Crystal structure of rubidium copper silver oxide, $Rb_3Cu_{0.5}Ag_{0.5}O_2$

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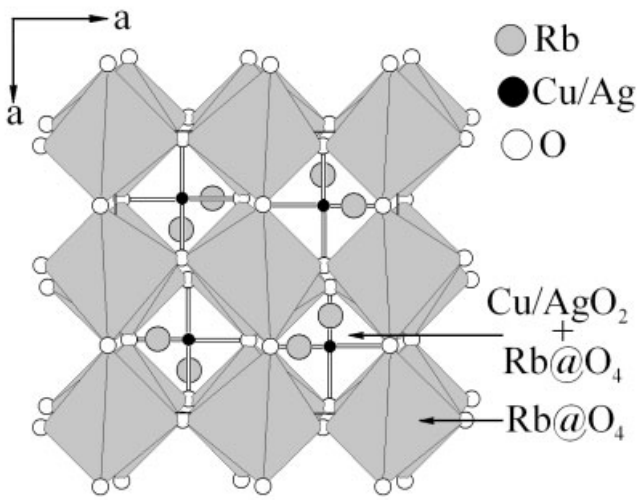

Abstract

$Ag_{0.5}Cu_{0.5}O_2Rb_3$, tetragonal, $P4_12_12$ (No. 92), a = 9.0169(3) Å, c = 14.1195(6) Å, V = 1148.0 Å^3, Z = 8, $R_{gt}(F)$ = 0.054, $wR_{ref}(F^2)$ = 0.150, T = 293 K.

Source of material

The title compound was obtained via the azide/nitrate route [1]. Starting materials for the preparation were the silver oxide (Sigma-Aldrich, 99%), RbN_3, $RbNO_3$ (Sigma-Aldrich, 99%), and activated CuO. Activated CuO was prepared by heating $CuC_2O_4 \cdot 0.5H_2O$ (Johnson Matthey, 99%) in a flow of oxygen at 623 K for 20 h. Rubidium azide was synthesised from aqueous HN_3 and rubidium carbonate (Johnson Matthey, 99%). The starting materials were mixed in the ratio required according to the equation: 31 RbN_3 + 5 $RbNO_3$ + 3 Ag_2O + 6 CuO = 12 $Rb_3Cu_{0.5}Ag_{0.5}O_2$ + 48 N_2. This mixture was milled in a ball mill, pressed in pellets, dried under vacuum at 423 K for 12 h, and placed under argon in a tightly closed steel container provided with a silver inlay [2]. In a flow of dry Ar the follow temperature profile was applied: 298 K→533 K (100 K/h), 533 K→653 K (5 K/h), 653 K→723 K (10 K/h), and subsequent annealing for 50 h at 723 K. The obtained colourless powder is sensitive to air and moisture. Single crystals have been grown by subsequent annealing of the pressed powder at 723 K for 500 h, in silver crucibles, which were sealed in glass ampules under dried Ar.

Discussion

Copper and silver are randomly distributed over one crystallographic position (occupation factor 0.50(1) for each element). Unexpectedly, $Rb_3Ag_{0.5}Cu_{0.5}O_2$ is neither isostructural to Rb_3AgO_2 [3] (orthorhombic, $P2_12_12_1$) nor to Rb_3CuO_2 [4] (monoclinic, $P2_1/c$), but instead adopts the structure of K_3CuO_2 [5]. Similar to all known cuprates(I) and argentates(I) with the formula A_3MO_2 (A = alkali metal, M = Cu or Ag), there are linear (∠O–M–O = 178.14°) isolated MO_2 anions. The M—O bond lengths are 1.904 Å and 1.910 Å, which corresponds approximately to the average of characteristic bond lengths Ag—O (2.00 Å – 2.04 Å) and Cu—O (1.78 Å – 1.84 Å) . The rubidium ions are tetrahedraly coordinated by oxygen ions. The $Rb_3Ag_{0.5}Cu_{0.5}O_2$ structure can be derived from that of Rb_2O (anti-fluorite) by substituting copper/silver for one fourth of the rubidium atoms and shifting copper/silver from the center of the tetrahedra to an adjacent edge, thus becoming two-fold coordinated. Along the [001] axis silver/copper atoms periodically substitute one half of the rubidium atoms. Along [100] and [010], mixed rows of Cu/Ag-Rb atoms alternate with rows containing only rubidium atoms. The same mode of substitution also can be applied, in order to derive the structure of K_3AgO_2, K_3CuO_2 and Na_3AgO_2 from the corresponding alkali metal oxides. This general rule of substitution is the same for $Rb_3Ag_{0.5}Cu_{0.5}O_2$, Rb_3AgO_2 [3], K_3AgO_2 [6], K_3CuO_2 [5] but different from Na_3AgO_2 [7,8].

Table 1. Data collection and handling.

Crystal:	colourless block, size 0.05 × 0.1 × 0.2 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	286.66 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS II, 360 images $\Delta\omega$ = 1°, $0 < \omega < 180°$, φ = 0°, 180°
$2\theta_{max}$:	59.22°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12051, 1618
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1250
$N(param)_{refined}$:	53
Programs:	SHELXL-97 [9], DIAMOND [10]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
Ag(1)	8*b*	0.50(1)	0.2612(1)	0.2625(1)	0.33452(6)	0.0235(3)
Cu(1)	8*b*	0.50	0.2612	0.2625	0.33452	0.0235

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rb(1)	8*b*	0.5350(1)	0.9398(1)	0.00163(7)	0.0288(5)	0.0289(5)	0.0263(6)	–0.0006(3)	–0.0008(5)	0.0011(5)
Rb(2)	8*b*	0.8465(2)	0.7366(2)	0.3915(1)	0.108(2)	0.0279(7)	0.0453(7)	0.0052(7)	–0.0217(8)	–0.0013(6)
Rb(3)	4*a*	0.9459(1)	0.9459(1)	0	0.0281(5)	U_{11}	0.0250(8)	–0.0010(5)	0.0031(5)	$-U_{13}$
Rb(4)	4*a*	0.5274(1)	0.5274(1)	0	0.0318(5)	U_{11}	0.0281(8)	0.0025(5)	–0.0024(5)	$-U_{13}$
O(1)	8*b*	0.238(1)	0.551(1)	0.9192(6)	0.022(4)	0.048(5)	0.041(4)	0.001(4)	–0.001(4)	–0.002(4)
O(2)	8*b*	0.9743(9)	0.241(1)	0.0837(6)	0.030(4)	0.026(4)	0.040(4)	0.006(3)	–0.006(3)	–0.006(4)

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