

$\text{Ba}_3\text{YRu}_{0.73(2)}\text{Al}_{1.27(2)}\text{O}_8$ and $\text{Ba}_5\text{Y}_2\text{Ru}_{1.52(2)}\text{Al}_{1.47(2)}\text{O}_{13.5}$: New Perovskite Ruthenates with Partial Octahedra Replacement

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Dark red single crystals of the new phases $\text{Ba}_3\text{YRu}_{0.73(2)}\text{Al}_{1.27(2)}\text{O}_8$ and $\text{Ba}_5\text{Y}_2\text{Ru}_{1.52(2)}\text{Al}_{1.47(2)}\text{O}_{13.5}$ have been grown from powder mixtures of BaCO_3 , Y_2O_3 , Al_2O_3 , and RuO_2 . The compositions given in the formulas result from the refinements of the crystal structures based on single crystal X-ray diffraction data (hexagonal $P6_3/mmc$ (No. 194), $Z = 2$, $\text{Ba}_3\text{YRu}_{0.73(2)}\text{Al}_{1.27(2)}\text{O}_8$: $a = 5.871(1)$, $c = 14.633(3)$ Å, $R1 = 0.035$, $wR2 = 0.069$ and $\text{Ba}_5\text{Y}_2\text{Ru}_{1.52(2)}\text{Al}_{1.47(2)}\text{O}_{13.5}$: $a = 5.907(1)$, $c = 24.556(5)$ Å, $R1 = 0.057$, $wR2 = 0.114$). $\text{Ba}_3\text{YRu}_{0.73(2)}\text{Al}_{1.27(2)}\text{O}_8$ crystallizes in a 6H perovskite structure, $\text{Ba}_5\text{Y}_2\text{Ru}_{1.52(2)}\text{Al}_{1.47(2)}\text{O}_{13.5}$ has been characterized as a 10H Perovskite. Due to similar spatial extensions of (Ru_2O_9) face-sharing pairs of octahedra and (Al_2O_7) vertex-sharing pairs of tetrahedra, both structures show partial mutual substitution of these units. Consequently, the title compounds may be written as $\text{Ba}_3\text{Y}(\text{Ru}_2\text{O}_9)_{1-x}(\text{Al}_2\text{O}_7)_x$, $x = 0.64(1)$ and $\text{Ba}_5\text{Y}_2\text{RuO}_6(\text{Ru}_2\text{O}_9)_{1-x}(\text{Al}_2\text{O}_7)_x$, $x = 0.74(1)$. This interpretation is supported by the results of electron probe microanalysis using wavelength-dispersive X-ray spectroscopy. An oxidation state of Ru close to +5 for the (Ru_2O_9) units, as can be derived from the distances $d(\text{Ru}-\text{Ru})$, additionally leads to similar charges of both the (Ru_2O_9) and the (Al_2O_7) units.

Key words: Crystal Structure, Solid State Synthesis, Ruthenium, Perovskite

Introduction

In recent years the electronic properties of oxoruthenates have stimulated a multitude of studies both in solid state chemistry and condensed matter physics since they include for example the occurrence of unconventional superconductors, metamagnets and itinerant ferromagnets. A large number of ternary and multinary ruthenates can be described in perovskite structures and variants thereof. One general feature is the occurrence of RuO_6 octahedra in face- or vertex-sharing arrangements together with units of a tetrahedrally coordinated metal. An extensive review on the crystal chemistry of ruthenates has recently appeared [1].

A second feature of oxoruthenate chemistry is the possibility to form mixed and intermediate valence states leading to a broad structural chemistry and a large compositional variability for many compounds. In the ternary system Ba-Ru-O the ruthenium atoms can exhibit average oxidation states in the range from +3.66 (in $\text{BaRu}_6\text{O}_{12}$ [2]) up to +5 (in $\text{Ba}_5\text{Ru}_2\text{O}_{10}$ and $\text{Ba}_5\text{Ru}_2\text{O}_{11}$ [3–5]). Ru in the oxidation state +4 is present in the different modifications of BaRuO_3 . The r.t. form resembles a 9R perovskite (stacking sequence hhc) with a three-dimensional framework $\infty[(\text{Ru}_3\text{O}_6\text{O}_{6/2})^{6-}]$ [6]. At $p = 15$ kbar, 9R BaRuO_3 transforms to the 4H (hc) structure type [7] (also prepared at ambient pressure [8]) with pairs of face-sharing octahedra (Ru_2O_9) being interconnected *via*

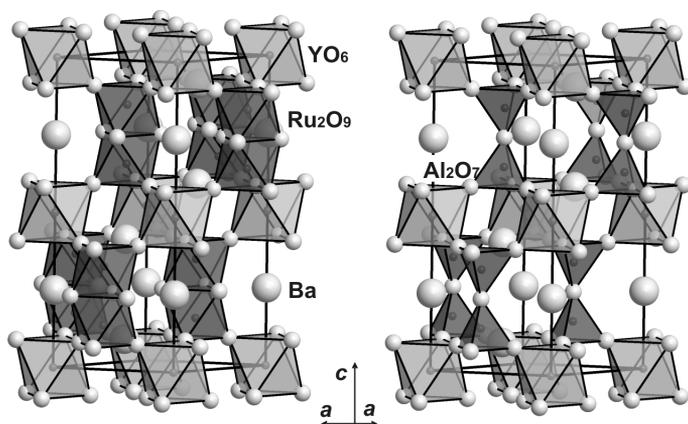


Fig. 1. Ba₃YRu_{0.73(2)}Al_{1.27(2)}O₈: Sections of the 6H perovskite crystal structure with (Ru₂O₉) units (dark grey) vertex-sharing with YO₆ octahedra (light grey), left, (Al₂O₇) units replacing the (Ru₂O₉) units, right, indicating the two ordered limiting structure models.

the corners, *i. e.* $\frac{3}{\infty}[(\text{Ru}_2\text{O}_3\text{O}_{6/2})^{4-}]$. A further transformation takes place at $p = 30$ kbar leading to 6H BaRuO₃ (hcc) with pairs of octahedra interconnected with further octahedra exclusively *via* corners, *i. e.* $\frac{3}{\infty}[(\text{Ru}_2\text{O}_3\text{O}_{6/2})^{4-}(\text{RuO}_{6/2})^{2-}]$ [7]. A study aiming on a phase diagram description has indicated a third transformation at $p \approx 120$ kbar leading to the cubic perovskite-type structure [9]. This crystal chemistry of barium oxoruthenates can be greatly expanded by the addition of further metals [1].

Results and Discussion

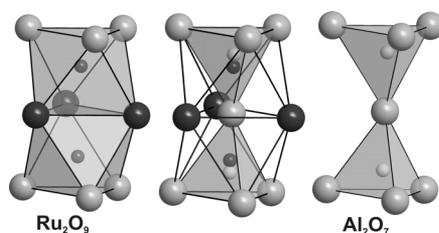
Ba₃YRu_{0.73(2)}Al_{1.27(2)}O₈

Ba₃YRu_{0.73(2)}Al_{1.27(2)}O₈ crystallizes in the space group $P6_3/mmc$ with the lattice parameters $a = 5.871(1)$, $c = 14.633(3)$ Å, $Z = 2$. The analogous ruthenium-free compound Ba₃YAl₂O_{7.5} was reported to crystallize in two modifications (orthorhombic and monoclinic) with similar unit cell parameters and volumes, but no simple crystallographic relationship [10] to the title phase. No further information on this compound could be extracted from the literature. The initial refinement of the crystal structure was carried out with the structure model of a 6H perovskite (Fig. 1, left). The 6H perovskite structure is characterized by metal-centered octahedra which share faces and vertices. The sequence ... ABACBC... (Jagodzinski notation *hcc*) of close-packed layers of oxygen and barium ions leads to layers of octahedra which share all vertices with pairs of octahedra formed by face-sharing. In accordance with a number of well known 6H perovskite ruthenates with general composition Ba₃MRu₂O₉ ($M = \text{Li}, \text{Na}, \text{Mg}, \text{Ca}, \text{In}$, and a large variety of $3d$ metals and rare earth metals) [1] and particularly the compound

Ba₃YRu₂O₉ [11], the pairs of octahedra were initially occupied by Ru and the additional octahedra by Y. The refinement cycles indicated less electron density within the pairs of octahedra, and indeed this site was found to be mixed occupied by Ru and Al in the following cycles. Occupation factors below unity occur for the oxygen site $6h$, which confirms a face-sharing of two octahedra. According to electron density maps there is a remaining peak in $(2/3, 1/3, 1/4)$ (= site $2d$), which is located in the center of the faces shared by the two octahedra. These results indicate a replacement of pairs of octahedra by pairs of tetrahedra. Additionally, the Ru or Al position was split into two partially occupied sites for Ru and Al, leading to interatomic distances for both RuO₆ octahedra and AlO₄ tetrahedra in the expected range (see below). Apparently, the Ba(2) atom site in direct neighborhood also reacts on the occurrence of pairs of octahedra or tetrahedra and consequently is also split into two positions along [001] resulting in the sites Ba(2a) and Ba(2b).

The final structure model of Ba₃YRu_{0.73(2)}Al_{1.27(2)}O₈ contains (Ru₂O₉) units which are partly replaced by (Al₂O₇) units. This fact is depicted in Fig. 1 showing a comparison of the structures with exclusively (Ru₂O₉) units (left) and exclusively (Al₂O₇) units (right), respectively. These pairs of polyhedra are connected *via* corners with two single layers of mutually isolated YO₆ octahedra. A similar partial replacement of octahedra was previously observed for the 6H perovskite α -Ba₂ScAlO₅ [12] with mixed occupation of face-sharing pairs of octahedra (Sc,Al)₂O₉ or vertex-sharing tetrahedra (Sc,Al)₂O₇, respectively. In general, replacement of single octahedra by single trigonal bipyramids or tetrahedra is well known in perovskite

Formula	Ba ₃ YRu _{0.73(2)} Al _{1.27(2)} O ₈	Ba ₅ Y ₂ Ru _{1.52(2)} Al _{1.47(2)} O _{13.5}
Cryst.size, mm ³	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.1
Crystal system	hexagonal	hexagonal
Space group	<i>P6₃/mmc</i> (No. 194)	<i>P6₃/mmc</i> (No. 194)
<i>a</i> , Å	5.871(1)	5.907(1)
<i>c</i> , Å	14.633(3)	24.556(5)
<i>V</i> , Å ³	436.81	742.03
<i>Z</i>	2	2
<i>D</i> _{calcd} , g cm ⁻³	7.039	5.641
<i>μ</i> (MoK _α), cm ⁻¹	31.881	22.634
<i>F</i> (000), e	639.26	1112.4
<i>hkl</i> range	±7, -8 → +6, ±20	-6 → +8, -8 → +7, ±33
((<i>sin θ</i>)/λ) _{max} , Å ⁻¹	0.735	0.617
Refl. measured	3146	5041
Refl. unique	275	427
<i>R</i> _{int}	0.029	0.043
Param. refined	28	32
<i>R</i> (<i>F</i>)/ <i>wR</i> (<i>F</i> ²) (all reflections)	0.035/0.069	0.057/0.114
GoF(<i>F</i> ²)	1.298	1.387
Δρ _{fin} (max/min), e Å ⁻³	1.35	2.57

Table 1. Measurement conditions and crystallographic data for Ba₃YRu_{0.73(2)}Al_{1.27(2)}O₈ and Ba₅Y₂Ru_{1.52(2)}Al_{1.47(2)}O_{13.5}.Fig. 2. Ba₃YRu_{0.73(2)}Al_{1.27(2)}O₈ and Ba₅Y₂Ru_{1.52(2)}Al_{1.47(2)}O_{13.5}: (Ru₂O₉) units (left) and (Al₂O₇) units (right) with a similar spatial extension, similar charge and possibility for mutual replacement. Middle: both units superimposed.

chemistry, both in a statistical disordered or an ordered manner [13, 14]. For a well known ordered example the mineral brownmillerite can be viewed as a variant of the cubic perovskite with every second layer of vertex-sharing octahedra replaced by parallel chains of vertex-sharing tetrahedra [15]. For the title compound Ba₃YRu_{0.73(2)}Al_{1.27(2)}O₈ the occupation of the centers of the octahedra or tetrahedra refines to about 60% Al and 40% Ru. The refinement of the oxygen positions results in a close to 50% replacement of pairs of octahedra by pairs of tetrahedra. With this information a speculation about the occupation of octahedra by Ru and of tetrahedra by Al is near at hand (Table 2): The composition might be written alternatively according to Ba₃Y(Ru₂O₉)_{1-x}(Al₂O₇)_x, *x* = 0.64, also indicating a solid solution series as suggested by chemical analysis results (see below). Fig. 2 (middle) shows an (Al₂O₇) unit inscribed into a (Ru₂O₉) unit including the necessary displacement of Al relative to the Ru

position along the crystallographic direction [001]. Such a correlation is even more pronounced for the second title compound Ba₅Y₂Ru_{1.52(2)}Al_{1.47(2)}O_{13.5} as will be discussed in the next paragraph.

The distances between Al and the bridging oxygen atom *d*(Al–O_{tet}) = 1.64(1) Å is clearly too short compared with similar distances for tetrahedrally coordinated Al (*e. g.* 1.76–1.78 Å in Na₅AlO₄ [16]). The main reason is the fixing of the bridging oxygen atom in a special position leading to a bond angle Al–O–Al of 180°, resulting in a large displacement parameter for oxygen, *i. e.* the tetrahedra are tilted against each other in the real structure. The distance of Al to the remaining oxygen atoms connecting to YO₆ octahedra *d*(Al–O_{tet}) = 1.766(8) Å are well in the expected range. On the other hand, the distances within the (Ru₂O₉) units with *d*(Ru–O_{oct}) = 1.928(7) Å (terminal), and 2.02(2) Å (bridging) are well in the predicted range. *E. g.* in Ba₃ZrRu₂O₉, with face-sharing (Ru₂O₉) pairs of octahedra, Ru⁴⁺–O distances of 1.99 Å were found [17], whereas the distances *d*(Y–O) in the YO₆ octahedra of 2.206(6) Å are comparable with those in Y₂O₃: *d*(Y–O) = 2.25–2.28 Å [18]. Selected distances are given in Table 3.

Unfortunately, chemical analysis data for the crystal used for structure refinements are not available. The data from several other crystals, however, support the above structure model. All crystals studied show an atomic metal ratio *n*(Ba) : *n*(Y) : *n*(Al + Ru) = 3 : 1 : 2 within experimental error, although mostly with a somewhat higher Al content. Typically, the composition results are in the range of Ba₃Y(Ru_{2-x}Al_x)O₉

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	Occupation	<i>U</i> _{eq} (Å ²)
Ba₃YRu_{0.73(2)}Al_{1.27(2)}O₈						
Ba(1)	2 <i>b</i>	0	0	1/4		0.0228(4)
Ba(2a)	4 <i>f</i>	1/3	2/3	0.0966(4)	1-occ(Ru)	0.020(1)
Ba(2b)	4 <i>f</i>	1/3	2/3	0.0761(6)	occ(Ru)	0.011(1)
Y	2 <i>a</i>	0	0	0		0.0103(4)
Ru*	4 <i>f</i>	1/3	2/3	0.6615(3)	0.364(8)	0.0075(9)
Al*	4 <i>f</i>	1/3	2/3	0.6382(7)	1-occ(Ru)	<i>U</i> _{eq} (Ru)
O(1a)*	6 <i>h</i>	0.486(2)	2 <i>x</i>	3/4	0.53(3)	0.025(5)
O(1b)*	2 <i>d</i>	1/3	2/3	1/4	0.41(7)	0.05(2)
O(2)	12 <i>k</i>	0.1740(7)	2 <i>x</i>	0.5899(4)		0.031(2)
Ba₅Y₂Ru_{1.52(2)}Al_{1.47(2)}O_{13.5}						
Ba(1)	2 <i>c</i>	1/3	2/3	1/4		0.0258(5)
Ba(2)	4 <i>e</i>	0	0	0.14484(6)		0.0165(4)
Ba(3)	4 <i>f</i>	1/3	2/3	0.54509(5)		0.0128(3)
Y(1)	4 <i>f</i>	1/3	2/3	0.10140(7)		0.0091(4)
Ru(1)	2 <i>a</i>	0	0	0		0.0070(5)
Ru(2)*	4 <i>f</i>	1/3	2/3	0.6953(3)	0.26(1)	0.007(1)
Al(2)*	4 <i>f</i>	1/3	2/3	0.6812(5)	1-occ(Ru(2))	<i>U</i> _{eq} (Ru(2))
O(1a)*	2 <i>d</i>	1/3	2/3	3/4	1-occ(Ru(2))	0.045(9)
O(1b)*	6 <i>h</i>	0.838(8)	2 <i>x</i>	1/4	occ(Ru(2))	<i>U</i> _{eq} (O(1a))
O(2)	12 <i>k</i>	0.1565(9)	2 <i>x</i>	0.0472(3)		0.017(2)
O(3)	12 <i>k</i>	0.507(1)	2 <i>x</i>	0.1542(4)		0.027(2)

Table 2. Crystal structure parameters of Ba₃YRu_{0.73(2)}Al_{1.27(2)}O₈ and Ba₅Y₂Ru_{1.52(2)}Al_{1.47(2)}O_{13.5}.

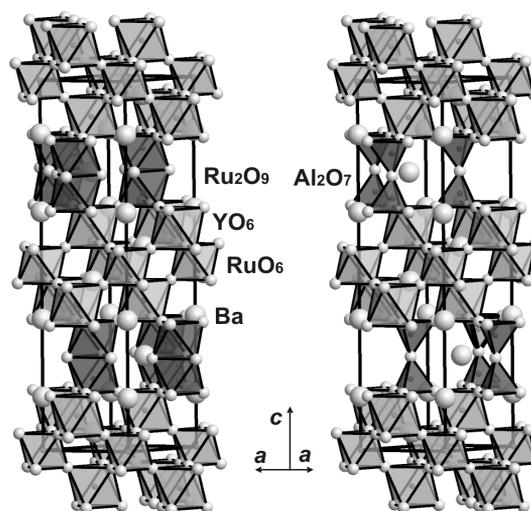
* Refined applying isotropic displacement parameters.

Table 3. Selected interatomic distances (Å) and angles (°) for Ba₃YRu_{0.73(2)}Al_{1.27(2)}O₈ and Ba₅Y₂Ru_{1.52(2)}Al_{1.47(2)}O_{13.5}.

Ba ₃ YRu _{0.73(2)} Al _{1.27(2)} O ₈			Ba ₅ Y ₂ Ru _{1.52(2)} Al _{1.47(2)} O _{13.5}			
Ba(1)	– O(2)	2.937(7)	6×	Ba(1)– O(3)	2.95(1)	6×
	– O(1a)	2.939(1)	6×	– O(1b)	2.954(1)	6×
Ba(2a)	– O(1a)	2.90(1)	3×	Ba(2)– O(2)	2.883(9)	3×
	– O(2)	2.9373(6)	6×	– O(3)	2.963(1)	6×
	– O(2)	3.173(8)	3×	– O(1b)	3.07(5)	3×
Ba(2b)	– O(2)	2.92(2)	3×	Ba(3)– O(2)	2.901(9)	3×
	– O(2)	2.9442(9)	6×	– O(2)	2.9558(6)	6×
	– O(1a)	3.14(1)	3×	– O(3)	3.14(1)	3×
Y	– O(2)	2.206(6)	6×	Y(1)– O(3)	2.20(1)	3×
Ru	– O(2)	1.928(7)	3×	– O(2)	2.245(9)	3×
	– O(1a)	2.02(2)	3×	Ru(1)– O(2)	1.977(9)	6×
Ru	– Ru	2.590(9)	1×	Ru(2)– O(3)	1.92(1)	3×
Al	– O(1b)	1.64(1)	1×	– O(1b)	2.21(7)	3×
	– O(2)	1.766(8)	3×	– Ru(2)	2.69(1)	1×
				Al(2)– O(1a)	1.69(1)	1×
				– O(3)	1.77(1)	3×

with $x = 1.60 - 1.90$. The apparently varying Al and Ru content also supports the view of statistic replacement of (Ru₂O₉) units by (Al₂O₇) units in favor of an ordered superstructure model. The variation of unit cell parameters within standard deviations of these crystals with different Al/Ru atomic ratios corroborates the proposed similar spatial extensions of (Ru₂O₉) and (Al₂O₇) units, necessary for partial statistical substitution together with only weakly locally disturbed crystal structures.

In compounds Ba₃MRu₂O₉ the distance $d(\text{Ru}-\text{Ru})$ within the pairs of octahedra depends

Fig. 3. Ba₅Y₂Ru_{1.52(2)}Al_{1.47(2)}O_{13.5}: Sections of the 10H perovskite crystal structure with (Ru₂O₉) units (dark grey) vertex-sharing with YO₆ octahedra (light grey), left (Al₂O₇) units replacing the (Ru₂O₉) units, right, indicating the two ordered limiting structure models. Additional RuO₆ octahedra (light grey) share vertices with YO₆ octahedra.

on the oxidation state of Ru. Provided oxidation states of Ba²⁺, Y³⁺, Al³⁺ and O²⁻, for the composition Ba₃YRu_{0.73(2)}Al_{1.27(2)}O₈ the oxidation state of Ru calculates to +4.4. In compounds Ba₃MRu₂O₉ a distance $d(\text{Ru}-\text{Ru})$ in the range of 2.5 to 2.6 Å is expected for Ru^{+4.5} [10,20]. In the investigated compound

the corresponding distance $d(\text{Ru-Ru})$ was found at 2.590(9) Å.

Ba₅Y₂Ru_{1.52(2)}Al_{1.47(2)}O_{13.5}

The features described above are similarly present in Ba₅Y₂Ru_{1.52(2)}Al_{1.47(2)}O_{13.5}. This phase crystallizes in a 10H perovskite stacking variant with the sequence ... ABCBACBABC... of close-packed layers formed by O²⁻ and Ba²⁺ (Jagodzinski notation *hcccc*). This stacking leads to three-layer blocks of vertex-sharing octahedra, which can be viewed as a section of the cubic perovskite connected *via* layers of pairs of octahedra. Electron densities led to the occupation of these units with Ru and Al. Further octahedra vertex-sharing with these pairs located in adjacent layers are occupied by Y. Finally, the remaining octahedra of perovskite-type slaps (vertex-sharing with the YO₆ octahedra) are occupied by Ru, sandwiched by the two layers of Y-centered octahedra. As discussed for the first title compound, again (Ru₂O₉) units are partly replaced by (Al₂O₇) units. Fig. 3 shows the comparison of the ideal crystal structure of a 10H perovskite with exclusively (Ru₂O₉) units (left) and with exclusively (Al₂O₇) units (right). The spatial extension of both building blocks is depicted in Fig. 2. The speculation on the occupation of octahedra exclusively by Ru and of tetrahedra solely by Al is confirmed by the occupation with about 26% Ru and 74% Al and concomitantly a proportion of about 74% tetrahedra (Table 2). The composition might thus be written as Ba₅Y₂RuO₆(Ru₂O₉)_{1-x}(Al₂O₇)_x, $x = 0.74(1)$. A variable oxygen content relative to the sum of the metal atoms in the formula was previously reported for (Ba,Sr)₅R_{2-x}Al₂Zr_{1+x}O_{13+x/2} ($R = \text{Gd-Lu, Y, Sc}$) in the 10H perovskite structure variant with exclusively (Al₂O₇) units. In this structure variant the extra oxygen atoms are introduced in a different position, which is only surrounded by Ba in a trigonal bipyramidal fashion in the nearly unchanged parent structure [21]. Occupation of this particular site is not indicated by the X-ray diffraction data for the title compound and structurally partially prohibited considering the resulting short distances $d(\text{O-O})$ at positions where an (Al₂O₇) unit is replaced by a (Ru₂O₉) unit.

Again the feature of a comparably short distance $d(\text{Al-O}) = 1.69(1)$ Å for the vertex-condensation of the tetrahedra is present together with the larger displacement parameter for the respective oxygen site, indicating a deviation from 180° for the Al-O-Al angle.

Such a deviation was previously reported at the bridging oxygen atom of (Al₂O₇) units in Ba₅In₂Al₂ZrO₁₃ with the 10H perovskite structure variant showing exclusively pairs of tetrahedra [22]. The bridging oxygen site was split into three positions with inter-site distances of about 0.7 Å, leading to an angle Al-O_{bridge}-Al of 152°.

As for Ba₃YRu_{0.73(2)}Al_{1.27(2)}O₈, chemical analysis data for the crystal used for structure refinements are not available. The atomic ratios $n(\text{Ba}) : n(\text{Y}) : n(\text{Ru} + \text{Al}) = 5 : 2 : 3$ were found within experimental error. The Ru content varied in the range of 0.15–1.35 in the formula unit. Again, the apparently varying Al and Ru contents support the view of statistic replacement of (Ru₂O₉) by (Al₂O₇) units in favor of a completely ordered superstructure model.

The Ru-Ru spacing of 2.69(2) Å within the (Ru₂O₉) units indicates an oxidation state of +5 according to the distance criterion [19, 20]. Provided the oxidation states of +2 for Ba, +3 for Y, and -2 for O, an average oxidation state of +4.3 of Ru is calculated from the composition. However, we observe two Ru sites in the crystal structure. Assuming an oxidation state of +4 for Ru(1) located in octahedra exclusively sharing vertices with YO₆ octahedra leads directly to an assignment of +5 for Ru(2) in the (Ru₂O₉) units. This oxidation state of Ru in the (Ru₂O₉) units additionally leads to similar charges for both the (Ru₂O₉) and the (Al₂O₇) units. All further distances are in the range known from similar compounds (compare Table 3 and previous section).

Conclusions

We present two new ruthenate phases with 6H and 10H perovskite structures. Due to extensive replacement of Ru by Al significant numbers of face-sharing pairs of octahedra (Ru₂O₉) are substituted by vertex-sharing pairs of tetrahedra (Al₂O₇). Due to the very similar size and charge of these two building blocks the replacement occurs without a major structural effect, but certainly leads to local distortions of the crystal structures. The oxidation state of Ru can reliably be established from the distances $d(\text{Ru-Ru})$ within the (Ru₂O₉) units.

Experimental Section

Synthesis

Dark red single crystals of the new compounds Ba₃YRu_{0.73(2)}Al_{1.27(2)}O₈ and

Ba₅Y₂Ru_{1.52(2)}Al_{1.47(2)}O_{13.5} have been grown from powder mixtures of BaCO₃ (MaTeck, 99.99%), Y₂O₃ (Alfa Aesar 99.98%), CuO (MaTeck, 99.99%), Al₂O₃ (Alfa Aesar 99.99%), RuO₂ (Berg- und Hüttenkombinat Freiberg, 99.9%), molar ratio Ba:Y:Cu:Al:Ru 5:2.4:1.2:0.86:0.46 and with addition of Pt for the first phase on ZrO₂ bars in alumina crucibles. The mixtures were heated to 1373 K and annealed for 17 h. Afterwards, they were cooled to ambient temperature with a rate of 600 K h⁻¹. Small red single crystals of the new compounds were found in the contact zones with the ZrO₂ bars. The bulk material contained a variety of mostly unknown phases.

Single crystal X-ray structure determination

Red single crystals were mechanically extracted from the surfaces of the respective samples. The measurements of intensity data were carried out at 295 K on a four-circle diffractometer Rigaku AFC-7, equipped with a Mercury CCD-detector (scan mode φ/ω , $\Delta = 0.6^\circ$, 120 s per image), using MoK α radiation ($\lambda = 0.71073$ Å). The positions of the metal atoms were established by Patterson Methods (SHELXS-97-2 [10]). The remaining atomic positions of oxygen were taken from difference Fourier syntheses. The final full-matrix least-squares refinements converged at $R1 = 0.035$, $wR2 = 0.069$ for Ba₃YRu_{0.73(2)}Al_{1.27(2)}O₈ and at $R1 = 0.057$, $wR2 = 0.114$ for Ba₅Y₂Ru_{1.52(2)}Al_{1.47(2)}O_{13.5} (SHELXL-97-2 [11]). Occupational factors of the metal atom sites were chosen as described in the discussion section. Crystallographic data and measurement conditions are summarized in Table 1. Positional and occupation parameters are given in Table 2. Structure refinements in non-centrosymmetric subgroups of $P6_3/mmc$, namely $P6_3mc$, $P\bar{6}2c$ and $P31c$, which

may lead to an ordered occupation of oxygen sites, did not resolve the disorder in the oxide substructure and did not lead to any higher partial order in the metal substructure. No indications for larger unit cells (superstructure reflections) or lower space group symmetry (extinctions) were observed.

Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-418121 (Ba₃YRu_{0.73(2)}Al_{1.27(2)}O₈) and CSD-418122 (Ba₅Y₂Ru_{1.52(2)}Al_{1.47(2)}O_{13.5}).

Electron probe X-ray microanalysis (EPMA)

The chemical compositions of several single crystals with identical lattice parameters within standard deviations of the determination on the single crystal diffractometer were measured by electron probe X-ray microanalysis (EPMA) using a wavelength-dispersive X-ray (WDX) spectrometer (SEM-Q, Applied Research Lab, USA). Pure metals Al and Cu as well as RuO₂ for Ru, ZrO₂ for Zr and YBa₂Cu₃O₇ for Ba and Y were applied as standard materials for quantification of the elements in a single crystal. Pt was not detected, Cu and Zr only occasionally and in negligible amounts. The oxygen content can not be reliably determined with this technique.

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