

distance of 2.302 (6) Å is much longer than all the other Li—O distances [1.925 (5) – 2.180 (6) Å] in the structure.

Structure analysis indicates that the composition of the compound proposed by us is correct. Differential thermal analysis (DTA), heating at a rate of 10 K min⁻¹, shows two endothermal peaks at 1125 (5) (peritectic reaction) and 1179 (5) K (melting point) in good agreement with Sastry & Hummel (1958).^{*} They also reported decomposition at 969 (4) K which is not observed in our experiment. The X-ray diffraction pattern of a powder specimen which was sintered at 903 K for 25 days shows that the compound remains stable below 969 (4) K in contradiction with the results of Sastry & Hummel (1958). The transmission spectrum of 3Li₂O·7B₂O₃ in the wavelength range 190–900 indicates that the B₃O₇ or B₃O₈ groups confer better ultraviolet transparency than that displayed by crystals containing planar B₃O₆ groups, such as BBO.^{*}

^{*} See deposition footnote.

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Structure of (La_xCa_{1-x})Ba₂Cu₂(Al_yCu_{1-y})O_{6.78} with $x = 0.52$ and $y = 0.64$

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Abstract. La_{0.515}(5)Ca_{0.485}(5)Ba₂Cu_{2.36}(1)Al_{0.64}(1)O_{6.78}(3), $M_r = 641.34$, tetragonal, $P4/mmm$, $a = 3.908$ (1), $c = 11.647$ (3) Å, $V = 177.88$ Å³, $Z = 1$, $D_x = 5.987$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 21.0$ mm⁻¹, $F(000) = 282.1$, $T = 296$ K, $R = 0.030$ for 240 unique reflections. The compound crystallizes in a variant of the YBa₂Cu₃O_{7-x} structure with La and Ca atoms on the Y sites and partial substitution of the Cu chain atoms by Al atoms. The Al content is higher than that previously observed in YBa₂Cu₃O_{7-x} single crystals.

Introduction. During our investigations on high- T_c superconductors it was attempted to reproduce the

synthesis of a YBa₂Cu₃O_{7-x} variant described by Carim, de Jong & de Leeuw (1988) and by Peng, Klavins, Shelton, Radousky, Hahn, Bernardez & Costantino (1989). The model concerning the mixed occupation of the three metal ions La, Ba and Ca on the Y and Ba sites given by these authors is inconsistent with the results presented here and with chemical expectations. While substitution of La by Ca has been widely studied (Nguyen, Er-Rakho, Michel, Choynet & Raveau, 1980), Ca atoms on the Ba positions are less probable. In order to clarify these inconsistencies, single-crystal investigations were carried out.

Experimental. Since no information about the crucible materials is given in the literature cited above, crystal growth experiments were performed in

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Table 1. Atomic parameters for $\text{La}_{0.515}\text{Ca}_{0.485}\text{Ba}_2\text{Cu}_{2.36}\text{Al}_{0.64}\text{O}_{6.78}$ with their *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}(\text{\AA}^2)$	S.o.f.
La	0.5	0.5	0.5	0.0062 (2)	0.515 (5)
Ca	0.5	0.5	0.5	0.0062 (2)	0.485 (5)
Ba	0.5	0.5	0.19132 (6)	0.0137 (2)	1
Cu(1)/Al	0	0	0	0.0315 (9)	0.65 (1)*
Cu(2)	0	0	0.3536 (1)	0.0061 (2)	1
O(1a)	0.094 (3)	0.094 (3)	0.133 (2)	0.023 (4)	0.162 (2)†
O(1b)	0	0	0.157 (2)	0.017 (5)	0.352 (8)
O(2+3)	0	0.5	0.3639 (5)	0.0084 (9)	1
O(4+5)	0.5	0	0	0.023 (4)	0.39 (2)

* Corresponding to a mixed occupation of Cu and Al in the ratio 1:1.77.

† Split position.

Table 2. Selected distances (\AA) for $\text{La}_{0.515}\text{Ca}_{0.485}\text{Ba}_2\text{Cu}_{2.36}\text{Al}_{0.64}\text{O}_{6.78}$

La—O(2+3)	2.516 (4)	Ba—O(4+5)	2.9637 (8)
Ca—O(2+3)	2.516 (4)	Cu(1)/Al—O(1a)	1.63 (2)
Ba—O(1a)	2.34 (1)	Cu(1)/Al—O(1a)	1.83 (2)
Ba—O(1a)	2.89 (1)	Cu(1)/Al—O(4+5)	1.9540 (5)
Ba—O(1a)	3.35 (1)	Cu(2)—O(2+3)	1.9577 (6)
Ba—O(1b)	2.792 (3)	Cu(2)—O(1b)	2.29 (2)
Ba—O(2+3)	2.803 (4)	Cu(2)—O(1a)	2.62 (2)

different crucibles. Until now, crystals suitable for X-ray investigations were obtained only from corundum crucibles. This gives rise to the question of whether aluminium is incorporated as known from $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Siegrist, Schneemeyer, Waszczak, Singh, Opila, Batlogg, Rupp & Murphy, 1987).

The crystal used for the structure determination was obtained from a mixture of 66% CuO, 15% CaCO_3 , 15% BaCO_3 and 4% $\text{LaO}_{1.5}$ (mol%). The well ground mixture was heated to 1323 K, soaked for 10 h and slowly cooled to 1173 K (cooling rate 1 K h^{-1}), then to room temperature at 10 K h^{-1} . EDX analyses of the crystal used showed significant amounts of aluminium in addition to the elements of the reaction mixture. Crystal dimensions in mm were 0.013 (001), 0.013 (00 $\bar{1}$), 0.140 (010), 0.070 (010), 0.075 (1 $\bar{1}$ 0) and 0.085 ($\bar{1}$ 20) (common centre to faces). The crystal quality was checked by the Laue method, and twinning as often observed for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Roth, Ewert, Heger, Hervieu, Michel, Raveau, D'Yvoire & Revcolevschi, 1987) was shown to be absent by precession photographs and ω scans. Accurate cell dimensions were obtained from least-squares refinements with 18 reflections in the range $24^\circ \leq 2\theta \leq 42^\circ$ on a Huber 511 four-circle diffractometer. 749 reflections in the range $3^\circ \leq 2\theta \leq 65^\circ$ were measured (*hkl*; $-5 \leq h \leq 5$, $0 \leq k \leq 5$, $0 \leq l \leq 17$) with the ω -scan technique leading to 240 unique reflections having $F_o > 3\sigma(F_o)$ (5 unobserved) after L_p and absorption correction (min. and max. transmission factors 0.09, 0.75), merging $R_{\text{int}} = 0.035$, *SHELX76* (Sheldrick, 1976). Three standard

reflections monitored at constant intervals showed no significant changes. Starting parameters used for the refinement (*SHELX76*) were from the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ structure. The refinement of the site occupation factors (s.o.f.'s) of La and Cu(1) atoms led to a significant decrease in the *R* value, while changes for the Ba s.o.f. were insignificant. The correct Cu/Al ratio at the position (0,0,0) was refined by varying the s.o.f. with the Cu scattering factor as well as by a constrained $\text{Cu}_x\text{Al}_{1-x}$ occupancy refinement, which leads to the same result. The position of the O(1) was split into two crystallographic sites O(1a) and O(1b). Using a split position ($2g \rightarrow 8r$) for O(1a) indicated by large thermal parameters U_{11} and U_{22} also improved the *R* value significantly. Refinement with anisotropic thermal parameters (on the basis of *F*, 33 parameters) and isotropic extinction (0.0126, *SHELX76*) converged at $R = 0.030$, $wR = 0.026$, [$w = k/\sigma^2(F_o)$, *k* determined by least-squares refinement] and led to the final parameters given in Table 1, $(\Delta/\sigma)_{\text{max}}$ in final cycle < 1 , max. electron density 2.09 e \AA^{-3} , scattering factors used as given in the literature (Cromer & Mann, 1968). Selected distances (Busing, Martin & Levy, 1971) are listed in Table 2,* a schematic presentation of the structure is given in Fig. 1.

* Lists of structure factors, anisotropic displacement parameters, and all bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53058 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

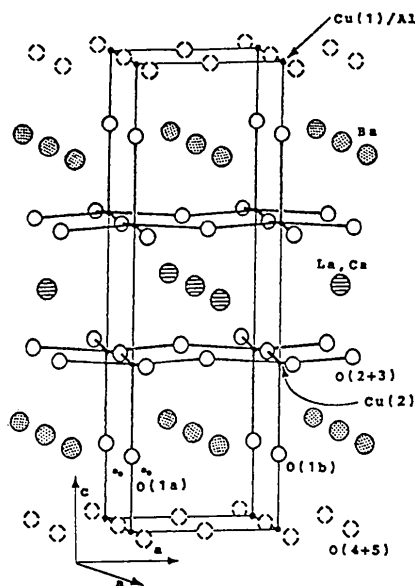


Fig. 1. Crystal structure of $\text{La}_{0.515}\text{Ca}_{0.485}\text{Ba}_2\text{Cu}_{2.36}\text{Al}_{0.64}\text{O}_{6.78}$. The O(1a) split position is shown only in the bottom left-hand corner of the unit cell. The O(4+5) is only partially occupied.

Discussion. The structure determined deviates distinctly from the stoichiometry and the model given by Carim, de Jong & de Leeuw (1988) and Peng *et al.* (1989). It was found that the Y sites were substituted by almost equal parts of Ca and La. The Cu(1) position shows a mixed occupancy by Cu and Al. The aluminium content is much higher than previously seen for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ -type single crystals. The two positions O(1a) and O(1b) are caused by different Cu—O and Al—O bond distances [Cu(1)—O(1b) = 1.88 (2) Å and Al—O(1a) = 1.63 (2) Å]. The occupation of these two O sites corresponds to the Cu to Al ratio. We observe a strikingly short distance between the Ba and the O(1a) site [Ba—O(1a) = 2.34 (1) Å] indicating a partial substitution of Ba by La. A mixing of these two elements on one site cannot be detected by X-ray analysis. X-ray photoelectron spectroscopy investigations are in progress.

No indication was found of either a superstructure (Carim, de Jonge & de Leeuw, 1988) or of orthorhombic symmetry in the case of the present investigations. From $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ it is known that Al doping causes a change in symmetry from orthorhombic to tetragonal. The compound investigated contains a considerable amount of Al. Investigations

into whether the tetragonal symmetry is caused by the Al content or is an intrinsic feature of the $(\text{La,Ca})\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ system are in progress.

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Structure Refinement of Pyrite-Type Ruthenium Disulfide, RuS_2 , and Ruthenium Diselenide, RuSe_2

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Abstract. RuS_2 : $M_r = 165.20$, cubic, $P\bar{a}3$, $a = 5.6106$ (3) Å, $V = 176.6$ Å³, $Z = 4$, $D_x = 6.21$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 104.32$ cm⁻¹, $F(000) = 304$, $T = 293$ K, $R = 0.021$ for 573 reflections. RuSe_2 : $M_r = 258.99$, cubic, $P\bar{a}3$, $a = 5.9336$ (4) Å, $V = 208.9$ Å³, $Z = 4$, $D_x = 8.23$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 414.10$ cm⁻¹, $F(000) = 448$, $T = 293$ K, $R = 0.021$ for 537 reflections. The intermolecular distances of the S_2 and Se_2 dumbbells are much smaller than the sums of the corresponding van der Waals radii. The intra-ionic Se—Se bond length of RuSe_2 [2.4532 (2) Å] resembles the sum of the covalent radii for tetrahedral coordination; the corresponding S—S

distance [2.1707 (8) Å, RuS_2] is smaller than that based on the covalent radii, but larger than both normal S—S single bonds and the S—S distances in ionic disulfides.

Introduction. Hitherto structure determinations of the pyrite-type ruthenium chalcogenides RuS_2 and RuSe_2 have been performed by X-ray powder methods (Sutarno, Knop & Reid, 1967; Stassen & Heyding, 1968). Because we need structural data of high quality for lattice dynamical calculations (Müller, 1990) we redetermined the crystal structures of these compounds on the basis of single-crystal X-ray measurements.