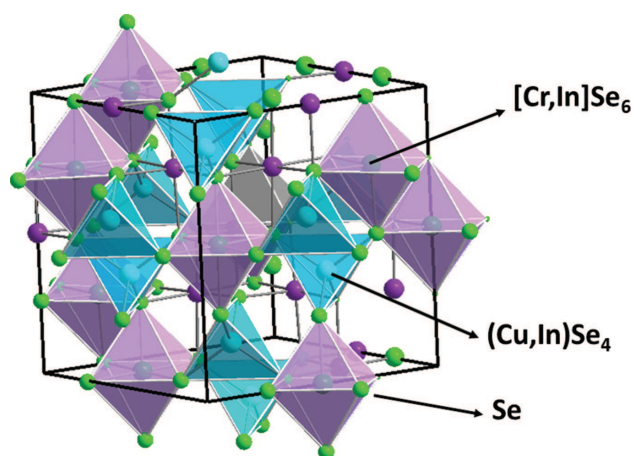


Silvana Moris, Patricia Barahona and Antonio Galdámez*

Crystal structure of $(\text{Cu}_{0.51}\text{In}_{0.49})_{\text{tet}}[\text{Cr}_{1.74}\text{In}_{0.26}]_{\text{oct}}\text{Se}_4$ selenospinel, $\text{Cu}_{0.51}\text{In}_{0.75}\text{Cr}_{1.74}\text{Se}_4$



<https://doi.org/10.1515/ncrs-2018-0426>

Received October 14, 2018; accepted December 17, 2018; available online January 24, 2019

Abstract

$\text{Cu}_{0.51}\text{In}_{0.75}\text{Cr}_{1.74}\text{Se}_4$, cubic, $Fd\bar{3}m$ (no. 227), $a = 10.6506(13)$ Å, $V = 1208.2$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0371$, $wR_{\text{ref}}(F^2) = 0.0912$, $T = 293(2)$ K.

CCDC no.: 1861215

The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

$\text{Cu}_{0.51}\text{In}_{0.75}\text{Cr}_{1.74}\text{Se}_4$ was prepared by directly combining high-purity elemental powders (99.99%, Aldrich) in stoichiometric amounts. All manipulations were carried out under argon atmosphere. The reaction mixtures were sealed in evacuated quartz ampoules and placed in a programmable furnace. The ampoules were then slowly heated at a rate of 2.5 °C/min, from room temperature until 500 °C for 2 hours, followed by

Table 1: Data collection and handling.

Crystal:	Black prism
Size:	$0.05 \times 0.04 \times 0.04$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	31.6 mm^{-1}
Diffractometer, scan mode:	D8 VENTURE Bruker AXS,
θ_{max} , completeness:	30.0° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	1089, 109, 0.040
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 109
$N(\text{param})_{\text{refined}}$:	10
Programs:	Bruker [1], SHELX [2], Olex2 [3], DIAMOND [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1 ^a	1/8	1/8	1/8	0.0031(11)
In1 ^b	1/8	1/8	1/8	0.0031(11)
Cr2 ^c	1/2	1/4	1/4	0.0082(13)
In2 ^d	1/2	1/4	1/4	0.0082(13)
Se1	0.26060(10)	x	x	0.0085(7)

^aOccupancy: 0.51(5), ^bOccupancy: 0.49(5), ^cOccupancy: 0.87(2),

^dOccupancy: 0.13(2).

a heating-rate of 1 °C/min up to the maximum temperature of 850 °C, and held for 7 days.

Experimental details

Three models were considered for the permutations of the metal atom positions in $(\text{A})_{\text{tet}}[\text{B}]_{\text{oct}}\text{Se}_4$ spinel-type: (1) indium and copper cations sharing the tetrahedral position $(\text{A})_{\text{tet}}$ -site; (2) indium and chromium cations sharing octahedral $[\text{B}]_{\text{oct}}$ -sites; and (3) indium sharing both tetrahedral $(\text{A})_{\text{tet}}$ - and octahedral $[\text{B}]_{\text{oct}}$ -sites. For the tetrahedral cation site, the sum of site occupation factors (SOF) was constrained to equal 1 (fully occupied) for $8a = (1-x)\text{Cu} + x\text{In}$. The sum of SOF in the octahedral cation site was constrained to equal 2 (fully occupied) for $16d = (2-y)\text{Cr} + y\text{In}$. Moreover, cations sharing the same site were constrained to have identical thermal displacements. A careful examination of the structural details, such as the thermal equivalent isotropic displacements U_{eq} , occupation sites, R_{gt} and wR_{ref} indices provided a strong indication

*Corresponding author: Antonio Galdámez, Universidad de Chile, Facultad de Ciencias, Departamento de Química, Casilla 653, Santiago Chile, e-mail: agaldamez@uchile.cl

Silvana Moris: Universidad Católica del Maule, Vicerectoría de Investigación y Postgrado, Talca, Chile

Patricia Barahona: Universidad Católica del Maule, Facultad de Ciencias Básicas, Talca, Chile

of crystal structure final refinement. The best convergence refinements was obtained in model (3).

Comment

The (Cu, In)_{tet}-Se distances in (Cu_{0.51}In_{0.49})_{tet}[Cr_{1.74}In_{0.26}]_{oct}Se₄ were consistent with the bond lengths of Cu_{0.5}In_{0.5}Cr_{2.0}Se₄ (2.475 Å) [5] and Cu_{0.46}In_{0.54}Cr_{2.08}Se₄ (2.433–2.507 Å) [6]. The [Cr, In]_{oct}-Se (2.5548 Å) bond distances are comparable with [Cr, M]_{oct}-Se bond lengths for CuCr_{1.5}Zr_{0.5}Se₄ (2.538 Å) and CuCr_{1.5}Sn_{0.5}Se₄ (2.5671 Å) [6]. The [Cr, In]_{oct}-Se bond length in the CdCr_{1.8}In_{0.19}Se₄ compound is 2.55413 Å [7]. Baur and Wildner *et al.* evaluated the degree of distortions of the tetrahedra and octahedra using distortion indices [8, 9]. These indices have been used in our research group for describing the polyhedra in CuCr_{2-x}Sn_xSe₄ [6], CuCr_{2-x}Ti_xSe₄ [10] and CuCr_{2-x}Zr_xSe₄ [6]. In (Cu_{1-x}In_x)_{tet}[Cr_{2-y}In_y]_{oct}Se₄, the (Cu, In)_{tet}Se₄ tetrahedra was ideal, with an angle of 109.47°. The [Cr, In]_{oct}Se₆ octahedron edge length distortion (EDL) indice is 4.5%. This value of octahedral distortion is approximately twice that of the compounds previously reported: CuCr_{2-x}Ti_xSe₄, CuCr_{2-x}Sn_xSe₄ and CuCr_{2-x}Zr_xSe₄. These materials obtained by ceramic synthesis present interesting magnetic properties such as other spinels substituted in A-site [11].

Acknowledgements: The authors thank FONDECYT Grant No. 1161020 and the Chilean-French International Associated Laboratory for Multifunctional Molecules and Materials (LIAM3-CNRS N°1027).

References

1. Bruker. Analytical X-ray Instruments Inc., Madison, WI, USA (2000).
2. Sheldrick, G. M.: SHELXL97. Program for the refinement of crystal structures. University of Göttingen, Stuttgart (1997).
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **42** (2009) 339–341.
4. Brandenburg, K.: DIAMOND. Visual crystal structure information system. Ver. 3.0., Crystal Impact, Bonn, Germany (2004).
5. Yokoyama, H.; Chiba, S.: Preparation and magnetic properties of a new selenide spinel Cu_{1/2}In_{1/2}Cr₂Se₄. *J. Phys. Soc. Jpn.* **27** (1969) 505.
6. Pinto, C.; Galdámez, A.; Barahona, P.; Moris, S.; Peña, O.: Crystal structure, Raman scattering and magnetic properties of CuCr_{2-x}Zr_xSe₄ and CuCr_{2-x}Sn_xSe₄ selenospinel. *J. Magn. Magn. Mater.* **456** (2018) 160–166.
7. Skrzypek, D.; Malicka, E.; Waskowska, A.; Widuch, S.; Cichon, A.; Mydlarz, T.: Structural and magnetic properties of Cd_xIn_yCr₂Se₄. *J. Cryst. Growth* **297** (2006) 419–425.
8. Baur, W. H.: The geometry of polyhedral distortions. Predictive relationships for the phosphate group. *Acta Crystallogr.* **B30** (1974) 1195–1215.
9. Wildner, M.: On the geometry of Co(II)O₆ in inorganic compounds. *Z. Kristallogr.* **202** (1992) 51–70.
10. Barahona, P.; Galdámez, A.; López-Vergara, F.; Manríquez, V.; Peña, O.: Crystal structure and magnetic properties of titanium-based CuTi_{2-x}M_xS₄ and CuCr_{2-x}Ti_xSe₄ chalcospinel. *J. Solid State Chem.* **212** (2014) 114–120.
11. Pinch, H. L.; Woods, M. J.; Lopatin, E.: Some new mixed A-site chromium chalcogenide spinels. *Mater. Res. Bull.* **5** (1970) 425–429.