR(F^2) = 0.028$
$S = 1.12$
227 reflections
9 parameters
$\Delta\rho_{\max} = 0.79$ e Å^{-3}
$\Delta\rho_{\min} = -1.27$ e Å^{-3}

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: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XtalDraw* (Downs & Hall-Wallace, 2003); software used to prepare material for publication: *SHELXTL* (Bruker, 1997).

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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

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.
Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2003). *SMART*. Version 6.0. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2005). *SAINT*. Version 6.0. Bruker AXS Inc., Madison, Wisconsin, USA.
Downs, R. T. & Hall-Wallace, M. (2003). *Am. Mineral.* **88**, 247–250.
Foecker, A. J. & Jeitschko, W. (2001). *J. Solid State Chem.* **162**, 69–78.
Furuseth, S., Kjekshus, A. & Andersen, A. F. (1969). *Acta Chem. Scand.* **23**, 2325–2334.
Garcia-Garcia, F. J., Larsson, A.-K., Noren, L. & Withers, R. L. (2004). *Solid State Sci.* **6**, 725–733.
Garg, G., Bobev, S. & Ganguli, A. K. (2001). *J. Alloys Compd*, **327**, 113–115.
Goodenough, J. B. (1967). *Solid State Commun.* **5**, 577–580.
Harris, D. C. (1970). *Can. Mineral.* **10**, 731–736.
Hazen, R. M. & Yang, H. (1999). *Am. Mineral.* **84**, 1956–1960.
Hollander, J. C. Th., Sawatzky, G. & Haas, C. (1974). *Solid State Commun.* **15**, 747–751.
Jendrzejewska, I. (2000). *J. Alloys Compd*, **305**, 90–92.
Juszczyk, S. & Gogolowicz, M. (1991). *J. Magn. Magn. Mater.* **92**, 388–396.
Kamat Dalal, V. N., Keer, H. V. & Biswas, A. B. (1971). *J. Inorg. Nucl. Chem.* **33**, 2839–2845.
Kim, D., Gedanken, A., Tver'yanovich, Y. S., Lee, D. W. & Kim, B. K. (2006). *Mater. Lett.* **60**, 2807–2809.
Lotgering, F. K. (1964). *Solid State Commun.* **2**, 55–56.
Lotgering, F. K. & Van Stapele, R. P. (1967). *Solid State Commun.* **5**, 143–146.
Machatschki, F. & Stradner, E. (1952). *Anz. Oesterr. Akad. Wiss. Math. Naturwiss. Kl.* **89**, 211–213.
Noh, H.-J., Kang, J.-S., Lee, S. S., Kim, G., Han, S.-W., Oh, S. J., Kim, J.-Y., Lee, H.-G., Yeo, S., Guha, S. & Cheong, S.-W. (2007). *Europhys. Lett.* **78**, 27004.
Okońska-Kozlowska, I., Kopyczok, J., Lutz, H. D. & Stingl, T. (1993). *Acta Cryst.* C**49**, 1448–1449.
Okońska-Kozlowska, I., Malicka, E., Waskowska, A., Heimann, J. & Mydlarz, T. (2001). *J. Solid State Chem.* **158**, 34–39.
Payer, A., Schmalz, M., Schollhorn, R., Schlogl, R. & Ritter, C. (1990). *Mater. Res. Bull.* **25**, 515–522.
Payer, A., Schollhorn, R., Ritter, C. & Paulus, W. (1993). *J. Alloys Compd*, **191**, 37–42.
Robinson, S. C. & Brooker, E. J. (1952). *Am. Mineral.* **37**, 542–544.
Rodic, D., Antic, B., Tellgren, R., Rundlof, H. & Blanusa, J. (1998). *J. Magn. Magn. Mater.* **187**, 88–92.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (2005). *SADABS*. Version 2.10. University of Göttingen, Germany.
Skrzypek, D., Malicka, E., Waskowska, A., Widuch, S., Cichon, A. & Mydlarz, T. (2006). *J. Cryst. Growth*, **297**, 419–425.
Williamson, D. P. & Grimes, N. W. (1974). *J. Phys. D Appl. Phys.* **7**, 1–6.
Yamashita, O., Yamaguchi, Y., Nakatani, I., Watanabe, H. & Masumoto, K. (1979). *J. Phys. Soc. Jpn*, **46**, 1145–1152.

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