# Ba<sub>3</sub>YRu<sub>0.73(2)</sub>Al<sub>1.27(2)</sub>O<sub>8</sub> and Ba<sub>5</sub>Y<sub>2</sub>Ru<sub>1.52(2)</sub>Al<sub>1.47(2)</sub>O<sub>13.5</sub>: New Perovskite Ruthenates with Partial Octahedra Replacement

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Dark red single crystals of the new phases Ba<sub>3</sub>YRu<sub>0.73(2)</sub>Al<sub>1.27(2)</sub>O<sub>8</sub> and Ba<sub>5</sub>Y<sub>2</sub>Ru<sub>1.52(2)</sub>Al<sub>1.47(2)</sub>O<sub>13.5</sub> have been grown from powder mixtures of BaCO<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and RuO<sub>2</sub>. The compositions given in the formulas result from the refinements of the crystal structures based on single crystal X-ray diffraction data (hexagonal *P*6<sub>3</sub>/*mmc* (No. 194), Z = 2, Ba<sub>3</sub>YRu<sub>0.73(2)</sub>Al<sub>1.27(2)</sub>O<sub>8</sub>: a = 5.871(1), c = 14.633(3) Å, R1 = 0.035, wR2 = 0.069 and Ba<sub>5</sub>Y<sub>2</sub>Ru<sub>1.52(2)</sub>Al<sub>1.47(2)</sub>O<sub>13.5</sub>: a = 5.907(1), c = 24.556(5) Å, R1 = 0.057, wR2 = 0.114). Ba<sub>3</sub>YRu<sub>0.73(2)</sub>Al<sub>1.27(2)</sub>O<sub>8</sub> crystallizes in a 6H perovskite structure, Ba<sub>5</sub>Y<sub>2</sub>Ru<sub>1.52(2)</sub>Al<sub>1.47(2)</sub>O<sub>13.5</sub> has been characterized as a 10H Perovskite. Due to similar spatial extensions of (Ru<sub>2</sub>O<sub>9</sub>) face-sharing pairs of octahedra and (Al<sub>2</sub>O<sub>7</sub>) vertex-sharing pairs of tetrahedra, both structures show partial mutual substitution of these units. Consequently, the title compounds may be written as Ba<sub>3</sub>Y(Ru<sub>2</sub>O<sub>9</sub>)<sub>1-x</sub>(Al<sub>2</sub>O<sub>7</sub>)<sub>x</sub>, x = 0.64(1) and Ba<sub>5</sub>Y<sub>2</sub>Ru<sub>0.6</sub>(Ru<sub>2</sub>O<sub>9</sub>)<sub>1-x</sub>(Al<sub>2</sub>O<sub>7</sub>)<sub>x</sub>, 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<sub>2</sub>O<sub>9</sub>) units, as can be derived from the distances *d*(Ru–Ru), additionally leads to similar charges of both the (Ru<sub>2</sub>O<sub>9</sub>) and the (Al<sub>2</sub>O<sub>7</sub>) 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 vertexsharing 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 BaRu<sub>6</sub>O<sub>12</sub> [2]) up to +5 (in Ba<sub>5</sub>Ru<sub>2</sub>O<sub>10</sub> and Ba<sub>5</sub>Ru<sub>2</sub>O<sub>11</sub> [3–5]). Ru in the oxidation state +4 is present in the different modifications of BaRuO<sub>3</sub>. The r.t. form resembles a 9R perovskite (stacking sequence hhc) with a three-dimensional framework  ${}^{3}_{\infty}[(Ru_{3}O_{6}O_{6/2})^{6-}]$  [6]. At p = 15 kbar, 9R BaRuO<sub>3</sub> transforms to the 4H (hc) structure type [7] (also prepared at ambient pressure [8]) with pairs of face-sharing octahedra (Ru<sub>2</sub>O<sub>9</sub>) being interconnected *via* 

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the corners, *i. e.*  ${}_{\infty}^{3}[(\text{Ru}_{2}\text{O}_{3}\text{O}_{6/2})^{4-}]$ . A further transformation takes place at p = 30 kbar leading to 6H BaRuO<sub>3</sub> (hcc) with pairs of octahedra interconnected with further octahedra exclusively *via* corners, *i. e.*  ${}_{\infty}^{3}[(\text{Ru}_{2}\text{O}_{3}\text{O}_{6/2})^{4-}(\text{Ru}\text{O}_{6/2})^{2-}]$  [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**

## $Ba_3YRu_{0.73(2)}Al_{1.27(2)}O_8$

Ba<sub>3</sub>YRu<sub>0.73(2)</sub>Al<sub>1.27(2)</sub>O<sub>8</sub> 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 Ba3YAl2O7.5 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 metalcentered octahedra which share faces and vertices. The sequence ... ABACBC... (Jagodinski 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  $Ba_3MRu_2O_9$  (M = Li, Na, Mg, Ca, In, and a large variety of 3d metals and rare earth metals) [1] and particularly the compound

Fig. 1. Ba<sub>3</sub>YRu<sub>0.73(2)</sub>Al<sub>1.27(2)</sub>O<sub>8</sub>: Sections of the 6H perovskite crystal structure with (Ru<sub>2</sub>O<sub>9</sub>) units (dark grey) vertex-sharing with YO<sub>6</sub> octahedra (light grey), left, (Al<sub>2</sub>O<sub>7</sub>) units replacing the (Ru<sub>2</sub>O<sub>9</sub>) units, right, indicating the two ordered limiting structure models.

 $Ba_3YRu_2O_9$  [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 RuO<sub>6</sub> octahedra and AlO<sub>4</sub> 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

Ba<sub>3</sub>YRu<sub>0.73(2)</sub>Al<sub>1.27(2)</sub>O<sub>8</sub> contains (Ru<sub>2</sub>O<sub>9</sub>) units which are partly replaced by (Al<sub>2</sub>O<sub>7</sub>) units. This fact is depicted in Fig. 1 showing a comparison of the structures with exclusively (Ru<sub>2</sub>O<sub>9</sub>) units (left) and exclusively (Al<sub>2</sub>O<sub>7</sub>) units (right), respectively. These pairs of polyhedra are connected *via* corners with two single layers of mutually isolated YO<sub>6</sub> octahedra. A similar partial replacement of octahedra was previously observed for the 6H perovskite  $\alpha$ -Ba<sub>2</sub>ScAlO<sub>5</sub> [12] with mixed occupation of face-sharing pairs of octahedra (Sc,Al)<sub>2</sub>O<sub>9</sub> or vertexsharing tetrahedra (Sc,Al)<sub>2</sub>O<sub>7</sub>, respectively. In general, replacement of single octahedra by single trigonal bipyramides or tetrahedra is well known in perovskite

	D- VD- A1 O	D- V D- Al O	Table 1 Measurement conditions
Formula	Ba <sub>3</sub> Y $Ru_{0.73(2)}AI_{1.27(2)}O_8$	Bas $r_2 Ru_{1.52(2)} AI_{1.47(2)} O_{13.5}$	and crystallographic data for
Cryst.size, mm <sup>3</sup>	$0.2 \times 0.2 \times 0.1$	$0.2 \times 0.2 \times 0.1$	Da VD Al O and
Crystal system	hexagonal	hexagonal	Ba <sub>3</sub> i $Ru_{0.73(2)}AI_{1.27(2)}O_8$ and
Space group	<i>P</i> 6 <sub>3</sub> / <i>mmc</i> (No. 194)	<i>P</i> 6 <sub>3</sub> / <i>mmc</i> (No. 194)	$Ba_5Y_2Ru_{1.52(2)}Al_{1.47(2)}O_{13.5}.$
<i>a</i> , Å	5.871(1)	5.907(1)	
<i>c</i> , Å	14.633(3)	24.556(5)	
<i>V</i> , Å <sup>3</sup>	436.81	742.03	
Ζ	2	2	
$D_{\rm calcd}, {\rm g}{\rm cm}^{-3}$	7.039	5.641	
$\mu$ (Mo $K_{\alpha}$ ), cm <sup>-1</sup>	31.881	22.634	
<i>F</i> (000), e	639.26	1112.4	
hkl range	$\pm 7, -8 \rightarrow +6, \pm 20$	$-6 \rightarrow +8, -8 \rightarrow +7, \pm 33$	
$((\sin\theta)/\lambda)_{\rm max}$ , Å <sup>-1</sup>	0.735	0.617	
Refl. measured	3146	5041	
Refl. unique	275	427	
R <sub>int.</sub>	0.029	0.043	
Param. refined	28	32	
$R(F)/wR(F^2)$ (all reflections)	0.035/0.069	0.057/0.114	
$GoF(F^2)$	1.298	1.387	
$\Delta \rho_{\rm fin}$ (max/min), e Å <sup>-3</sup>	1.35	2.57	



Fig. 2. Ba<sub>3</sub>YRu<sub>0.73(2)</sub>Al<sub>1.27(2)</sub>O<sub>8</sub> and  $Ba_5Y_2Ru_{1.52(2)}Al_{1.47(2)}O_{13.5}$ : (Ru<sub>2</sub>O<sub>9</sub>) units (left) and (Al<sub>2</sub>O<sub>7</sub>) 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  $Ba_3YRu_{0.73(2)}Al_{1.27(2)}O_8$  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 Ba<sub>3</sub>Y(Ru<sub>2</sub>O<sub>9</sub>)<sub>1-x</sub>(Al<sub>2</sub>O<sub>7</sub>)<sub>x</sub>, x = 0.64, also indicating a solid solution series as suggested by chemical analysis results (see below). Fig. 2 (middle) shows an (Al<sub>2</sub>O<sub>7</sub>) unit inscribed into a (Ru<sub>2</sub>O<sub>9</sub>) 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 Ba<sub>5</sub>Y<sub>2</sub>Ru<sub>1.52(2)</sub>Al<sub>1.47(2)</sub>O<sub>13.5</sub> 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 Na<sub>5</sub>AlO<sub>4</sub> [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 YO<sub>6</sub> octahedra  $d(Al-O_{tet}) = 1.766(8)$  Å are well in the expected range. On the other hand, the distances within the  $(Ru_2O_9)$  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 Ba<sub>3</sub>ZrRu<sub>2</sub>O<sub>9</sub>, with face-sharing (Ru<sub>2</sub>O<sub>9</sub>) pairs of octahedra, Ru<sup>4+</sup>–O distances of 1.99 Å were found [17], whereas the distances d(Y-O) in the YO<sub>6</sub> octahedra of 2.206(6) Å are comparable with those in  $Y_2O_3$ : 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  $Ba_3Y(Ru_{2-x}Al_x)O_y$ 

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Atom	Site	x	у	z	Occupation	$U_{\rm eq}({\rm \AA}^2)$	
Ba <sub>3</sub> YRu <sub>0.73(2)</sub> Al <sub>1.27(2)</sub> O <sub>8</sub>							
Ba(1)	2b	0	0	1/4		0.0228(4)	
Ba(2a)	4f	1/3	2/3	0.0966(4)	1-occ(Ru)	0.020(1)	
Ba(2b)	4f	1/3	2/3	0.0761(6)	occ(Ru)	0.011(1)	
Y	2a	0	0	0		0.0103(4)	
Ru*	4f	1/3	2/3	0.6615(3)	0.364(8)	0.0075(9)	
Al*	4f	1/3	2/3	0.6382(7)	1-occ(Ru)	$U_{\rm eq}({\rm Ru})$	
O(1a)*	6h	0.486(2)	2x	3/4	0.53(3)	0.025(5)	
O(1b)*	2d	1/3	2/3	1/4	0.41(7)	0.05(2)	
O(2)	12k	0.1740(7)	2x	0.5899(4)		0.031(2)	
$Ba_5Y_2Ru_{1,52(2)}Al_{1,47(2)}O_{13,5}$							
Ba(1)	2c	1/3	2/3	1/4		0.0258(5)	
Ba(2)	4e	Ó	Ó	0.14484(6)		0.0165(4)	
Ba(3)	4f	1/3	2/3	0.54509(5)		0.0128(3)	
Y(1)	4f	1/3	2/3	0.10140(7)		0.0091(4)	
Ru(1)	2a	Ó	Ó	0		0.0070(5)	
Ru(2)*	4f	1/3	2/3	0.6953(3)	0.26(1)	0.007(1)	
$Al(2)^*$	4f	1/3	2/3	0.6812(5)	$1 - \operatorname{occ}(\operatorname{Ru}(2))$	$U_{\rm eq}({\rm Ru}(2))$	
O(1a)*	2d	1/3	2/3	3/4	1-occ(Ru(2))	0.045(9)	
O(1b)*	6h	0.838(8)	2x	1/4	occ(Ru(2))	$U_{eq}(O(1a))$	
O(2)	12k	0.1565(9)	2x	0.0472(3)		0.017(2)	
O(3)	12k	0.507(1)	2x	0.1542(4)		0.027(2)	

\* Refined applying isotropic displacement parameters.

Table 3. Selected interatomic distances (Å) and angles (°) for
$Ba_3YRu_{0.73(2)}Al_{1.27(2)}O_8$ and
$Ba_5Y_2Ru_{1.52(2)}Al_{1.47(2)}O_{13.5}.$

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

with x = 1.60 - 1.90. The apparently varying Al and Ru content also supports the view of statistic replacement of (Ru<sub>2</sub>O<sub>9</sub>) units by (Al<sub>2</sub>O<sub>7</sub>) 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 (Ru<sub>2</sub>O<sub>9</sub>) and (Al<sub>2</sub>O<sub>7</sub>) units, necessary for partial statistical substitution together with only weakly locally disturbed crystal structures.

In compounds  $Ba_3MRu_2O_9$  the distance d(Ru-Ru) within the pairs of octahedra depends



Fig. 3. Ba<sub>5</sub>Y<sub>2</sub>Ru<sub>1.52(2)</sub>Al<sub>1.47(2)</sub>O<sub>13.5</sub>: Sections of the 10H perovskite crystal structure with (Ru<sub>2</sub>O<sub>9</sub>) units (dark grey) vertex-sharing with YO<sub>6</sub> octahedra (light grey), left (Al<sub>2</sub>O<sub>7</sub>) units replacing the (Ru<sub>2</sub>O<sub>9</sub>) units, right, indicating the two ordered limiting structure models. Additional RuO<sub>6</sub> octahedra (light grey) share vertices with YO<sub>6</sub> octahedra.

on the oxidation state of Ru. Provided oxidation states of  $Ba^{2+}$ ,  $Y^{3+}$ ,  $Al^{3+}$  and  $O^{2-}$ , for the composition  $Ba_3YRu_{0.73(2)}Al_{1.27(2)}O_8$  the oxidation state of Ru calculates to +4.4. In compounds  $Ba_3MRu_2O_9$  a distance d(Ru-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(Ru-Ru) was found at 2.590(9) Å.

## $Ba_5Y_2Ru_{1.52(2)}Al_{1.47(2)}O_{13.5}$

The features described above are similarly present in  $Ba_5Y_2Ru_{1.52(2)}Al_{1.47(2)}O_{13.5}$ . This phase crystallizes in a 10H perovskite stacking variant with the sequence ... ABCBACBABC... of close-packed layers formed by  $O^{2-}$  and  $Ba^{2+}$  (Jagodinski 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 vertexsharing with these pairs located in adjacent layers are occupied by Y. Finally, the remaining octahedra of perovskite-type slaps (vertex-sharing with the YO<sub>6</sub> octahedra) are occupied by Ru, sandwiched by the two layers of Y-centered octahedra. As discussed for the first title compound, again (Ru<sub>2</sub>O<sub>9</sub>) units are partly replaced by (Al<sub>2</sub>O<sub>7</sub>) units. Fig. 3 shows the comparison of the ideal crystal structure of a 10H perovskite with exclusively (Ru<sub>2</sub>O<sub>9</sub>) units (left) and with exclusively (Al<sub>2</sub>O<sub>7</sub>) 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 Ba<sub>5</sub>Y<sub>2</sub>RuO<sub>6</sub>(Ru<sub>2</sub>O<sub>9</sub>)<sub>1-x</sub>(Al<sub>2</sub>O<sub>7</sub>)<sub>x</sub>, x = 0.74(1). A variable oxygen content relative to the sum of the metal atoms in the formula was previously reported for  $(Ba,Sr)_5R_{2-x}Al_2Zr_{1+x}O_{13+x/2}$  (*R* = Gd–Lu, Y, Sc) in the 10H perovskite structure variant with exclusively  $(Al_2O_7)$  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(O-O) at positions where an  $(Al_2O_7)$ unit is replaced by a (Ru<sub>2</sub>O<sub>9</sub>) unit.

Again the feature of a comparably short distance d(AI-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  $(Al_2O_7)$  units in  $Ba_5In_2Al_2ZrO_{13}$ with the 10H perovskite structure variant showing exclusively pairs of tetrahedra [22]. The bridging oxygen site was split into three positions with intersite distances of about 0.7 Å, leading to an angle  $Al-O_{bridge}$ -Al of 152°.

As for Ba<sub>3</sub>YRu<sub>0.73(2)</sub>Al<sub>1.27(2)</sub>O<sub>8</sub>, chemical analysis data for the crystal used for structure refinements are not available. The atomic ratios n(Ba) : n(Y) : n(Ru + 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  $(Ru_2O_9)$  by  $(Al_2O_7)$  units in favor of a completely ordered superstructure model.

The Ru–Ru spacing of 2.69(2) Å within the (Ru<sub>2</sub>O<sub>9</sub>) 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 YO<sub>6</sub> octahedra leads directly to an assignment of +5 for Ru(2) in the (Ru<sub>2</sub>O<sub>9</sub>) units. This oxidation state of Ru in the (Ru<sub>2</sub>O<sub>9</sub>) units additionally leads to similar charges for both the (Ru<sub>2</sub>O<sub>9</sub>) and the (Al<sub>2</sub>O<sub>7</sub>) 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 ( $Ru_2O_9$ ) are substituted by vertex-sharing pairs of tetrahedra ( $Al_2O_7$ ). 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(Ru-Ru) within the ( $Ru_2O_9$ ) units.

#### **Experimental Section**

Synthesis

Dark red single crystals of the new compounds  $Ba_3YRu_{0.73(2)}Al_{1.27(2)}O_8$  and

Ba<sub>5</sub>Y<sub>2</sub>Ru<sub>1.52(2)</sub>Al<sub>1.47(2)</sub>O<sub>13.5</sub> have been grown from powder mixtures of BaCO<sub>3</sub> (MaTeck, 99.99%), Y<sub>2</sub>O<sub>3</sub> (Alfa Aesar 99.98%), CuO (MaTeck, 99.99%), Al<sub>2</sub>O<sub>3</sub> (Alfa Aesar 99.99%), RuO<sub>2</sub> (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 ZrO<sub>2</sub> 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<sup>-1</sup>. Small red single crystals of the new compounds were found in the contact zones with the ZrO<sub>2</sub> 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 CCDdetector (scan mode  $\varphi/\omega$ ,  $\Delta = 0.6^{\circ}$ , 120 s per image), using Mo $K_{\alpha}$  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 Ba<sub>3</sub>YRu<sub>0.73(2)</sub>Al<sub>1.27(2)</sub>O<sub>8</sub> and at R1 = 0.057, wR2 = 0.114 for Ba<sub>5</sub>Y<sub>2</sub>Ru<sub>1.52(2)</sub>Al<sub>1.47(2)</sub>O<sub>13.5</sub> (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  $P6_3mc$ ,  $P\overline{6}2c$  and P31c, which

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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\_anfor derung.html) on quoting the deposition numbers CSD-418121 (Ba<sub>3</sub>YRu<sub>0.73(2)</sub>Al<sub>1.27(2)</sub>O<sub>8</sub>) and CSD-418122 (Ba<sub>5</sub>Y<sub>2</sub>Ru<sub>1.52(2)</sub>Al<sub>1.47(2)</sub>O<sub>13.5</sub>).

### 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 (SEMQ, Applied Research Lab, USA). Pure metals Al and Cu as well as RuO<sub>2</sub> for Ru, ZrO<sub>2</sub> for Zr and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> 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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