inorganic compounds

Disordered La$_3$Cu$_{4.88}$Se$_7$

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The crystal structure of copper(I) lanthanum selenide, La$_3$Cu$_{4.88}$Se$_7$, obtained from the La$_2$Se$_3$–Cu$_2$Se quasi-binary system, has been investigated using X-ray single-crystal diffraction. The positions of the La and Se atoms are ordered and lie on mirror planes, whereas all positions for the Cu atoms are partially occupied. The crystal is built from edge-sharing [LaSe$_6$] and [LaSe$_7$] polyhedra. The five positions for the Cu atoms determine an ionic diffusion pathway in the structure.

Comment

The design of functional materials with increasingly complex compositions has become a primary direction in modern science and technology. Among multicomponent systems, much attention has been paid to complex rare-earth-based chalcogenides owing to their specific thermal, electrical, magnetic and optical properties. An example is prospective applications of various chalcogenide materials in the field of IR and nonlinear optics (Gulay & Daszkiewicz, 2011; Mitchell & Ibers, 2002).

So far, only La$_5$CuSe$_8$ and LaCuSe$_2$ have been synthesized from the La$_2$Se$_3$–Cu$_2$Se system (Julien-Pouzol & Guittard, 1968; Ijjaali *et al.*, 2004) and these have been fully characterized, crystallizing in the space groups $I\bar{4}3d$ and $P2_1/c$, respectively. Julien-Pouzol & Guittard (1972) reported the existence of crystals of a compound with orthorhombic symmetry. Lattice parameters $a = 7.74$ Å, $b = 24.67$ Å and $c = 7.01$ Å were determined using the Weissenberg method and a formula La$_5$Cu$_{13}$Se$_{14}$ was proposed. However, its crystal structure has not been reported until now.

The compound turns out to have the stoichiometry La$_3$Cu$_{4.88}$Se$_7$ and the asymmetric unit contains two La sites, five Cu sites and four Se sites. The site of each Cu atom is partially occupied. The nonstoichiometry here can be explained by the presence of mixed-valence Cu^{I}/Cu^{II}. The La1

and Se2 atoms lie on a mirror plane. Each of the formally La^{III} and Cu atoms is surrounded by four Se^{2-} anions at distances that agree well with the sum of the respective ionic radii (Wiberg, 1995). The Se atoms form a distorted trigonal prism around the La1 atom and a distorted monocapped trigonal prism around the La2 atom. Two trigonal prisms centred by La1 are surrounded on two sides by two monocapped trigonal prisms centred by La2. These six trigonal prisms (2La1 + 4La2) form large structural [La$_6$Se$_{28}$] building blocks which are related to one another by inversion symmetry (Fig. 1). Since each La atom is connected to the adjacent La atom by two bridging Se atoms, the crystal lattice is built by the edge-sharing [LaSe$_6$] and [LaSe$_7$] polyhedra. On the other hand, the Se atoms exhibit distorted tetrahedral coordination around the Cu1–Cu4 atoms. The remaining Cu5 atom has a triangular environment and is located very close to the plane built by three Se atoms.

Overall, the crystal structure of La$_3$Cu$_{4.88}$Se$_7$ is structurally related to Pt$_3$Sr$_7$ (Fornasini & Palenzona, 1983; ICSD, 2010) (Fig. 1). In Pt$_3$Sr$_7$, atom Pt1 is surrounded by seven Sr atoms which form a monocapped [PtSr$_7$] trigonal prism, and each Pt2
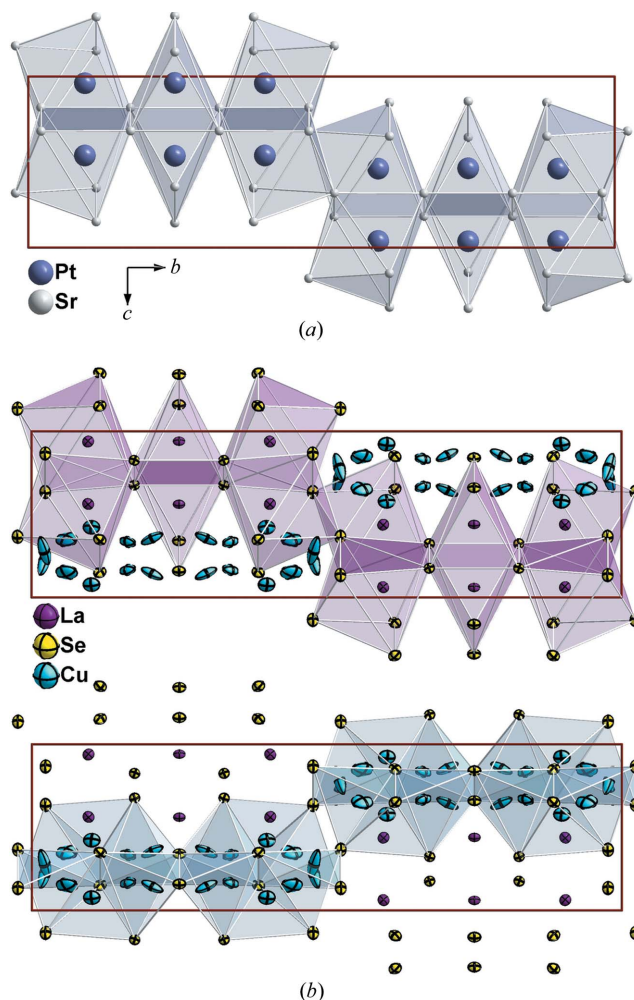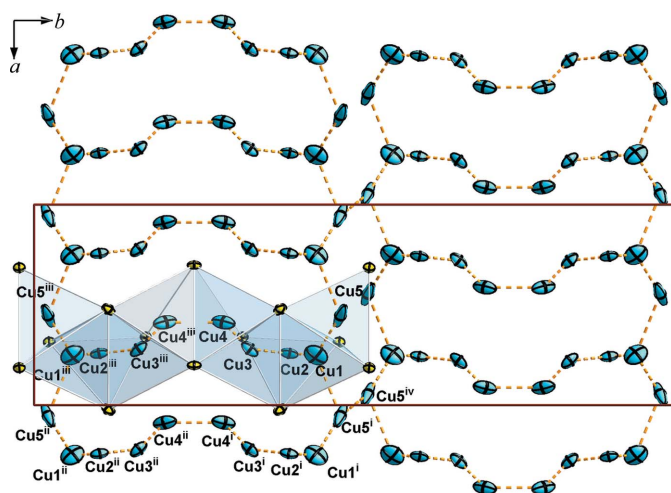

Figure 1
The unit cell and coordination polyhedra of (*a*) the Pt and Sr atoms in Pt$_3$Sr$_7$ and (*b*) the La^{3+} and Cu$^+$ ions in La$_3$Cu$_{4.88}$Se$_7$.

Figure 2
Diffusion pathway of the copper ions in $La_3Cu_{4.88}Se_7$. [Symmetry codes: (i) $x + \frac{1}{2}, y, -z + \frac{3}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x, -y + \frac{1}{2}, z$; (iv) $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$.]

atom is surrounded by six Sr atoms which form a [PtSr₆] trigonal prism. Those polyhedra are connected to each other by edges, creating a Pt₆Sr₂₈ building block. Since the positions of the Pt and Sr atoms correspond with the positions of the La and Se ions in the title compound, an identical building block of [La₆Se₂₈] exists in $La_3Cu_{4.88}Se_7$. Furthermore, since this building block is created by edge-sharing polyhedra, voids exist inside the block near the faces of the [LaSe₆] and [LaSe₇] polyhedra. These voids are filled by the Cu⁺ ions, because Cu⁺ has a relatively small ionic radius and the [La₆Se₂₈] building block is deficient in positive charge. So it appears that the role of voids in the stiff structural base of [La₆Se₂₈] is as important as the Cu⁺ ions occupying disordered positions (Gulay & Daszkiewicz, 2011).

From the bond-valence-sum (BVS) point of view, the five Cu⁺ ions are overbonded, because the BVS for these ions is greater than the formal oxidation state, +1 (Table 1) (Brown, 1996). These values remain greater than 1 even if the longest Cu—Se distance is not taken into the calculation of the BVS for Cu1–Cu4. In the case of Cu5, the BVS is less than 1 for two coordination spheres. However, the longest Cu—Se distance for each Cu-atom position should be included in the coordination sphere, because the longest Cu—Se distance still contributes 0.198 (for Cu4)–0.396 (for Cu5) of a valence unit. All the Cu-atom positions create a ring with the shortest spacing between Cu⁺ ion sites ranging from 1.148 (11) (for the Cu1/Cu2 sites) to 2.557 (10) Å [for the Cu1/Cu5ⁱ sites; symmetry code: (i) $x + \frac{1}{2}, y, -z + \frac{3}{2}$] (Fig. 2). The total occupation of the Cu⁺ ions in the ring is 8.0 over 18 positions. Adjacent rings are joined together forming a ribbon along the a axis. The longest Cu···Cu distance along this direction corresponds to the longest distance in the ring, *viz.* 2.557 (10) Å (for Cu1···Cu5ⁱ). The ribbon is transformed by the inversion and the shortest interribbon distance is 3.311 (6) Å [for Cu5ⁱ···Cu5ⁱᵛ; symmetry code: (iv) $-x + \frac{3}{2}, -y + 1, z - \frac{1}{2}$] (Fig. 2). If the copper ions move through the Cu1–Cu5 positions, the intra-ring (Cu1···Cu5) and inter-

ribbon (Cu5···Cu5) distances appear to play an important role in ionic diffusion. If the energy barriers associated with these distances are overcome, ionic conductivity of the $La_3Cu_{4.88}Se_7$ compound will be observed.

Experimental

The sample of composition $La_3Cu_{4.88}Se_7$ was prepared by the melting of high-purity (better than 99.9 wt%) elements in an evacuated silica tube. The ampoule was heated at a rate of 30 K h⁻¹ in a tube furnace to a temperature of 1420 K and kept at this temperature for 3 h. Afterwards the ampoule was cooled slowly (at a rate of 10 K h⁻¹) to 870 K and annealed at this temperature for 720 h. After annealing, the sample was quenched in air. A diffraction-quality single crystal was selected from the sample.

Crystal data

$La_3Cu_{4.88}Se_7$	$V = 1304.3\ (3)$ Å³
$M_r = 1279.53$	$Z = 4$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 7.6785\ (11)$ Å	$\mu = 36.88$ mm⁻¹
$b = 24.523\ (3)$ Å	$T = 295$ K
$c = 6.9265\ (10)$ Å	$0.06 \times 0.06 \times 0.03$ mm

Data collection

Kuma KM-4 diffractometer with a CCD area detector	13882 measured reflections
	1518 independent reflections
Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2007)	1058 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.102$
$T_{min} = 0.110,\ T_{max} = 0.384$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	99 parameters
$wR(F^2) = 0.051$	$\Delta\rho_{max} = 2.36$ e Å⁻³
$S = 1.01$	$\Delta\rho_{min} = -1.56$ e Å⁻³
1518 reflections	

Table 1
Bond-valence-sums (BVS) for the symmetry-independent Cu⁺ and La³⁺ ions in $La_3Cu_{4.88}Se_7$.

CN = coordination number.

Atom	CN	BVS	Atom	CN	BVS
Cu1	3	1.103	Cu4	3	1.041
Cu1	4	1.317	Cu4	4	1.238
Cu2	3	1.139	Cu5	2	0.825
Cu2	4	1.368	Cu5	3	1.221
Cu3	3	1.107	La1	6	2.845
Cu3	4	1.324	La2	7	2.835

Two positions for La, five for Cu and four for Se were determined. The site-occupancy factor for each Cu-atom position was refined as a free parameter. Attempts to use a SUMP restraint (*SHELXL* manual; Sheldrick, 2008) to make the total number of Cu atoms integral always resulted in nonpositive definite anisotropic displacement parameters. The structure was checked with *PLATON* (Spek, 2009) and no additional symmetry elements were found.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg,

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