

Crystal Structure of Dicalcium Cuprate, Ca_2CuO_3 Michael Hjorth^a and Jens Hyldtoft^{b,*}^aChemistry Department B, The Technical University of Denmark, DK-2800 Lyngby and ^bNKT A/S, R&D Department, Bldg. 61, NKT Allé 1, DK-2605 Brøndby, DenmarkHjorth, M. and Hyldtoft, J., 1990. Crystal Structure of Dicalcium Cuprate, Ca_2CuO_3 . – Acta Chem. Scand. 44: 516–518.

When one attempts to prepare superconducting bismuth calcium copper oxides¹ using solid-state synthesis, various other oxides occur among the reaction products, e.g. dicalcium cuprate.² The structure of Ca_2CuO_3 was reported by Teske and Müller-Buschbaum,³ who characterized the structure from a very small data set (86 reflections). When characterizing the reaction products from solid-state syntheses, a good knowledge of possible reaction products is important; thus it was considered worthwhile to refine the structure from a larger data set.

In the present work, the structure was refined from single-crystal X-ray diffraction data collected on an automatic four-circle diffractometer, and microcrystals from the sample were examined using high-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED). The electron microscopy study provides information on defects in the crystals, thus contributing to a better understanding of metal oxide structures.

Energy-dispersive X-ray analysis (EDX) indicated significant amounts of strontium and traces of bismuth, as also seen in Ref. 2, and thus the X-ray investigation was carried out with both calcium and strontium on the calcium site, giving the composition $\text{Ca}_{1.82}\text{Sr}_{0.18}\text{CuO}_3$.

Experimental

Golden needle-shaped single crystals of dicalcium cuprate were found when attempting to prepare one of the superconducting phases in the newly discovered Bi-system¹ by the following procedure.

A grey powder was obtained by dissolving the nitrates of Bi, Sr, Ca and Cu in ethylene glycol with a molar ratio 4:3:3:4, adding citric acid, and by a slow heating to 800 °C to decompose the nitrates.^{4,5} The powder was pressed to a pellet and sintered in air for 40 h at 860 °C.

The crystals appeared on the surface of the pellet and could easily be removed from the sample.

Single-crystal X-ray data were collected with an Enraf-Nonius CAD4 diffractometer, and were corrected for background, Lorentz, polarization and absorption effects. Sta-

tistical analysis of psi-scans of eight different reflections were used to check the crystal dimensions used for absorption correction. A summary of the experimental conditions is given in Table 1. Systematic absences indicated an *I*-centred space group, and the space group *Immm* is sup-

Table 1. Crystal data and experimental conditions.

Formula	$\text{Ca}_{1.82(5)}\text{Sr}_{0.179(5)}\text{CuO}_3$
Formula weight	200.2
Space group	<i>Immm</i>
Unit cell/Å	$a = 3.2781(4)$, $b = 3.7870(4)$, $c = 12.277(1)$
Unit cell volume/Å ³	152.40(5)
Formula units per unit cell	2
Calculated density/g cm ⁻³	4.363(1)
Radiation	Mo <i>K</i> α
Wavelength/Å	0.71073
Temperature/K	293(1)
Crystal shape	Prismatic
Crystal size/mm	0.024×0.194×0.070
Diffractometer	Enraf-Nonius CAD4
Determination of unit cell:	
Number of reflections used	24
θ-range/°	9.98 to 14.77
Intensity data collection:	
Maximum sin θ/Å ⁻¹	1.08
Range of <i>h</i> , <i>k</i> and <i>l</i>	0 to 7; -8 to 8; 0 to 26
Standard reflections	0 2 0, 1 1 6 and 1 2 3
Intensity instability	Insignificant Δ <i>I</i> < 3σ(<i>I</i>)
No. of collected reflections	973
No. of unique reflections	492
No. of observed reflections	373
Criterion for significance	<i>I</i> > 3σ(<i>I</i>)
Internal <i>R</i>	0.017
Absorption correction:	
Linear absorption coefficient/cm ⁻¹	102.7
Transmission factor range	0.45–0.77
Structure refinement:	
Minimization of	Sum of $w(\Delta F)^2$
Anisotropic model for	All atoms
Number of refined parameters	17
Extinction parameter	8(1)×10 ²
Maximum correction	1.12
Weighting scheme	(σ _{<i>F</i>} ² + 0.0001 <i>F</i> ²) ⁻¹
Final <i>R</i>	0.019
Final <i>R</i> _w	0.022

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Table 2. Fractional coordinates and thermal parameters for Ca_2CuO_3 with estimated standard deviations in parentheses.

Atom	x	y	z	U_{eq}^a
Ca	$\frac{1}{2}$	0	0.15016(3)	0.0061(1)
Cu	0	$\frac{1}{2}$	0	0.0051(1)
O1	$\frac{1}{2}$	0	0.3402(1)	0.0080(4)
O2	0	0	0	0.0081(6)

$$^a U_{\text{eq}} = \frac{1}{6\pi^2} \sum \beta_{ij} a_i a_j$$

ported by the outcome of the refinement, thus verifying the space group of Ref. 3.

The structure was refined using the coordinates of Teske and Müller-Buschbaum³ as a starting point. The calculations were carried out with the least-squares program UP-ALS⁶ including an isotropic type I extinction parameter,⁷ and the crystal showed only very small extinction effects (cf. Table 1). Scattering factors for neutral atoms were taken from Ref. 8. Final atomic coordinates and thermal parameters are listed in Table 2. Listings of observed and calculated structure factors as well as anisotropic temperature factors are available from the authors on request.

For the electron micrographs, SAED images and EDX analyses, a 400 kV Jeol JEM 4000EX microscope with a resolving power of approximately 1.4 Å, and a 300 kV Philips EM430 instrument with resolving power of approximately 2.3 Å, have been used.

Discussion

The structure of Ca_2CuO_3 can be considered as built of edge-sharing oxygen coordination polyhedra; calcium is seven-coordinated in a monocapped trigonal prism and copper is four-coordinated in a distorted square plane. The trigonal prisms share triangular faces in the *a* direction and edges in the *b* direction to build a layer of equally orientated calcium polyhedra. Two of the calcium layers, related by a mirror plane, share the free edge of the trigonal prism, giving double layers in which there are tunnels where the copper atoms are placed. This sandwich is then stacked along the *c* axis to give the three-dimensional structure (Fig. 1). The bond lengths in the coordination polyhedra are given in Table 3, and are close to those of Ref. 3. The

Table 3. Bond distances and multiplicities in the coordination polyhedra of Ca_2CuO_3 .

Bond	Distance	Multiplicity
Ca–O1	2.3336(14) Å	–
Ca–O2	2.4667(3) Å	2×
Ca–O1	2.5071(2) Å	4×
Cu–O2	1.8935(2) Å	2×
Cu–O1	1.9613(14) Å	2×

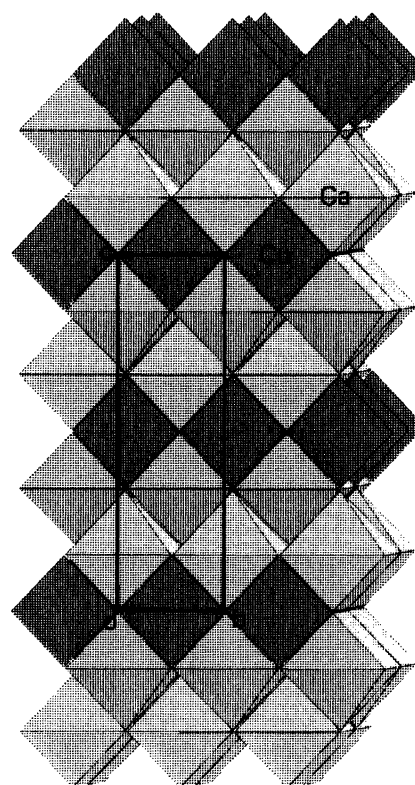


Fig. 1. Polyhedral plot¹² of Ca_2CuO_3 with the *b* axis horizontal and *c* axis vertical. The plot is slightly rotated to visualize the packing along the *a* axis.

strontium refines to occupy 9.0(3) % of the calcium position.

Empirical bond-valences have been estimated using the functions and parameters of Brown and Altermatt,⁹ in order to compare the metal–oxygen bond distance distribution with that observed in other metal oxide structures. The values obtained are 2.03 for copper and 1.83 for calcium; thus copper has a coordination in agreement with that observed in the structures from which Brown and Altermatt derived their parameters, whereas calcium has longer bonds than expected from this approach. The discrepancy concerning calcium may be ascribed to the large coordination number of the small Ca^{2+} ion. When calculating the bond-valence parameter for Sr^{2+} in the isotypic compound Sr_2CuO_3 ,¹⁰ the value 1.98 is obtained, indicating that the Sr^{2+} ion suits the seven-coordination better than the Ca^{2+} ion when applying these bond-valence parameters. Discrepancies of this type have often been seen when calculating bond-valence parameters for unusual coordinations of metal ions (e.g. Ref. 11).

In Fig. 2 the electron micrograph and electron diffraction patterns are seen, and it is noted that the high-resolution image [Fig. 2(a)] shows no defects, except for a thin disordered layer at the surface. Selected-area electron diffraction images [Figs. 2(b) and (c)] are very sensitive to local defects; thus, as no streaks or superlattice spots are ob-

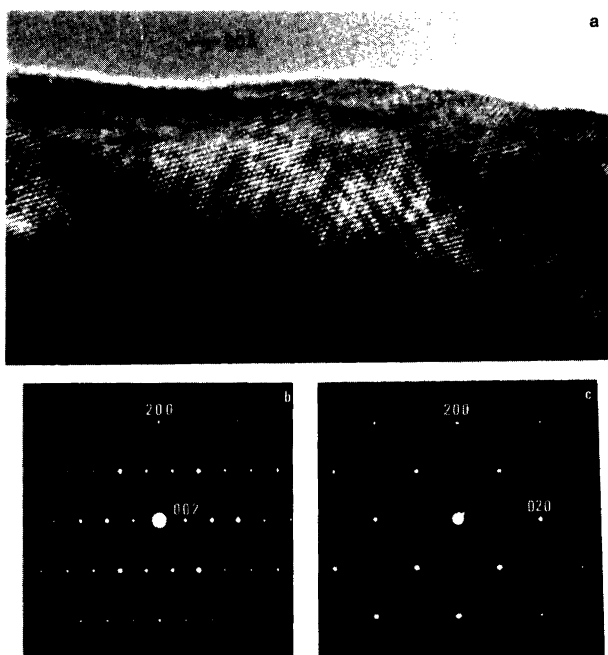


Fig. 2. Electron micrograph and selected-area diffraction (SAED) patterns of Ca_2CuO_3 . The electron micrograph (a) is taken with the beam parallel to the $[010]$ direction and shows no defects except for a thin disordered surface layer [corresponding SAED in (b)]. The SAED patterns [(b) and (c)] show no streaks or superlattice spots, thus indicating no local defects in the selected crystals.

served, it is concluded that the crystals examined are homogeneous with very few defects. On this basis it may be expected that the crystals in general are well ordered; this is consistent with the X-ray refinement, which gives reasonable values of all thermal parameters.

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