JOURNAL OF
Materials
CHEMISTRY

Synthesis and structure of $La_{14}V_6CuO_{36.5}$: a transparent Cu(I) vanadate containing $[OCuO]^{3-}$ sticks†

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Received 30th March 2002, Accepted 14th October 2002
First published as an Advance Article on the web 29th October 2002

The title compound, $La_{14}V_6CuO_{36.5}$, was prepared from a stoichiometric mixture of La_2O_3, V_2O_5, and CuO at 1050–1080 °C. The compound forms transparent, pale green crystals and was characterized by wavelength dispersive spectroscopy and single crystal X-ray diffraction. The structure contains isolated VO_4^{3-} tetrahedra and $[OCuO]^{3-}$ sticks dispersed in a lanthanum oxide network. Films of $La_{14}V_6CuO_{36.5}$ were grown on R-plane sapphire by using pulsed laser deposition. Rutherford backscattering spectroscopic and X-ray diffraction analyses of the films showed oriented growth of the title phase, a ~5 eV optical band gap and n-type conductivity. The compound is an example of a transparent copper(I) oxide.

Introduction

Although the cuprous ion is quite common in molecular inorganic chemistry, the linear $[OCuO]^{3-}$ cuprous ion is far less common in solid state compounds.[1] This unit has been identified in the parent binary oxide, Cu_2O,[2] two high T_c superconductivity-related cuprates, $YBa_2Cu_3O_6$ [3] and $Pb_2Sr_2(Ca,Y)Cu_3O_8$,[4] the $CuMO_2$ delafossites (M = Al, Fe, Sc, Co, Rh, Ga, Y, lanthanide),[5] $SrCu_2O_2$,[6] and the recently reported $Sr_5(VO_4)_3(CuO)$ phase with linear $[CuO]^-$ chains.[7] The ternary alkali metal copper oxides with the general formulae ACuO (A = Li, Na, K, Rb, Cs),[8] $A_3Cu_5O_4$ (A = K, Rb, Cs),[9] and A_3CuO_2 (A = Na, K, Rb)[10] represent a distinct class of Cu(I) oxide system where the characteristic unit is the bent $[OCuO]^{3-}$ (170° < O–Cu–O < 180°). $Na_5[CuO_2](OH)_2$ also belongs to this class, with an O–Cu–O angle of ~170°, and is the first example of a Cu(I) oxide hydroxide.[11] Interestingly, some of these compounds have potential or proven electronic applications.[2–6,12] The superconductors are, of course, important electronic materials, whereas the delafossites have recently been identified as prototypes for the elusive p-type transparent conductors.[12] In particular, the $CuAlO_2$ phase is optically transparent, with a bandgap of 3.5 eV, but has a room temperature conductivity of ~1 S cm^{-1}. Although the conductivity is 2–3 orders of magnitude lower than is necessary for most device applications, it demonstrates that p-type transparent conductors are potentially accessible.[12] Recent studies on $CuScO_{2+x}$ films demonstrated that conductivities as high as 30 S cm^{-1} were accessible.[5e] The key feature in the $CuMO_2$ delafossites is the presence of the linear $[OCuO]^{3-}$ sticks that are diluted with MO_6 octahedra. The latter give the compounds their transparent nature whereas the $[OCuO]^{3-}$ sticks provide p-type conductivity.

Herein, we describe the synthesis, structure, and optical spectrum of a new copper vanadate, $La_{14}V_6CuO_{36.5}$, that contains isolated VO_4^{3-} tetrahedra and $[OCuO]^{3-}$ sticks. It is an example of a Cu(I) oxide and a transparent Cu–O material, and shows n-type conductivity regardless of the annealing conditions.

Experimenal

General

La_2O_3 was dried at 950 °C before each use. All other chemicals were purchased from Cerac and used without further purification. Powder X-ray diffraction patterns were collected at 25 °C using a Bruker D8 diffractometer (Cu-Kα radiation). Powder patterns were obtained in 48 h runs using a step width of 0.02° between $10° \leqslant 2\theta \leqslant 90°$. Wavelength dispersive spectroscopy (WDS) was performed on $La_{14}V_6CuO_{36.5}$ using a JEOL JXA-8900 microprobe analyzer. $LaPO_4$, V, and Cu were used as standards.

Synthesis

The title compound was prepared from an intimately ground mixture of La_2O_3 (99.9%), V_2O_5 (99.9%), and CuO (99.99%) in the stoichiometric molar ratio 7 : 3 : 1. The mixture was loaded into an alumina crucible and heated for 36 h at 1100 °C. After cooling to room temperature (5 °C min^{-1}), the mixture was reground and refired at 1100 °C for an additional 12 h. The sample was then cooled to room temperature at a rate of 1 °C min^{-1}. The resulting product is a homogeneous pale green crystalline solid that is single phase.

For fabrication of thin films, a sintered target of the title compound was used for pulsed laser deposition onto R-plane (1102) sapphire substrates. KrF excimer laser pulses of wavelength 248 nm were focused onto the target at an energy density of approximately 1 J cm^{-2}. The target–substrate distance was 4 cm. The substrate was held at 750 °C in 100 mTorr of O_2 partial pressure. Following the deposition, the films were cooled down to room temperature in 200 Torr of O_2. The film thickness was nominally 1000 Å.

Crystallography

A colorless block with dimensions 0.163 × 0.132 × 0.116 mm^3 was placed and optically centered on a Bruker SMART CCD system at −80 °C. The initial unit cell was indexed using a least-squares analysis of a random set of reflections collected from three series of 0.3° wide ω scans (25 frames per series) that were well distributed in reciprocal space. Data frames were

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†Electronic supplementary information (ESI) available: powder XRD pattern of $La_{14}V_6CuO_{36.5}$ and simulated pattern from the single crystal data. See http://www.rsc.org/suppdata/jm/b2/b203257k/

DOI: 10.1039/b203257k

collected (Mo-Kα) with 0.3° wide ω-scans, 15 s frame^{-1}, 606 frames per series. Five complete series were collected, providing a complete sphere of data to $2\theta_{\max} = 55°$. A total of 13 640 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method, as incorporated into the program SADABS;[13] 4110 reflections were unique [R(int) = 0.0324].

The SHELXTL program package[14] was implemented to solve and refine the structure. System symmetry and lack of systematic absences indicated the possible space groups to be either the centrosymmetric space group $P\bar{1}$ (no. 2) or the acentric space group $P1$ (no. 1), with the intensity statistics indicating the former. The structure was determined by direct methods with the successful location of nearly all atoms using the program XS. After locating all atoms and refining with anisotropic thermal parameters, it became evident that one of the vanadium atoms was disordered over two sites; it was subsequently modeled as such. The resulting occupancies were V1a : V1b 0.23 : 0.77. Oxygen O20 was also found to be half-occupied. The final structure was refined to convergence ($\Delta/\sigma \leqslant 0.001$) with $R(F) = 2.81\%$, $wR(F^2) = 6.25\%$, GOF = 1.083 for all 4110 unique reflections [$R(F) = 2.57\%$, $wR(F^2) = 6.13\%$, for those 3844 data with $I > 2\sigma(I)$]. A final difference-Fourier map showed many large peaks near the heavy atoms, but these are assumed to be ghosts due to the highly absorbing nature of the compound ($\mu = 18.35$ mm^{-1}).

CCDC reference number 183159.

See http://www.rsc.org/suppdata/jm/b2/b203257k/ for crystallographic data in CIF or other electronic format.

Results and discussion

$La_{14}V_6CuO_{36.5}$ forms cleanly from stoichiometric ratios of the binary oxides at 1100 °C, but also crystallizes as a decomposition byproduct of $La_3VCu_2O_9$ at high temperatures. The individual crystallites are transparent, very pale green needles (essentially colorless) and were characterized by wavelength dispersive spectroscopic analysis (WDS) and single crystal X-ray diffraction. The semi-quantitative WDS analysis confirmed the presence of La, V, and Cu and gave compositions (atom%; La, 25.7; V, 9.0; Cu, 1.8) in good agreement with the formula determined from the single crystal structure determination (atom%; La, 24.3; V, 10.4; Cu, 1.7).

The title compound is triclinic, space group $P\bar{1}$, and contains 7 La^{3+} ions, 3 V^{5+} ions and 0.5 Cu^{+} ions in the asymmetric unit. A summary of the crystallographic data is given in Table 1, and fractional coordinates and bond distances are listed in Tables 2 and 3, respectively. A view down the b axis of the unit cell is shown in Fig. 1. The structure contains isolated VO_4^{3-} tetrahedra and linear $[OCuO]^{3-}$ units linked together by a lanthanum oxide network. For V(2) and V(3), the VO_4^{3-} tetrahedra are quite regular, with V–O contacts in the range 1.68–1.76 Å and O–V–O angles in the range 99.6–122°. Bond valence analysis[15] of these atoms gave valencies of +5.06 and +5.09, respectively. The V(1) atom is disordered over two sites, V(1A) and V(1B), as shown in Fig. 2. The two sites are separated by 0.817(5) Å and, therefore, cannot be occupied at the same time. The V(1B) site is 75% occupied and defines a very regular tetrahedron [V–O (av.) = 1.70 Å, O–V–O (av.) = 110°]. O(19) is also partially occupied and was refined at 75% based on the V(1B) occupancy, its thermal parameters, and overall charge considerations. The V(1A) site is only 25% occupied and is in a highly distorted pseudo-tetrahedral environment (see Fig. 2). The O(20) atoms are only 0.699 Å apart and are only 50% occupied (*i.e.* there is one oxygen present at a time). In general, the bond lengths and angles in the VO_4^{3-} tetrahedra are similar to those in $LaVO_4$ (V–O = 1.693–1.724 Å; O–V–O = 100.78–115.72°).[16]

Table 1 Crystal data for $La_{14}V_6CuO_{36.5}$

Empirical formula	$CuLa_{14}O_{36.5}V_6$
Formula weight	2905.92
Temperature/K	173(2)
Wavelength (Mo-Kα)/Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 9.7375(11) Å b = 9.9167(11) Å c = 10.3684(12) Å α = 88.083(2)° β = 64.141(2)° γ = 87.847(2)°
Volume/Å^3	900.16(18)
Z	1
Density (calc.)/g cm^{-3}	5.361
Absorption coefficient/mm^{-1}	18.350
F(000)	1261
θ Range for data collection/°	2.06–27.50
Index ranges	$-12 \leqslant h \leqslant 12$ $-12 \leqslant k \leqslant 12$ $-13 \leqslant l \leqslant 13$
Reflections collected	13 640
Independent reflections	4110 [R(int) = 0.0324]
Data/restraints/parameters	4110/0/278
Goodness-of-fit on F^2	1.083
Final R indices [$I > 2\sigma(I)$] (3844 data)	$R1$ = 0.0257, $wR2$ = 0.0613
R Indices (all data)	$R1$ = 0.0281, $wR2$ = 0.0625
Extinction coefficient	0.00445(10)
Largest diff. peak and hole/e Å^{-3}	3.301 and −3.435

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (× 10^3 Å) for $La_{14}V_6CuO_{36.5}$

	x	y	z	U(eq)
La(1)	6598(1)	6889(1)	554(1)	4(1)
La(2)	6454(1)	9960(1)	2740(1)	6(1)
La(3)	9009(1)	10001(1)	−1273(1)	4(1)
La(4)	8929(1)	3378(1)	987(1)	4(1)
La(5)	9208(1)	6753(1)	−3493(1)	5(1)
La(6)	8234(1)	6465(1)	3250(1)	11(1)
La(7)	3683(1)	6836(1)	4627(1)	15(1)
Cu(1)	5000	10 000	0	13(1)
V(2)	7935(1)	3622(1)	−2164(1)	5(1)
V(3)	8027(1)	10024(1)	5135(1)	5(1)
V(1A)	5082(5)	6245(4)	−3275(5)	6(1)
V(1B)	5280(2)	6599(1)	−2663(2)	6(1)
O(1)	10649(5)	6018(4)	−6147(4)	9(1)
O(2)	3833(5)	9560(4)	4569(4)	10(1)
O(3)	8689(5)	9057(4)	3579(4)	9(1)
O(4)	8753(4)	5883(4)	941(4)	5(1)
O(6)	6487(5)	9388(4)	520(4)	6(1)
O(7)	6227(5)	7575(4)	2966(4)	7(1)
O(8)	3616(5)	7053(4)	2227(4)	11(1)
O(9)	7533(5)	5148(4)	−1383(4)	12(1)
O(10)	8176(5)	9274(4)	−3450(4)	11(1)
O(11)	11221(5)	9189(4)	−1019(4)	6(1)
O(12)	11474(5)	5904(4)	−3361(4)	7(1)
O(13)	8975(5)	7632(4)	−1373(4)	5(1)
O(14)	8814(5)	2603(4)	−1346(4)	11(1)
O(15)	8775(5)	11590(4)	4789(4)	11(1)
O(16)	4065(6)	7615(4)	−3243(5)	15(1)
O(17)	4203(6)	5356(6)	−1768(6)	34(1)
O(18)	7022(6)	6233(8)	−4042(6)	45(2)
O(19)	5705(10)	7407(7)	−1508(8)	53(2)
O(20)	5277(18)	5054(17)	−5352(12)	68(5)

The remainder of the structure is crystallographically well behaved. Three of the lanthanum ions, La(2), La(3), and La(7), are at the center of seven-coordinate monocapped trigonal prisms whereas the remaining ions reside in eight-coordinate bicapped trigonal prisms. Bond valence analyses[15] for all the La ions fall in the range +2.83 to +3.17.

The copper atom in the linear $[OCuO]^{3-}$ ion (Fig. 3) resides on an inversion center and has a Cu–O distance of 1.831(4) Å, which is typical for two-coordinate Cu(I). The bond valence

Table 3 Bond lengths for $La_{14}V_6CuO_{36.5}$

La(1)–O(13)	2.427(4)	La(6)–O(4)	2.309(4)
La(1)–O(4)	2.472(4)	La(6)–O(7)	2.331(4)
La(1)–O(6)	2.476(4)	La(6)–O(12)	2.361(4)
La(1)–O(7)	2.481(4)	La(6)–O(18)	2.534(5)
La(1)–O(17)	2.497(5)	La(6)–O(3)	2.683(4)
La(1)–O(9)	2.522(4)	La(6)–O(1)	2.703(4)
La(1)–O(8)	2.656(4)	La(6)–O(14)	2.854(4)
La(1)–O(19)	2.666(6)	La(6)–O(20)	2.979(19)
La(2)–O(11)	2.354(4)	La(6)–V(2)	3.3931(11)
La(2)–O(6)	2.375(4)	La(6)–V(1A)	3.578(4)
La(2)–O(7)	2.378(4)	La(7)–O(20)	2.313(13)
La(2)–O(2)	2.464(4)	La(7)–O(20)	2.351(13)
La(2)–O(16)	2.464(4)	La(7)–O(12)	2.437(4)
La(2)–O(2)	2.736(4)	La(7)–O(7)	2.443(4)
La(2)–O(3)	2.783(4)	La(7)–O(8)	2.520(4)
La(3)–O(13)	2.357(4)	La(7)–O(16)	2.542(4)
La(3)–O(11)	2.389(4)	La(7)–O(15)	2.655(4)
La(3)–O(6)	2.431(4)	La(7)–O(2)	2.708(4)
La(3)–O(11)	2.448(4)	Cu(1)–O(6)	1.831(4)
La(3)–O(14)	2.581(4)	Cu(1)–O(6)′	1.831(4)
La(3)–O(3)	2.635(4)	V(2)–O(9)	1.692(4)
La(3)–O(10)	2.833(4)	V(2)–O(8)	1.702(4)
La(4)–O(4)	2.391(4)	V(2)–O(14)	1.727(4)
La(4)–O(13)	2.421(4)	V(2)–O(1)	1.727(4)
La(4)–O(12)	2.445(4)	V(3)–O(10)	1.683(4)
La(4)–O(4)	2.484(4)	V(3)–O(15)	1.700(4)
La(4)–O(11)	2.554(4)	V(3)–O(2)	1.735(4)
La(4)–O(14)	2.612(4)	V(3)–O(3)	1.757(4)
La(4)–O(16)	3.009(5)	V(1A)–V(1B)	0.831(5)
La(4)–O(17)	3.026(6)	V(1A)–O(16)	1.644(6)
La(5)–O(13)	2.307(4)	V(1A)–O(17)	1.658(7)
La(5)–O(12)	2.390(4)	V(1A)–O(18)	1.700(7)
La(5)–O(15)	2.481(4)	V(1A)–O(20)	2.10(2)
La(5)–O(18)	2.506(6)	V(1A)–O(20)	2.42(2)
La(5)–O(1)	2.601(4)	V(1B)–O(17)	1.628(5)
La(5)–O(9)	2.613(4)	V(1B)–O(19)	1.664(6)
La(5)–O(10)	2.654(4)	V(1B)–O(18)	1.711(6)
La(5)–O(1)	2.776(4)	V(1B)–O(16)	1.808(5)

for the copper atom, +1.07, supports the oxidation state assignment. The $[OCuO]^{3-}$ ions are relatively isolated in the lanthanum oxide network and connect adjacent LaO layers (Fig. 3). The Cu–O bond distances in $YBa_2Cu_3O_6$ (1.792, 1.81 Å),[17,18] $CuAlO_2$ (1.861 Å)[5] and $Sr_5(VO_4)_3CuO$ (1.854 Å)[7] are quite similar to the 1.831(4) Å distance in the title compound. The latter value is close to the Shannon[19] radii sum of 1.84 Å for Cu^+ (0.46 Å) and O^{2-} (1.38 Å).

Films of the $La_{14}V_6CuO_{36.5}$ were prepared in order to assess the transport and optical properties of the compound. The films were prepared by pulsed laser deposition (PLD) from a bulk $La_{14}V_6CuO_{36.5}$ target to give nominally 1000 Å thick samples on a sapphire substrate (the XRD pattern of the $La_{14}V_6CuO_{36.5}$ powder and the simulated pattern from the single crystal data are given in the ESI). Unlike the light green bulk material, the films are transparent and colorless at room temperature. They have been characterized by XRD, Rutherford backscattering spectroscopy (RBS), and optical spectroscopy. The RBS analysis gave a composition of $La_{12}V_6CuO_{37}$, which is very close to that of the target. XRD analysis of the annealed films (O_2, 750 °C) showed significant preferred orientation, but indicated that the sample remained intact. We have measured the absorption spectrum using optical transmission. The absorption edge of the film is ~300 nm (Fig. 4), which corresponds to a 4.5–5 eV optical band gap. However, various annealing treatments of the films and bulk material did not significantly alter the respective absorption edges. Seebeck effect measurements indicated that the carriers of the present films are n-type, regardless of annealing conditions. The large gap is not unexpected in view of the large separation of Cu(I) centers in the structure.

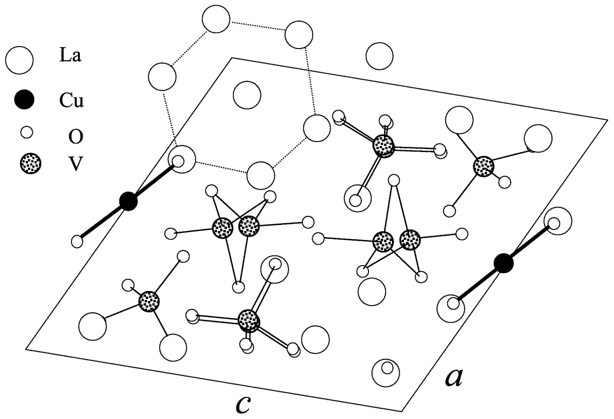

Fig. 1 Projection of the $La_{14}V_6CuO_{36.5}$ structure viewed down the *b* axis. Some oxygen atoms and La–O bonds omitted for clarity. The dotted lines emphasize the pseudo-hexagonal arrays of La^{3+} ions in the *a*–*c* plane.

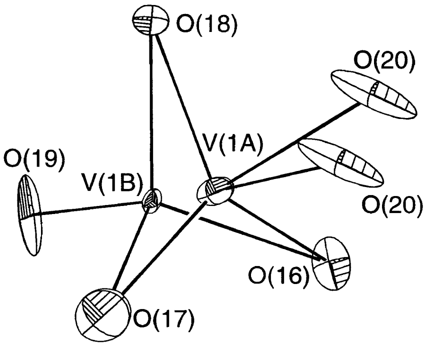

Fig. 2 ORTEP drawing of the V(1A)–V(1B) disordered site in $La_{14}V_6CuO_{36.5}$.

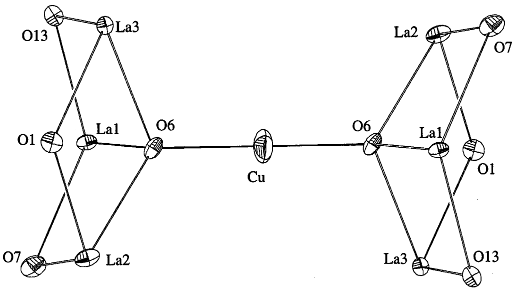

Fig. 3 ORTEP drawing of the CuO_2^{3-} units in the La–O network of $La_{14}V_6CuO_{36.5}$.

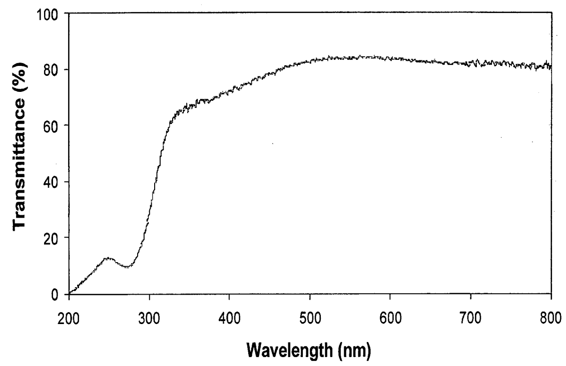

Fig. 4 Transmittance spectrum for a 100 nm thick LVCO film on a sapphire substrate. The transmittance of sapphire has been removed from the data.

$La_{14}V_6CuO_{36.5}$ is a unique oxide containing isolated VO_4^{3-} tetrahedra and CuO_2^{3-} sticks. The only other oxide known in the La–V–Cu–O system, $La_3VCu_2O_9$,[20–22] is related to $La_4MoCu_3O_{12}$,[23] contains Cu(II) and adopts a $YAlO_3$-related superstructure, where Cu(II) exists in a fivefold (trigonal bipyramidal) coordination.[21,22] Although the chemical composition of the title oxide is closely related to the composition of the oxide-ion conductor $Bi_4V_{2-x}Cu_xO_{11-y}$,[24] the La–O framework is not similar to the two-dimensional [Bi_2O_2] layers found in copper-substituted $Bi_4V_2O_{11}$, nor is it similar to that in $La_{11}(V^{4+})(V^{5+})_3O_{26}$, where La occurs in three different coordination environments.[25] The lack of p-type conductivity and the large optical gap in $La_{14}V_6CuO_{36.5}$ is presumably due to the low concentration of the Cu(I) centers relative to the Cu(I) p-type conductors.[4–6]

Acknowledgements

We are grateful to the NSF-DMR for support of this work and the LINK Foundation for a fellowship to Z. S. G. The authors are grateful to Mr Scott Sirchio for help with the WDS experiments. The work at Bangalore is supported by the Department of Science and Technology, Government of India.

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