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Preparation and crystal structure of members of the solid solution phase $Ba_5Ru_{2-x}Al_{1+x-y}Cu_yO_{11}$ with $x = 0.378$, $y = 0.085$ and $x = 0.5$, $y = 0$

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Abstract

Single crystals of the new phase $Ba_5Ru_{2-x}Al_{1+x-y}Cu_yO_{11}$ ($x = 0.378$, $y = 0.085$) have been grown from a powder mixture of $BaCO_3$, RuO_2 and CuO in an alumina crucible. The new compound crystallizes isostructurally to $Ba_5Ir_2AlO_{11}$. The crystal structure was determined by X-ray single-crystal diffraction technique and refined to a composition of $Ba_5Ru_{1.622(8)}Al_{1.29(1)}Cu_{0.085(6)}O_{11}$ (orthorhombic, *Pnma* (No. 62), $a = 18.615(4)$ Å, $b = 5.771(1)$ Å, $c = 11.098(2)$ Å, $Z = 4$, $R_1 = 0.048$, $wR_2 = 0.075$). The composition of the new compound obtained from crystal structure refinement is in good agreement with the result of electron probe microanalysis using wavelength-dispersive X-ray spectroscopy. Octahedra $[RuO_6]$ are connected via faces forming pairs. The central positions of the octahedra pairs are statistically occupied by Ru and Al atoms. These octahedra pairs are interconnected to one-dimensional chains extending along [010] via tetrahedra $[Al_{1-y}Cu_yO_4]$. Isotypic $Ba_5Ru_{1.5}Al_{1.5}O_{11}$ is a further member of the solid solution with the lattice parameters $a = 18.6654(5)$ Å, $b = 5.7736(1)$ Å, $c = 11.0693(3)$ Å according to Rietveld refinement on a microcrystalline sample.

Keywords: Crystal structure; Solid-state synthesis; Ruthenium

1. Introduction

Ruthenium-based oxides exhibit a variety of unusual physical properties, which are often attributed to different types of the crystal structures, e.g., pyrochlores [1–3], perovskites [4,5], and perovskite-related phases [6,7]. Indeed, the three-dimensional perovskite-type oxide $SrRuO_3$ is a metallic ferromagnet below approximately 160 K [5], and the layered compound Sr_2RuO_4 with the K_2NiF_4 structure is a superconductor ($T_c = 0.93$ K) [6]. New ruthenates possessing a superconducting or magnetically ordered state are of interest from the viewpoint of material design. Initially, it is necessary to study phase formation and phase relations in relevant systems and to determine compositions and crystal structures of new compounds. In this work, we describe the synthesis and crystal structure of two new ruthenates.

To our knowledge no crystal structure data on quinquenary compounds containing Ba, Ru, Al, Cu and O were reported so far. There are also no compounds mentioned in the quarternary systems Ba–Ru–Al–O and Ru–Al–Cu–O. In the system Ba–Al–Cu–O, a compound with the formula $Al_6Ba_{46}Cu_{24}O_{84}$ has been described [8,9]. For Ba–Ru–Cu–O one compound, $Ba_3Ru_2^{V}CuO_9$, has been reported [10]. In the crystal structure of this compound, two $[RuO_6]$ octahedra share faces forming octahedra pairs $[Ru_2O_9]$. These structural units are interconnected via CuO_6 octahedra, which share corners with the $[Ru_2O_9]$ octahedra pairs. Several ternary barium ruthenates are known with octahedrally coordinated Ru atoms (compare Table 1).

$BaRu_6O_{12} = Ba_{1.33}Ru_8O_{16}$ has been described to crystallize in an ordered stoichiometric hollandite structure type [11], which contains double strings of edge-sharing octahedra $[RuO_6]$ being interconnected by

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Table 1
Structural units in ternary barium ruthenates, for more details see text

Compound	Oxidation state of Ru	Structural units	Reference
$BaRu_6O_{12}$	+3.66 (average oxidation state)	${}^{2}_{\infty}[RuO^{1/3-}_{6/3}]$	[11]
$BaRuO_3$	+4	9R : ${}^{3}_{\infty}[Ru_3O_6O^{6-}_{6/2}]$	[12–15]
		4H : ${}^{3}_{\infty}[Ru_2O_3O^{4-}_{6/2}]$	
		6H : ${}^{3}_{\infty}([Ru_2O_3O^{4-}_{6/2}]\,[RuO^{2-}_{6/2}])$	
		3C : ${}^{2}_{\infty}[RuO^{2-}_{6/2}]$	
$Ba_4Ru_3O_{10}$	+4	${}^{2}_{\infty}[Ru_3O_8O^{8-}_{4/2}]$	[16]
$Ba_5Ru_2O_{10} = Ba_5[Ru_2O_9]O$	+5	${}^{0}[Ru_2O_9^{8-}]$	[17,18]
$Ba_5Ru_2O_{11} = Ba_5[Ru_2O_9]O_2$	+5	${}^{0}[Ru_2O_9^{8-}]$	[19]
$Ba_5Ru_3O_{12}$	+5/+4/+5[a]	${}^{0}[Ru_3O_{12}^{10-}]$	[16]

[a] Ru^{5+}–Ru^{4+}–Ru^{5+}.

corner-sharing of oxygen atoms. The octahedral framework forms tunnels, which accommodate the Ba cations. The average oxidation state for Ru in this compound is +3.66. In $BaRu^{IV}O_3$, a close-packed stacking of close-packed BaO_3 layers is observed. The $[RuO_6]$ octahedra are in strings of three sharing faces, which are interconnected by corner-sharing [12]. $BaRuO_3$ crystallizes in a perovskite-related hexagonal layer structure, i.e., $BaRuO_3$ has a 9R polytype structure with *hhchhchhc* stacking sequences. This structure transforms to a 4H structure (*hchc*) at a pressure of $P = 15$ kbar and to a 6H structure (*cchcch*) at $P = 30$ kbar [13]. A phase diagram study indicated a further transformation to the cubic perovskite structure type at $P \approx 120$ kbar [14]. The 4H $BaRuO_3$ has also been prepared at ambient pressure by Hong and Sleight [15]. $Ba_4Ru_3^{IV}O_{10}$ contains short chains of three face-sharing $[RuO_6]$ octahedra, which are interconnected via terminal corners [16]. $Ba_5Ru_2^{V}O_{10} = Ba_5[Ru_2O_9]O$ contains octahedra pairs $[Ru_2O_9]$ and additional oxygen atoms exclusively surrounded by barium [17,18]. In the barium ruthenium(V) oxide $Ba_5Ru_2^{V}O_{11} = Ba_5[Ru_2O_9]O_2$ identical octahedra pairs occur. The charge balance is realized by additional peroxide ions [19]. The crystal structure of $Ba_5Ru_3O_{12}$ consists of isolated trimeric units $[Ru_3O_{12}]$ of face-sharing octahedra separated by barium atoms. Dussarrat et al. [16] concluded that the trimeric unit corresponds to Ru^{V}–Ru^{IV}–Ru^{V} based on distances and valence bond calculations.

2. Experimental

2.1. Synthesis

Single crystals of the new compound $Ba_5Ru_{2-x}Al_{1+x-y}Cu_yO_{11}$ ($x = 0.378$, $y = 0.085$) were prepared from powders of $BaCO_3$ (MaTeck, 99.99%), RuO_2 (Berg- und Hüttenkombinat Freiberg, 99.9%) and CuO (MaTeck, 99.99%) with a molar ratio of Ba–Ru–Cu of 4:1:2. The components were mixed in an agate mortar and placed in an alumina crucible. The mixture was heated to 1373 K and annealed for 17 h. Afterwards, it was cooled down to ambient temperature with a rate of 600 K/h. Small single crystals of the new compound were found at the contact with the crucible. The aluminum necessary to form this compound originates from the crucible.

Further attempts for preparation of single phase products were performed for the compositions $Ba_5Ru_{2-x}Al_{1+x-y}Cu_yO_{11}$ with $x = 0$ and $y = 1$, $x = 0$ and $y = 0$, $x = 0.5$ and $y = 0$ at different temperatures $T = 1373$, 1473 and 1623 K. The pellets were placed on ZrO_2 bars inside alumina crucibles to prevent the contact between sample and the crucible. Annealing times of about 100 h were chosen. Additional experiments substituting some Al by Ga were also performed under identical conditions.

2.2. Single-crystal X-ray structure determination

A black needle-like crystal (approximate dimensions: ∅ 3.5 μm, length 110 μm) was mechanically extracted from the matrix surface. The measurement of the intensity data was carried out at 295 K on a four circle diffractometer Rigaku AFC-7, equipped with a Mercury CCD-detector, using Mo*K*α-radiation ($\lambda = 0.7107$ Å). The positions of barium and ruthenium atoms were established by Patterson method (SHELXS-97-2 [20]). The remaining atomic positions were taken from Fourier difference syntheses. The final full-matrix least-squares refinement converged to $R_1 = 0.048$, $wR_2 = 0.075$ (SHELXL-97-2 [21]). The crystallographic data and measurement conditions are summarized in Table 2. Atomic parameters and anisotropic displacement parameters are given in Table 3a.

2.3. Electron probe X-ray microanalysis (EPMA)

The chemical composition of a different isolated single crystal was measured by electron probe X-ray microanalysis (EPMA) using a wavelength-dispersive X-ray (WDX) spectrometer (SEMQ, Applied Research Lab, USA). Pure metals Al and Cu as well as RuO_2 for

Table 2
Measurement conditions and crystallographic data for $Ba_5Ru_{1.622}Al_{1.29}Cu_{0.085}O_{11}$ and $Ba_5Ru_{1.5}Al_{1.5}O_{11}$

Formula	$Ba_5Ru_{1.622(8)}Al_{1.29(1)}Cu_{0.085(6)}O_{11}$	$Ba_5Ru_{1.5}Al_{1.5}O_{11}$
Formula weight	1066.89	1054.71
Crystal size	Diameter: 3.5 μm, length: 110 μm	Microcrystalline powder
Color	Black	Black
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma* (No. 62)	*Pnma* (No. 62)
a (Å)	18.615(4)	18.6654(5)
b (Å)	5.771(1)	5.7736(1)
c (Å)	11.098(2)	11.0693(3)
V (Å^3)	1192.23	1192.90
Z	4	4
Density $\rho_{calc.}$ (g cm^{-1})	5.944	5.873
μ	18.54 mm^{-1}	
Diffractometer	Rigaku AFC-7, Mercury-CCD	X'Pert, PW3040/00
Monochromator	Graphite	Graphite
Radiation	Mo$K\alpha$	Co$K\alpha$
Temperature (K)	295	295
2θ range	up to 68.1	$10° \leqslant 2\theta \leqslant 130°$
Absorption correction	Multi-scan	
$h\,k\,l$ ranges	$-27 \leqslant h \leqslant 27$, $-8 \leqslant k \leqslant 5$, $-16 \leqslant l \leqslant 16$	
Scan mode, step Δ, time	φ/ω, $\Delta = 0.6°$, 90 s per image	$\theta/2\theta$, $\Delta = 0.03°$, 60 s per step
No. of measured reflections	12,625	
No. of unique reflections	2444	
No. of observed reflections	2106	
$R_{int.}$	0.0442	
No. of refined parameters	79	
Refinement method	Full matrix least squares	Least squares
R_1 (all data, 2444)	0.064	
R_1 ($F_o > 4\sigma$, 2106 data)	0.048	
wR_2 (all data)	0.075	
Goodness of fit (all data)	1.229	
Largest peak in the Fourier difference map	2.07 e Å^{-3} (0.51 Å from O(4))	
$R_{exp.}$		0.037
R_p		0.075
wR_p		0.098
R_B		0.085
R_F		0.047

Ru and O and $YBa_2Cu_3O_7$ for Ba were applied as standard materials for quantification of the elements in a single crystal. The characteristic wavelengths of Al-$K\alpha$-, Cu-$K\alpha$-, O-$K\alpha$-, Ba-$L\alpha$- and Ru-$L\alpha$-lines were used. Five independent measurements at different positions on the crystal were averaged. The chemical composition of the single crystal was calculated with the program LOVSCOTT [22].

2.4. X-ray powder diffraction measurements

X-ray powder diffraction patterns were obtained on an X'Pert diffractometer PW3040/00 (Philips) using Co$K\alpha$ radiation ($\lambda = 1.7903$ Å, for further measurement conditions and crystallographic data compare Table 2). The X-ray data were collected using Bragg–Brentano geometry in a range from 10° to 130° (2θ) with a step width of 0.03°. Phase analysis was performed using the program HighScore (Philips) [23]. The Rietveld refinement of the single phase product $Ba_5Ru_{1.5}Al_{1.5}O_{11}$ with Si as internal standard was carried out with the program Fullprof [24]. Atomic parameters are summarized in Table 3b. The comparison between the observed and the calculated powder pattern and the difference curve is shown in Fig. 1.

3. Results and discussion

$Ba_5Ru_{1.622}Al_{1.29}Cu_{0.085}O_{11}$ crystallizes in the orthorhombic space group *Pnma* (No. 62) with lattice parameters $a = 18.615(4)$ Å, $b = 5.771(1)$ Å and $c = 11.098(2)$ Å, $Z = 4$, obtained from single-crystal diffraction data refinements. The compound is an isotype of $Ba_5Ir_2AlO_{11}$ reported by Lang and Müller-Buschbaum [25]. Preparation attempts aimed for single phase members of the solid solution phase led to the following results: Samples with $x = 0$, $y = 1$ ("$Ba_5Ru_2CuO_{11}$") and $x = 0$, $y = 0$ ("$Ba_2Ru_2AlO_{11}$") contain several phases ($x = 0$, $y = 1$: $Ba_5Ru_2O_{10}$,

Table 3
Crystal structure parameters of (a) $Ba_5Ru_{1.622(8)}$ $Al_{1.29(1)}Cu_{0.085(6)}O_{11}$ and (b) $Ba_5Ru_{1.5}Al_{1.5}O_{11}$

(a)

Atom	Site	x	y	z	Occupation	U_{eq} (10^{-2} Å^2)
Ba(1)	4*c*	0.13831(3)	1/4	0.69066(5)	1.0	0.97(1)
Ba(2)	4*c*	0.17492(3)	1/4	0.05034(5)	1.0	1.16(1)
Ba(3)	4*c*	0.47231(3)	1/4	0.60570(5)	1.0	1.22(1)
Ba(4)	4*c*	0.43120(4)	1/4	0.97201(6)	1.0	1.76(1)
Ba(5)	4*c*	0.24922(3)	1/4	0.37606(5)	1.0	1.23(1)
Ru(1)/Al(1)	4*c*	0.43139(4)	1/4	0.29411(7)	0.927(4)/0.073	0.70(2)
Ru(2)/Al(2)	4*c*	0.06481(5)	1/4	0.29744(8)	0.695(4)/0.305	0.68(3)
Al(3)/Cu(1)	4*c*	0.3112(1)	1/4	0.7417(2)	0.915(6)/0.085	1.05(8)
O(1)	4*c*	0.0287(4)	1/4	0.1237(7)	1.0	1.2(1)
O(2)	4*c*	0.3480(4)	1/4	0.1912(7)	1.0	1.3(1)
O(3)	4*c*	0.0929(4)	1/4	0.4598(7)	1.0	1.6(1)
O(4)	4*c*	0.2723(4)	1/4	0.6001(7)	1.0	1.8(2)
O(5)	4*c*	0.2535(4)	1/4	0.8622(8)	1.0	2.1(2)
O(6)	8*d*	0.4845(3)	0.0200(9)	0.1818(5)	1.0	1.41(9)
O(7)	8*d*	0.1326(3)	0.0027(9)	0.2525(5)	1.0	1.5(1)
O(8)	8*d*	0.3982(3)	0.0128(9)	0.3961(5)	1.0	1.5(1)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba(1)	0.0083(2)	0.0101(3)	0.0108(3)	0	0.0003(2)	0
Ba(2)	0.0140(2)	0.0130(3)	0.0078(2)	0	0.0014(2)	0
Ba(3)	0.0123(2)	0.0127(3)	0.0118(3)	0	0.0023(2)	0
Ba(4)	0.0221(3)	0.0170(3)	0.0138(3)	0	0.0003(2)	0
Ba(5)	0.0170(2)	0.0110(3)	0.0090(2)	0	−0.0006(2)	0
Ru(1)/Al(1)	0.0080(3)	0.0058(4)	0.0073(3)	0	0.0001(2)	0
Ru(2)/Al(2)	0.0077(4)	0.0056(5)	0.0071(4)	0	0.0005(3)	0
Al(3)/Cu(1)	0.013(1)	0.010(1)	0.008(1)	0	0.0000(9)	0

(b)

Atom	Site	x	y	z	Occupation	B
Ba(1)	4*c*	0.1392(3)	1/4	0.6915(5)	1.0	1.19(3)
Ba(2)	4*c*	0.1745(2)	1/4	0.0491(5)	1.0	1.19(3)
Ba(3)	4*c*	0.4735(3)	1/4	0.6040(5)	1.0	1.19(3)
Ba(4)	4*c*	0.4322(3)	1/4	0.9711(5)	1.0	1.19(3)
Ba(5)	4*c*	0.2494(3)	1/4	0.3766(5)	1.0	1.19(3)
Ru(1)/Al(1)	4*c*	0.4313(4)	1/4	0.2926(6)	0.90(1)/0.10	1.13(1)
Ru(2)/Al(2)	4*c*	0.0636(5)	1/4	0.297(1)	0.72(1)/0.28	1.13(1)
Al(3)	4*c*	0.310(1)	1/4	0.747(2)	1.0	1.13(1)
O(1)	4*c*	0.028(2)	1/4	0.112(4)	1.0	0.0(2)
O(2)	4*c*	0.346(2)	1/4	0.186(4)	1.0	0.0(2)
O(3)	4*c*	0.085(2)	1/4	0.448(4)	1.0	0.0(2)
O(4)	4*c*	0.276(2)	1/4	0.594(4)	1.0	0.0(2)
O(5)	4*c*	0.256(2)	1/4	0.850(4)	1.0	0.0(2)
O(6)	8*d*	0.483(2)	0.006(5)	0.185(3)	1.0	0.0(2)
O(7)	8*d*	0.141(2)	0.010(6)	0.248(2)	1.0	0.0(2)
O(8)	8*d*	0.404(2)	0.023(6)	0.405(2)	1.0	0.0(2)

Ba_2CuO_3 and further phases, which could not be identified; $x = 0$, $y = 0$: phase isotypic to $Ba_5Ir_2AlO_{11}$, $Ba_4Ru_3O_{10}$, barium-aluminates and further phases). $Ba_5Ru_{1.5}Al_{1.5}O_{11}$ ($x = 0.5$, $y = 0$) was a single-phase powder sample, which is also an isotype of $Ba_5Ir_2AlO_{11}$ with $a = 18.6654(5)$ Å, $b = 5.7736(1)$ Å and $c = 11.0693(3)$ Å. It is also possible to substitute Al in the compound $Ba_5Ru_{1.622}Al_{1.29}Cu_{0.085}O_{11}$ by Ga. $Ba_5Ru_{1.622}Al_{0.65}Ga_{0.64}Cu_{0.085}O_{11}$ also crystallizes in the $Ba_5Ir_2AlO_{11}$ structure type with the lattice parameters $a = 18.7143(3)$ Å, $b = 5.79023(8)$ Å, $c = 11.1062(2)$ Å. The lattice parameters are slightly larger than those of $Ba_5Ru_{1.622}Al_{1.29}Cu_{0.085}O_{11}$, which is in good agreement with the ionic radii of Al and Ga according to Shannon [26] (Al^{3+} (CN = 4):0.39 Å, Ga^{3+} (CN = 4):0.47 Å; Al^{3+} (CN = 6):0.535 Å, Ga^{3+} (CN = 6):0.620 Å).

In the crystal structures of $Ba_5Ru_{1.622}Al_{1.29}Cu_{0.085}O_{11}$ and $Ba_5Ru_{1.5}Al_{1.5}O_{11}$, the Ru atoms are coordinated octahedrally by six O atoms. Two octahedra are connected via face-sharing, thus forming octahedra

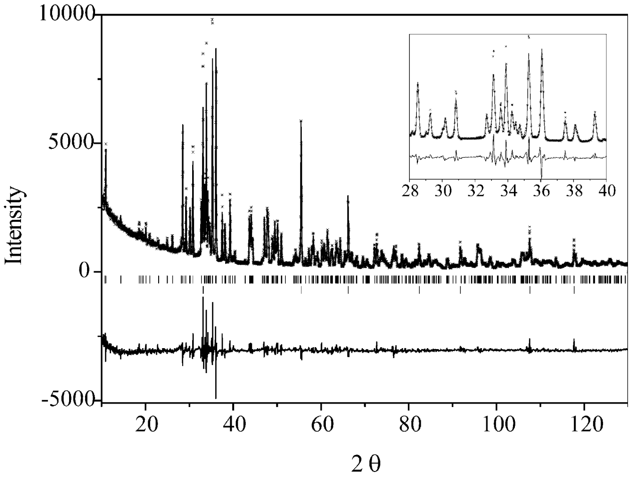

Fig. 1. X-ray powder diffraction pattern of $Ba_5Ru_{1.5}Al_{1.5}O_{11}$ with silicon as internal standard (experimental data (*), calculated (line) and difference curve). The tick marks indicate Bragg reflections of $Ba_5Ru_{1.5}Al_{1.5}O_{11}$ (top, rel. intensity$\geqslant$1%) and Si (bottom). The inset shows a part of the refined pattern.

pairs [Ru_2O_9]. Such fragments are known from several compounds $Ba_3MRu_2O_9$ with a variety of alkali, alkaline-earth, transition and rare-earth metals M [10,27–39]. In the title compounds, the octahedra pairs are interconnected by tetrahedral units [$Al_{1-y}Cu_yO_4$] forming one-dimensional chains extending along [010]. The central positions of the octahedra are statistically occupied by Ru and Al atoms. The central position (Ru(1)) of the octahedron which is not connected to the tetrahedra shows only a slight substitution by aluminum atoms (7.3%/10%) while the other octahedron (Ru(2)) is occupied by 30.5%/28.0% aluminum. The crystal structure is visualized in Fig. 2 (top) as well as the one-dimensional chains (bottom).

Bond distances and angles are summarized in Table 4.

Due to the higher reliability of the positional parameters from single-crystal X-ray diffraction data obtained on $Ba_5Ru_{1.622}Al_{1.29}Cu_{0.085}O_{11}$, in the following the crystal structure is analyzed based on these data. The distances d(Ru–O) vary in the range from 1.881(5) to 2.072(5) Å for Ru(1) and from 1.876(8) to 2.042(7) Å for Ru(2). The shorter distances d(Ru(1)–O) were observed for the three terminal oxygen atoms whereas longer Ru–O distances d(Ru(1)–O) were obtained for the face-connecting oxygen atoms. For Ru(2), only one terminal oxygen atom with the shortest distance d(Ru(2)–O(3)) = 1.876(8) Å is observed. The oxygen atoms which belong to the connection forming the octahedra pairs are those showing the largest distance d(Ru(2)–O) > 2 Å. Two further Ru–O distances d(Ru(2)–O(7)) = 1.970(5) Å belong to oxygen atoms which are additionally corner-sharing with the tetrahedra [$Al_{1-y}Cu_yO_4$]. The average distances $\bar{d}(Ru-O)$ of 1.977 and 1.981 Å for Ru(1) and Ru(2), respectively, are close to the average values known for Ru^V in $Ba_3MRu_2O_9$ with M = Co, Ni, Cu [10] (compare Table 4). These average distances $\bar{d}(Ru-O)$ are smaller than the corresponding values $\bar{d}(Ir-O)$ in $Ba_5Ir_2AlO_{11}$ (2.03 and 1.99 Å, respectively). This result is in good agreement with the ionic radii of Ru^V (0.565 Å for CN = 6) and Ir^{IV} (0.625 Å, CN = 6), Ir^V (0.57 Å, CN = 6) [26]. Even more significant for the decision between different oxidation states of Ru is the variation of Ru–Ru distances, which increase with increasing oxidation state. The distance d(Ru–Ru) of 2.683(1) Å in the crystal structure of $Ba_5Ru_{2-x}Al_{1+x-y}Cu_yO_{11}$ ($x = 0.378$, $y = 0.085$) indicates Ru^V as can be taken from Fig. 3 and Table 5.

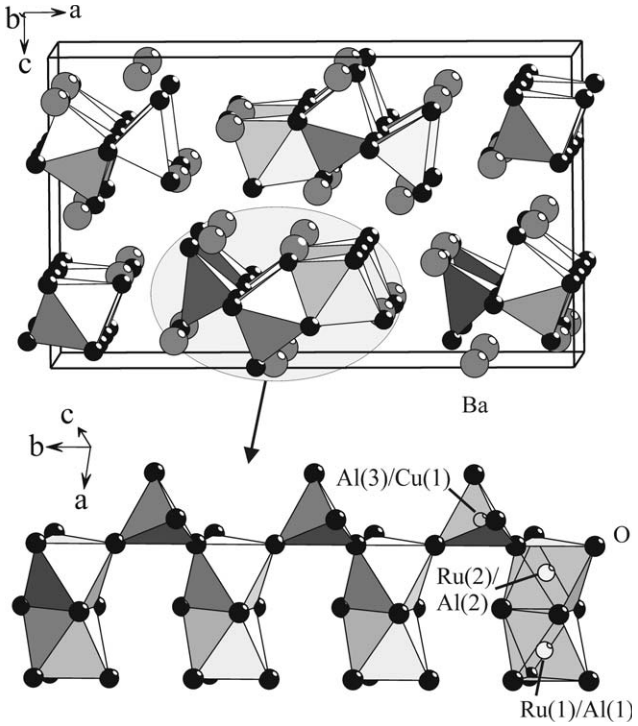

Fig. 2. Part of the crystal structure of $Ba_5Ru_{2-x}Al_{1+x-y}Cu_xO_{11}$ (top) and one-dimensional chains $[Ru_{2-x}Al_{1+x-y}Cu_yO_{11}]^{10-}$ (bottom).

Provided Ba^{2+}, Al^{3+}, Cu^{2+} and O^{2-}, the oxidation state for Ru from the refined composition $Ba_5Ru_{1.622(8)}Al_{1.29(1)}Cu_{0.085(6)}O_{11}$ is calculated to be +4.9. This is in good agreement with the analyses of distances. It is also justifiable to assume Cu in the oxidation state +2, because of its tetrahedral coordination. Cu^I prefers linear coordination while for Cu^{III}, square-planar as well as octahedral coordination environment have been reported [41]. +2 is the oxidation state for Cu with the largest variety of coordination polyhedra. Besides the square-planar coordination (isolated or interconnected), also pyramidal, octahedral and tetrahedral coordination is possible. Especially for vanadates ($Cu_2V_2O_7$ [42], α-$Cu^{II}VO_3$ [43], $Cu_xV_4O_{11}$ [44]) and for $(Ba,Sr)CuAl_{10}O_{17}$ [45] tetrahedral coordination has been reported.

Table 4
Selected interatomic distances (Å) and angles (deg) for $Ba_5Ru_{1.622(8)}Al_{1.29(1)}Cu_{0.085(6)}O_{11}$ (left) and $Ba_5Ru_{1.5}Al_{1.5}O_{11}$ (right)

Ba(1)–O(4)	2.690(8)		2.77(4)	
Ba(1)–O(3)	2.698(8)		2.88(4)	
Ba(1)–O(6)	2.768(5)	2 ×	2.72(4)	2 ×
Ba(1)–O(8)	2.822(5)	2 ×	2.95(3)	2 ×
Ba(1)–O(5)	2.867(8)		2.80(4)	
Ba(1)–O(2)	2.8968(8)	2 ×	2.901(4)	2 ×
Ba(2)–O(5)	2.550(8)		2.68(4)	
Ba(2)–O(8)	2.661(5)	2 ×	2.68(3)	2 ×
Ba(2)–O(7)	2.773(5)	2 ×	2.68(3)	2 ×
Ba(2)–O(1)	2.841(7)		2.82(4)	
Ba(2)–O(4)	3.098(3)	2 ×	3.07(1)	2 ×
Ba(3)–O(1)	2.754(7)		2.60(4)	
Ba(3)–O(8)	2.848(5)	2 ×	2.78(4)	2 ×
Ba(3)–O(1)	2.8925(7)	2 ×	2.888(1)	2 ×
Ba(3)–O(7)	2.932(5)	2 ×	3.06(3)	2 ×
Ba(3)–O(6)	2.939(5)	2 ×	2.88(3)	2 ×
Ba(3)–O(8)	3.031(5)	2 ×	2.87(3)	2 ×
Ba(4)–O(6)	2.794(5)	2 ×	2.77(3)	2 ×
Ba(4)–O(6)	2.857(5)	2 ×	2.91(3)	2 ×
Ba(4)–O(2)	2.884(7)		2.87(4)	
Ba(4)–O(3)	2.923(1)	2 ×	2.916(6)	2 ×
Ba(4)–O(7)	3.078(5)	2 ×	3.20(3)	2 ×
Ba(4)–O(3)	3.104(7)		2.99(4)	
Ba(5)–O(4)	2.523(8)		2.46(4)	
Ba(5)–O(2)	2.755(7)		2.78(4)	
Ba(5)–O(5)	2.8901(7)	2 ×	2.904(5)	2 ×
Ba(5)–O(7)	2.937(5)	2 ×	2.84(3)	2 ×
Ba(5)–O(3)	3.054(7)		3.17(4)	
Ba(5)–O(8)	3.101(5)	2 ×	3.18(4)	2 ×
Ru(1)/Al(1)–O(8)	1.881(5)	2 ×	1.88(3)	2 ×
Ru(1)/Al(1)–O(2)	1.927(7)		1.98(4)	
Ru(1)/Al(1)–O(1)	2.028(7)		2.09(4)	
Ru(1)/Al(1)–O(6)	2.072(5)	2 ×	2.08(3)	2 ×
Ru(1)/Al(1)–Ru(2)/Al(2)	2.683(1)		2.66(1)	
Ru(2)/Al(2)–O(3)	1.876(8)		1.72(5)	
Ru(2)/Al(2)–O(7)	1.970(5)	2 ×	2.07(4)	2 ×
Ru(2)/Al(2)–O(6)	2.013(5)	2 ×	2.07(3)	2 ×
Ru(2)/Al(2)–O(1)	2.042(7)		2.15(5)	
Ru(2)/Al(2)–Ru(1)/Al(1)	2.683(1)		2.66(1)	
Al(3)/Cu(1)–O(5)	1.716(9)		1.52(5)	
Al(3)/Cu(1)–O(4)	1.730(9)		1.81(5)	
Al(3)/Cu(1)–O(7)	1.798(5)	2 ×	1.76(4)	2 ×
O(1)–Ru(1)–O(6)	81.1(2)	2 ×		
O(1)–Ru(1)–O(8)	91.3(2)	2 ×		
O(2)–Ru(1)–O(6)	91.6(2)	2 ×		
O(2)–Ru(1)–O(8)	95.3(2)	2 ×		
O(6)–Ru(1)–O(6)	79.7(3)			
O(6)–Ru(1)–O(8)	93.0(2)	2 ×		
O(8)–Ru(1)–O(8)	93.4(2)			
O(1)–Ru(1)–O(2)	170.4(3)			
O(6)–Ru(1)–O(8)	170.1(2)	2 ×		
O(1)–Ru(2)–O(6)	82.2(2)	2 ×		
O(1)–Ru(2)–O(7)	88.4(2)	2 ×		
O(3)–Ru(2)–O(6)	95.6(2)	2 ×		
O(3)–Ru(2)–O(7)	93.7(2)	2 ×		
O(6)–Ru(2)–O(6)	82.5(3)			
O(6)–Ru(2)–O(7)	91.6(2)	2 ×		
O(7)–Ru(2)–O(7)	92.9(3)			
O(1)–Ru(2)–O(3)	177.0(3)			
O(6)–Ru(2)–O(7)	169.5(2)	2 ×		
O(4)–Al(3)–O(5)	116.5(4)			
O(4)–Al(3)–O(7)	107.7(2)	2 ×		
O(5)–Al(3)–O(7)	108.2(2)	2 ×		
O(7)–Al(3)–O(7)	108.4(4)			

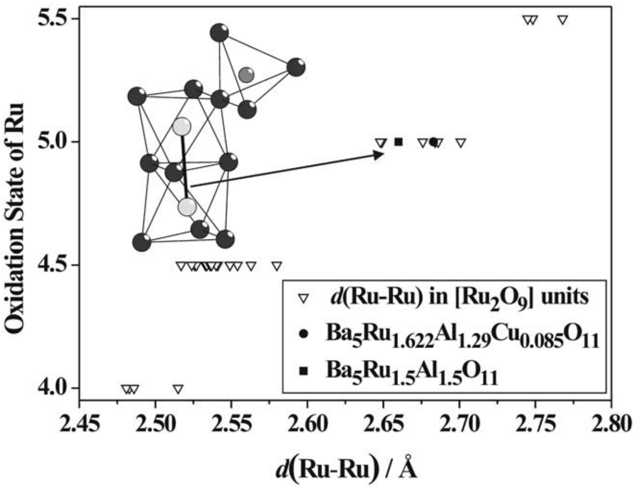

Fig. 3. Distance d(Ru–Ru) within octahedra pairs [Ru_2O_9] via oxidation state of Ru in these [Ru_2O_9] units. The inset shows a part of the crystal structure of $Ba_5Ru_{2-x}Al_{1+x-y}Cu_xO_{11}$. References for d(Ru–Ru) can be taken from Table 5.

Typical coordination environments for aluminum atoms are octahedral or tetrahedral as observed in the presented structure solution. An example for the combination of tetrahedral and octahedral coordination of Al is (Ba,Sr)$CuAl_{10}O_{17}$ [45]. The average distance $\bar{d}$(Al–O) in aluminates is between 1.700 and 1.825 Å for coordination number CN = 4. The average value of $\bar{d}(\mathrm{Al-O}) = 1.761$ Å as observed in the title compound is well within this range. The tetrahedrally coordinated Al site is partially occupied by Cu atoms.

For Ba atoms different coordinations were found with coordination numbers CN = 8 (Ba(2)), CN = 9 (Ba(1), Ba(5)), CN = 10 (Ba(4)) and CN = 11 (Ba(3)). Interestingly, in $Ba_5Ru_{2-x}Al_{1+x-y}Cu_yO_{11}$ ($x = 0.378$, $y = 0.085$) two relative short distances d(Ba–O) were observed: d(Ba(2)–O(5)) = 2.550(8) Å and d(Ba(5)–O(4)) = 2.523(8) Å. In comparison, the shortest Ba–O distance in $Ba_5Ru_2O_{10}$ is 2.494 Å. The corresponding distances in the isotype $Ba_5Ir_2AlO_{11}$ are also quite short (2.51(4) Å, 2.53(5) Å) [25].

As can be taken from Table 4, the relations are similar in the crystal structure of $Ba_5Ru_{1.5}Al_{1.5}O_{11}$.

Table 5
Average distance $\bar{d}$(Ru–O) and distance d(Ru–Ru) in $Ba_3MRu_2O_9$ in dependence of the Ru oxidation state

M	Oxidation state of Ru	Average distance Ru–O (Å)	Ru–Ru distance (Å)	Reference
Li^+	+5.5	1.946	2.768(1)	[27]
Na^+	+5.5	1.944	2.7482(9)	[27]
Na^+	+5.5	1.944	2.745(1)	[28]
Ca^{2+}	+5	1.952	2.649(2)	[29]
Ca^{2+}	+5	1.949	2.648(2)	[30]
Sr^{2+}	+5	1.965	2.676(6)	[31]
Ti^{4+}	+4	1.998	2.515(6)	[32]
Fe	[a]	1.984	2.607(9)	[10]
Co^{2+}	+5	1.970	2.684(4)	[10]
Ni^{2+}	+5	1.968	2.686(4)	[10]
Cu^{2+}	+5	1.964	2.701(4)	[10]
In^{3+}	+4.5	1.983	2.517(7)	[10]
In^{3+}	+4.5	1.985	2.563(4)	[34]
Bi	*	1.93	2.50(1)	[40]
Y^{3+}	+4.5	2.00	2.526(5)	[33]
Y^{3+}	+4.5	1.981	2.540(2)	[34]
La^{3+}	+4.5	1.977	2.554(3)	[34]
Ce^{4+}	+4	2.00	2.483(3)	[35]
Ce^{4+}	+4	1.993	2.481(3)	[36]
Pr^{4+}	+4	1.989	2.486(2)	[36]
Nd^{3+}	+4.5	1.979	2.524(4)	[37]
Sm^{3+}	+4.5	1.977	2.533(1)	[35]
Sm^{3+}	+4.5	1.978	2.536(3)	[34]
Eu^{3+}	+4.5	1.976	2.537(4)	[34]
Gd^{3+}	+4.5	2.00	2.534(5)	[33]
Tb^{4+}	+4	1.992	2.493(6)	[36]
Dy^{3+}	+4.5	1.971	2.527(1)	[35]
Er^{3+}	+4.5	1.973	2.534(1)	[35]
Yb^{3+}	+4.5	1.976	2.541(3)	[30]
Lu^{3+}	+4.5	1.980	2.549(3)	[34]

[a] Due to the element combination no unambiguous oxidation state assignment is possible.

The composition of $Ba_5Ru_{1.622(8)}Al_{1.29(1)}Cu_{0.085(6)}O_{11}$ obtained from single-crystal X-ray diffraction refinement was confirmed by electron probe microanalysis. The composition calculated from WDX results is $Ba_{5\pm0.3}Ru_{1.77\pm0.07}Al_{1.4\pm0.1}Cu_{0.19\pm0.01}O_{10.9\pm0.4}$. Considering the principally larger errors for Ba and Ru content from use of $L\alpha$-lines compared to, e.g., the values for Al and Cu derived from $K\alpha$-lines, the result from WDX studies is in good agreement with the composition of the single-crystal refinement.

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