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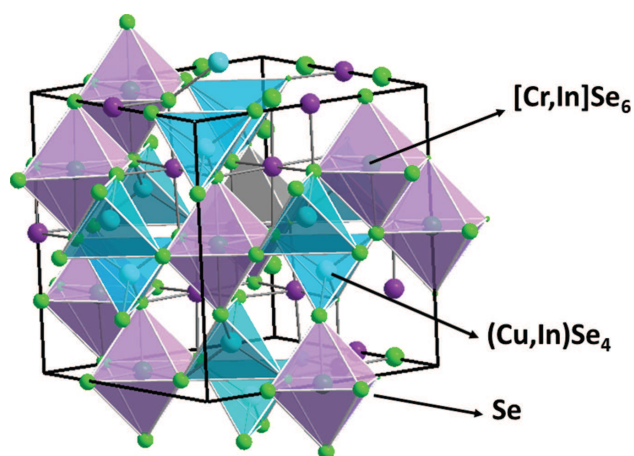
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Crystal structure of $(Cu_{0.51}In_{0.49})_{tet}[Cr_{1.74}In_{0.26}]_{oct}$ Se_4 selenospinel, $Cu_{0.51}In_{0.75}Cr_{1.74}Se_4$

$[Cr,In]Se_6$

$(Cu,In)Se_4$

Se

Abstract

$Cu_{0.51}In_{0.75}Cr_{1.74}Se_4$, cubic, $Fd\bar{3}m$ (no. 227), $a = 10.6506(13)$ Å, $V = 1208.2$ Å^3, $Z = 8$, $R_{gt}(F) = 0.0371$, $wR_{ref}(F^2) = 0.0912$, $T = 293(2)$ K.

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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

$Cu_{0.51}In_{0.75}Cr_{1.74}Se_4$ 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

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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%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	1089, 109, 0.040
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 109
$N(param)_{refined}$:	10
Programs:	Bruker [1], SHELX [2], Olex2 [3], DIAMOND [4]

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

Atom	x	y	z	U_{iso}*/U_{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)

[a]Occupancy: 0.51(5), [b]Occupancy: 0.49(5), [c]Occupancy: 0.87(2), [d]Occupancy: 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 $(A)_{tet}[B]_{Oct}Se_4$ spinel-type: (1) indium and copper cations sharing the tetrahedral position $(A)_{tet}$-site; (2) indium and chromium cations sharing octahedral $[B]_{Oct}$-sites; and (3) indium sharing both tetrahedral $(A)_{tet}$- and octahedral $[B]_{Oct}$-sites. For the tetrahedral cation site, the sum of site occupation factors (SOF) was constrained to equal 1 (fully occupied) for $8a = (1-x)\,Cu + x\,In$. The sum of SOF in the octahedral cation site was constrained to equal 2 (fully occupied) for $16d = (2-y)\,Cr + y\,In$. 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

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

Comment

The $(Cu, In)_{tet}$-Se distances in $(Cu_{0.51}In_{0.49})_{tet}[Cr_{1.74}In_{0.26}]_{oct}Se_4$ were consistent with the bond lengths of $Cu_{0.5}In_{0.5}Cr_{2.0}Se_4$ (2.475 Å) [5] and $Cu_{0.46}In_{0.54}Cr_{2.08}Se_4$ (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 $CuCr_{1.5}Zr_{0.5}Se_4$ (2.538 Å) and $CuCr_{1.5}Sn_{0.5}Se_4$ (2.5671 Å) [6]. The $[Cr,In]_{oct}$-Se bond length in the $CdCr_{1.8}In_{0.19}Se_4$ 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 $CuCr_{2-x}Sn_xSe_4$ [6], $CuCr_{2-x}Ti_xSe_4$ [10] and $CuCr_{2-x}Zr_xSe_4$ [6]. In $(Cu_{1-x}In_x)_{tet}[Cr_{2-y}In_y]_{Oct}Se_4$, the $(Cu,In)_{tet}Se_4$ tetrahedra was ideal, with an angle of 109.47°. The $[Cr,In]_{oct}Se_6$ octahedron edge length distortion (EDL) indice is 4.5%. This value of octahedral distortion is approximately twice that of the compounds previously reported: $CuCr_{2-x}Ti_xSe_4$, $CuCr_{2-x}Sn_xSe_4$ and $CuCr_{2-x}Zr_xSe_4$. These materials obtained by ceramic synthesis present interesting magnetic properties such as other spinels substituted in A-site [11].

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