

BaFe_{3.39(5)}Ru_{2.61(5)}O₁₁ and BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁ Preparation, Crystal Structures, and Magnetic and Transport Properties of Quaternary Transition Metal Oxoruthenates

Barbara Schüpp-Niewa^a, Larisa Shlyk^b, Sergej Kryukov^b, Lance E. De Long^b, and Rainer Niewa^a

^a Department Chemie, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

^b Department Physics & Astronomy, University of Kentucky, Lexington, KY 40506, USA

Reprint requests to Prof. Dr. Rainer Niewa. Fax: +49 (89) 289 13762.
E-mail: rainer.niewa@ch.tum.de

Z. Naturforsch. **2007**, 62b, 753 – 758; received February 8, 2007

Black plate-like single crystals of BaFe_{3.39(5)}Ru_{2.61(5)}O₁₁ and BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁ were grown from a BaCl₂ flux [hexagonal, space group *P6₃/mmc* (No. 194), Fe: *a* = 5.856(1), *c* = 13.587(1) Å, *R*1 = 0.029, *wR*2 = 0.084; Co: *a* = 5.842(1), *c* = 13.573(3) Å, *R*1 = 0.033, *wR*2 = 0.075]. The crystal structures contain two crystallographic sites with mixed Ru and Fe/Co occupation of different level in octahedral coordination and one site purely occupied by the respective 3*d* metal. The latter position is in trigonal bipyramidal coordination, with some indication for a displacement of the metal atom towards tetrahedral coordination. According to the charge balance, the ruthenium atoms are incorporated with different electronic situations in the two Ru containing sites. The Co compound may be described as containing Co²⁺ and Ru⁵⁺ next to Ru³⁺. Magnetic susceptibility data support this assignment. According to magnetization measurements on oriented crystals, BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁ is a soft ferromagnetic material with low coercive field and a spontaneous magnetization below *T*_c = 105 K. It behaves as an electric conductor. However, BaFe_{3.39(5)}Ru_{2.61(5)}O₁₁ is a narrow band semiconductor material with ferrimagnetic ordering at *T*_c = 440 K.

Key words: Oxoruthenates, Ferrates, Cobaltates, Magnetism, Crystal Structure

Introduction

Recently oxoruthenates have attracted considerable attention due to their electronic and magnetic properties. Those 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 octahedrally coordinated Ru connected with additional tetrahedrally coordinated metal species. An extensive review on the crystal chemistry of ruthenates has recently appeared [1]. We have put some effort in the growth of large single crystals of barium ruthenates containing a further transition metal of the third period of the PSE, with the aim of elucidating the crystal structures and magnetic properties of these attractive compounds. One focus has been set on the interdependence of magnetic properties and chem-

ical composition known to be frequently in a delicate balance in oxoruthenates.

Results and Discussion

Crystal structure and composition

In systems of the type Ba*M*₂Ru₄O₁₁ compounds with *M* = Mn, Fe, Co are known. Already the first report on BaFe₂Ru₄O₁₁ indicated the presence of Fe-Ru mixed occupied crystallographic positions [2]. Particularly the Mn-containing compound was recently studied in detail with focus on the Mn-Ru distribution in the crystal structure and the magnetic structure and properties [3]. All reported samples were previously produced in microcrystalline form from “appropriate ratios” of starting materials, leading to single phase materials with the reported ideal compositions. Crystals grown from a BaCl₂ flux in this work are inherently not restricted to a fixed composition.

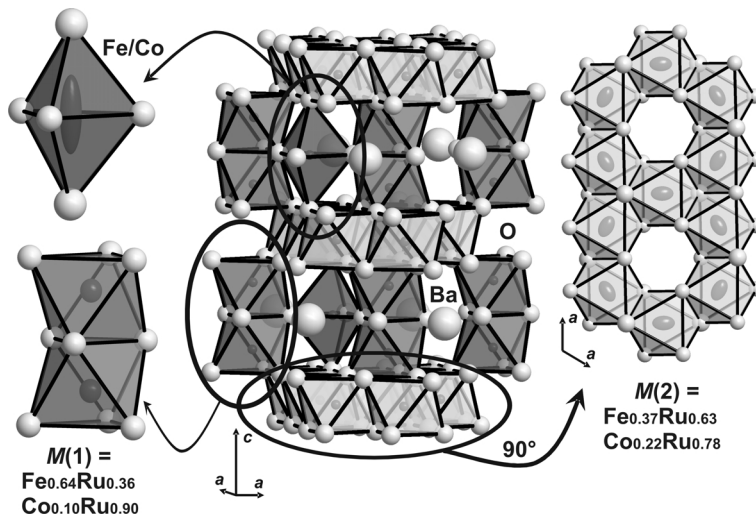


Table 1. Crystal structure data for BaFe_{3.39(5)}Ru_{2.61(5)}O₁₁ and BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁.

Formula	BaFe _{3.39(5)} Ru _{2.61(5)} O ₁₁	BaCo _{1.85(6)} Ru _{4.15(6)} O ₁₁
Crystal size, mm ³	0.08 × 0.05 × 0.001	0.05 × 0.03 × 0.001
Crystal system	hexagonal	hexagonal
Space group	<i>P6₃/mmc</i>	<i>P6₃/mmc</i>
<i>a</i> , Å	5.856(1)	5.842(1)
<i>c</i> , Å	13.587(1)	13.573(3)
<i>V</i> , Å ³	403.5	398.2
<i>Z</i>	2	2
<i>D</i> _{calcd} , g cm ⁻³	6.32	7.02
<i>μ</i> (MoK _α), mm ⁻¹	15.5	16.3
<i>F</i> (000), e	694.0	753.0
<i>hkl</i> Range	±7, ±7, ±17	±7, ±7, ±17
2 θ _{max} , deg	55.85	55.72
Refl. measured	6001	5990
Refl. unique	217	216
<i>R</i> _{int}	0.045	0.047
Param. refined	22	22
<i>R</i> (<i>F</i>)/ <i>wR</i> (<i>F</i> ²)	0.029/0.084	0.033/0.075
(all refl.)		
GoF (<i>F</i> ²) ^a	1.413	1.053
$\Delta\rho_{fin}$ (max/min), e Å ⁻³	1.30	0.86

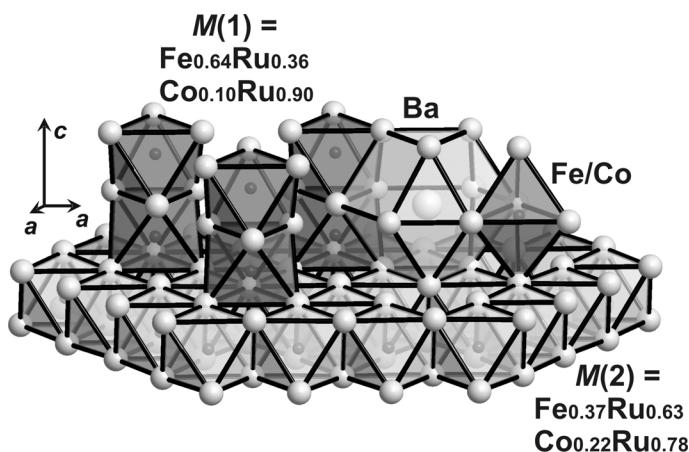
The crystal structures of compounds of the type BaM₂Ru₄O₁₁ were previously described in detail [2, 3]. Tables 1 and 2 give selected data on the crystal structure determinations and refinements. Ba and O form the motif of a distorted hexagonal close packing with Ba consequently located in *anti*-cuboctahedral coordination by O (see Figs. 1 and 2). Ru and Fe/Co occupy octahedral and trigonal bipyramidal interstices of this packing exclusively formed by O. Two crystallographic positions are mixed occupied by *M* and Ru in different ratios and surrounded octahedrally by O,

localized in the centers of 10 of 24 available octahedral holes of the hexagonal packing (including those formed with participation of Ba). In every third layer, 3/4 of the octahedral holes are occupied by *M*(2) forming layers of edge-sharing octahedra. These layers are interconnected in the third dimension by *M*(1)O₆ octahedra, which share faces with the unoccupied octahedra within the layers. The *M*(1)O₆ octahedra themselves share faces, leading to pairs of octahedra. Within the layers with *M*(1) sites (two out of three layers) only 1/4 of the octahedral holes are occupied. In this way the pairs of octahedra are not directly interconnected, but separated by the barium ions. As a remarkable feature of the structure, O(3) as a part of the close packing connects four octahedra *via* vertices, but does not coordinate to Ba. The crystal structure is completed by sites purely occupied by Fe or Co. These *d*-metal species are in trigonal bipyramidal surrounding by O (*i.e.* in voids of two face-sharing tetrahedra) located within the layer of the pairs of octahedra. Earlier refinements based on powder diffraction data indicated small intermixing of Ru in this position, but the data presented did not indicate any increased electron density. In the refinement in space group *P6₃/mmc* this transition metal atom is located on a mirror plane. Close inspection of the displacement parameters reveals elongation of the ellipsoid in [001] and indicates a dislocation in the sense of a preference for a tetrahedrally coordinated position rather than a five-fold coordinated site. A refinement with a split position, as was suggested *e.g.* for isotypic BaTi₂Fe₄O₁₁ and BaSn₂Fe₄O₁₁ [4], or alternatively in the corresponding non-centrosymmetric

Table 2. Crystal structure parameters of BaFe_{3.39(5)}Ru_{2.61(5)}O₁₁ (first row of parameters) and BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁ (second row of parameters in italics).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} (Å ²)	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Ba(1)	2 <i>c</i>	1/3	2/3	1/4	0.0112(4) <i>0.0149(5)</i>	0.0116(5) <i>0.0141(3)</i>	<i>U</i> ₁₁	0.0104(6) <i>0.0163(6)</i>	0	0	1/2 <i>U</i> ₁₁
<i>M</i> (1) ^a	4 <i>e</i>	0	0	0.14844(9) <i>0.15158(7)</i>	0.0086(5) <i>0.0105(5)</i>	0.0081(6) <i>0.0101(5)</i>	<i>U</i> ₁₁ <i>0.0111(6)</i>	0.0096(7) <i>0.0091(6)</i>	0 <i>0.0002(3)</i>	0	1/2 <i>U</i> ₁₁
<i>M</i> (2) ^a	6 <i>g</i>	1/2	0	0	0.0132(4) <i>0.0177(4)</i>	0.0130(5) <i>0.0162(5)</i>	0.0232(7) <i>0.0335(7)</i>	0.0069(6) <i>0.0091(6)</i>	0.0016(3) <i>0.0002(3)</i>	1/2 <i>U</i> ₂₃	1/2 <i>U</i> ₂₂
Fe(3) <i>Co</i> (3)	2 <i>d</i>	2/3	1/3	1/4	0.0341(9) <i>0.0176(5)</i>	0.0067(8) <i>0.0053(7)</i>	<i>U</i> ₁₁	0.089(3) <i>0.042(1)</i>	0	0	1/2 <i>U</i> ₁₁
O(1) ^b	12 <i>k</i>	0.1706(3) <i>0.1704(4)</i>	2 <i>x</i>	0.0803(3) <i>0.0797(3)</i>	0.0105(9) <i>0.0125(9)</i>						
O(2) ^b	6 <i>h</i>	0.3051(9) <i>0.299(1)</i>	1/2 <i>x</i>	1/4	0.010(1) <i>0.014(1)</i>						
O(3) ^b	4 <i>f</i>	2/3	1/3	0.4165(6) <i>0.4198(5)</i>	0.015(1) <i>0.023(2)</i>						

^a For BaFe_{3.39(5)}Ru_{2.61(5)}O₁₁: *M*(1) = 0.64(1) Fe, 0.36 Ru; *M*(2) = 0.37(1) Fe, 0.63 Ru; for BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁: *M*(1) = 0.10(1) Co, 0.90 Ru; *M*(2) = 0.22(1) Co, 0.78 Ru.

Fig. 2. Arrangement of coordination polyhedra of transition metal atoms and Ba in BaFe_{3.39(5)}Ru_{2.61(5)}O₁₁ and BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁.

space group *P6₃mc* and with a mirror plane as twin law did not lead to a significant improvement of the results. For the isostructural vanadate PbV₆O₁₁ the non-centrosymmetric structure was observed at ambient temperature, probably caused by steric influence of the electron lone pair of Pb²⁺ [5]. PbV₆O₁₁ as well as the corresponding vanadates NaV₆O₁₁ and SrV₆O₁₁ suffer a displacive phase transition from centric to non-centric structures on temperature reduction below 560 K (Pb), 245 K (Na) and 320 K (Sr), respectively [6]. Analyses of single crystal X-ray diffraction data collected on the Fe containing crystal at 150 K did not give any indication of an enhancement of displacement of the Fe site in question.

Different levels of occupation of the two sites *M*(1) (Fe_{0.64(1)}, Ru_{0.36} or Co_{0.10(1)}, Ru_{0.90}) and *M*(2) (Fe_{0.37(1)}, Ru_{0.63}; Co_{0.22(1)}, Ru_{0.78}) with Ru and

M = Fe, Co as compared to literature reports lead to compositions deviating from the ideal compositions BaFe₂Ru₄O₁₁ and BaCo₂Ru₄O₁₁. Additionally, homogeneity ranges in the sense of Ba*M*_{2±x}Ru_{4±x}O₁₁ become likely. For *M* = Fe the composition calculated from the refinement of X-ray diffraction data is BaFe_{3.39(5)}Ru_{2.61(5)}O₁₁ in contrast to an approximate composition of BaFe_{2.7}Ru_{3.3}O₁₁ from μ -probe data. Comparably small isotropic displacement parameters for the *M*(1) and *M*(2) position in the refinement of the diffraction data may suggest a somewhat higher occupation with Ru, also indicated by the fact that the result from μ -probe data exactly matches the molar ratio used in the preparation. X-Ray powder diffraction patterns showed only weak reflections of an unknown second phase (unit cell parameters from powder least squares refinements: *a* = 5.830(1), *c* =

Table 3. Selected distances (Å) for BaFe_{3.39(5)}Ru_{2.61(5)}O₁₁ and BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁ with estimated standard deviations in parentheses.

	BaFe _{3.39(5)} Ru _{2.61(5)} O ₁₁	BaCo _{1.85(6)} Ru _{4.15(6)} O ₁₁	
Ba(1) –O(1)	2.836(3)	2.825(3)	6×
–O(2)	2.932(3)	2.926(3)	6×
M(1) –M(1)	2.760(2)	2.652(2)	1×
–O(1)	1.962(3)	1.978(4)	3×
–O(2)	2.073(4)	2.012(5)	3×
M(2) –O(1)	1.996(2)	1.984(3)	4×
–O(3)	2.036(4)	2.003(4)	2×
M(3) –O(2)	1.834(5)	1.860(6)	3×
–O(3)	2.262(8)	2.288(7)	2×

13.5852(5) Å) and are strongly textured according to (00l) as may be expected from the hexagonal platelet shape of the crystals. As an important conclusion, the studied crystals clearly do not represent the composition BaFe₂Ru₄O₁₁ proposed in the literature, but contain a significantly higher molar ratio $n(\text{Fe})/n(\text{Ru})$. However, for $M = \text{Co}$ the composition obtained in the structure refinements with BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁ exactly matches the composition found from μ -probe data with BaCo_{1.8}Ru_{4.2}O₁₁ and shows a minor but significant deviation from the ideal composition in direction of a smaller ratio $n(\text{Co})/n(\text{Ru})$. Remarkably, the occupation of the $M(2)$ site with Ru and 3d metal exactly matches the one reported for BaMn₂Ru₄O₁₁ [3]. The deviation in the composition consequently originates from a higher Ru occupation (less Co as compared to Mn) of the $M(1)$ site.

Distances between Ba and O are in the range expected for highly coordinated Ba. Distances $d(M\text{--}O)$ are slightly shorter in the Co compound as compared to the Fe compound as a result of the higher occupation with Ru in high oxidation state in the Co compound. Distances $d(\text{Co}(3)\text{--}O)$, however, are longer than $d(\text{Fe}(3)\text{--}O)$ as one would expect for low oxidation state low spin atoms [7]. Selected interatomic distances are presented in Table 3.

The distance $d(\text{Ru}\text{--}\text{Ru})$ within the pairs of octahedra was shown to be indicative of the oxidation state of ruthenium [8, 9]. For the present crystal structures we have to consider the possibility of Ru in different oxidation states for sites $M(1)$ (face-sharing octahedra) and $M(2)$ (no face sharing) because intermediate as well as mixed valence situations were frequently observed for oxoruthenates [1]. In the Fe containing compound the distance was refined to $d(M(1)\text{--}M(1)) = 2.760(2)$ Å. This distance is located at the short end of the range for which one would expect an oxida-

tion state of +5.5 for Ru. Within the frame of simple charge balance calculations and provided that an oxidation state of +5 is valid for Ru on the $M(2)$ site (no face sharing with other occupied octahedra) for the composition BaFe_{3.39(5)}Ru_{2.61(5)}O₁₁ from structure refinements this would lead to an oxidation state close to +2 for Fe. However, with an occupation of $M(1)$ with 0.64(1) Fe and 0.36 Ru this distance is highly dominated by Fe–Fe and Fe–Ru contacts and does not necessarily give valuable information about pure Ru–Ru interactions. For BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁ the situation is reversed: with an occupation of the site $M(1)$ with 0.10(1) Co and 0.90 Ru the distance $d(M(1)\text{--}M(1)) = 2.652(2)$ Å can be viewed as close to a pure Ru–Ru distance. This value is at the lower end expected for Ru in an oxidation state of +5. The charge balance then leads to Co close to +2 if $M(2)$ contains Ru in the oxidation state +3. This result is in good agreement with the magnetic susceptibility data (see below).

Magnetic properties

The magnetic susceptibility measurements of a BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁ single crystal have revealed a spontaneous magnetization below $T_c = 105$ K (Fig. 3). According to previous studies, this material can be considered a soft ferromagnetic material with low coercive field [3]. The title compounds contain ferromagnetically aligned moments located on the Co (Fe) and Ru atoms, which lead to an overall ferromagnetic order *via* superexchange through the oxygen atoms. As shown in the inset of Fig. 3, the in-

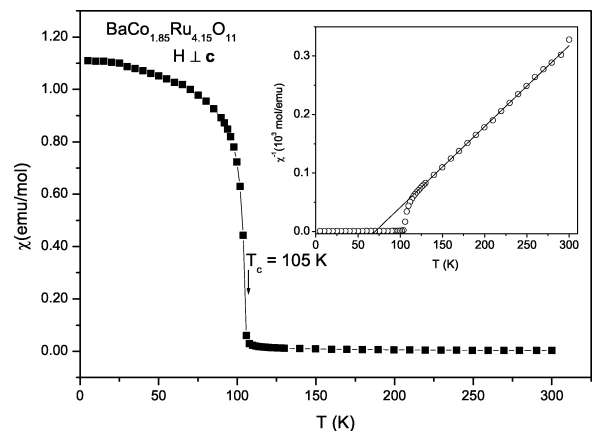


Fig. 3. BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁: dc susceptibility in an external magnetic field $\mu_0 H = 0.05$ T ($H \perp c$). The inset shows the inverse magnetic susceptibility vs. temperature. The solid line is a fit of the data to the Curie-Weiss law.

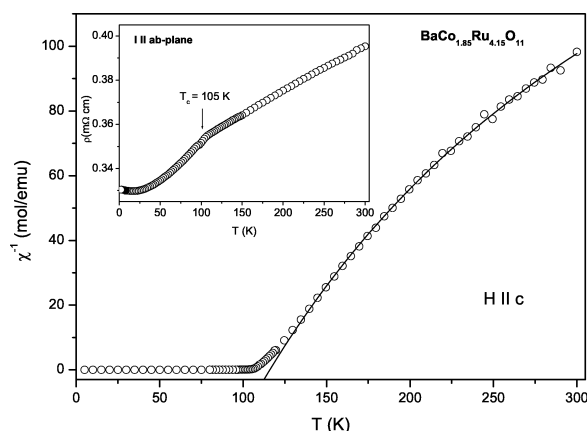


Fig. 4. BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁: Inverse magnetic susceptibility vs. temperature in an external magnetic field $\mu_0 H = 0.05$ T (H||c). The inset shows the temperature dependence of the resistivity (I||ab plane). The arrow designates the temperature of magnetic ordering at $T_c = 105$ K.

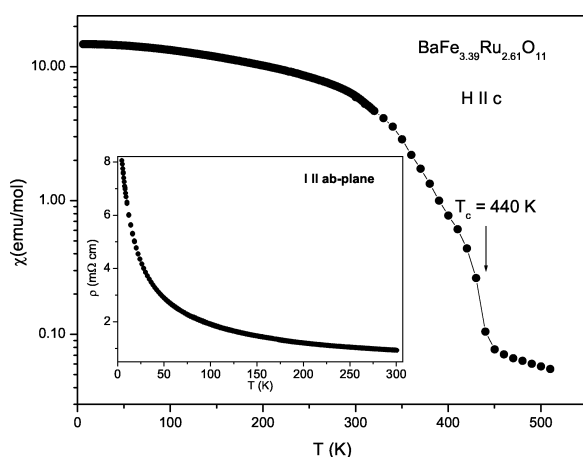


Fig. 5. BaFe_{3.39(5)}Ru_{2.61(5)}O₁₁: fc dc susceptibility in an applied magnetic field $\mu_0 H = 0.1$ T (H||c). The inset shows the temperature dependence of the resistivity (I||ab plane).

verse of the field-cooled (fc) dc susceptibility (H \perp c) exhibits an abrupt change in slope above 100 K and a linear behavior above 120 K. A Curie-Weiss fit of the data in the temperature interval $120 < T < 300$ K gives a Weiss constant $\theta_p = 70$ K and an effective magnetic moment of $2.41 \mu_B$. The susceptibility of the single crystal BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁ is strongly anisotropic and is much higher for H||c. Above 150 K the susceptibility follows a modified Curie-Weiss law with a temperature-independent term $\chi_0 = 3.8 \times 10^{-3}$ mol/emu, $\theta_p = 115$ K, and $\mu_{\text{eff}} = 3.08 \mu_B$ (Fig. 4). Fitting with a spatial average $\chi =$

$(\chi_{\parallel} + 2\chi_{\perp})/3$ of the Curie-Weiss law above 150 K yields $\mu_{\text{eff}} = 2.78 \mu_B$. An estimation of the theoretical effective magnetic moment can be obtained using an expression $\mu_{\text{eff}} = [n_1 \mu_B (\text{Co}^{2+})^2 + n_2 \mu_B (\text{Ru}^{3+})^2 + n_3 \mu_B (\text{Ru}^{5+})^2]^{1/2}$, where n_1 , n_2 and n_3 are fractions of Co²⁺, Ru³⁺ and Ru⁵⁺ moments per mol of material, respectively. Effective magnetic moments for spin-only Ru³⁺ ($S = 1/2$), Ru⁵⁺ ($S = 3/2$) and Co²⁺ ($S = 1/2$) yield a value of $\mu_{\text{eff}} = 2.81 \mu_B$, which is in good agreement with the experimental result. This result can be taken as a support of the oxidation state discussion in the previous paragraph. The temperature dependence of the fc dc susceptibility of BaFe_{3.39(5)}Ru_{2.61(5)}O₁₁ shows that in this sample ferrimagnetism develops below $T_c = 440$ K (Fig. 5). Due to the very high Curie temperature of this compound we were not able to extract the parameters of magnetic interactions from a high-temperature fit of the reciprocal susceptibility to the Curie-Weiss law.

Electric conductivity

The different 3d- (Co, Fe) and 4d-metal (Ru) contents apparently have a profound effect on the electronic properties. Measurements of the electrical resistivity reveal that the Co-poor phase BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁ behaves as an electric conductor (inset in Fig. 4), while the Fe-rich phase BaFe_{3.39(5)}Ru_{2.61(5)}O₁₁ is a narrow band semiconductor (inset in Fig. 5). The respective compounds with ideal compositions, BaFe₂Ru₄O₁₁ and BaCo₂Ru₄O₁₁, were both described as poor metals, since they exhibited a very weak semiconductor-like temperature dependence of the resistance in measurements taken on pressed pellets of microcrystalline material [3]. The difference in the resistivity behavior of the Co- and Fe-containing samples may be a consequence of different electronic structures of these metals. As a possible explanation, we suggest that the presence of an extra electron in BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁ closes a gap at the Fermi surface of BaFe_{3.39(5)}Ru_{2.61(5)}O₁₁.

Experimental Section

Preparation

For the preparation of BaFe_{3.39(5)}Ru_{2.61(5)}O₁₁, 2.23 g (11.3 mmol) BaCO₃, 0.452 g (3.40 mmol) RuO₂ and 0.222 g (1.39 mmol) Fe₂O₃ were mixed with about 1.5 g of BaCl₂ used as an agent to initiate crystal growth. The powders were heated to 1350 °C and kept at this temperature for several days. Then the furnace was slowly cooled to r. t. Black hexag-

onal platelets with maximum sizes of 2 mm and a thickness of about 0.05 mm were obtained.

Starting materials for BaCo_{1.85(6)}Ru_{4.15(6)}O₁₁ were 2.23 g (11.3 mmol) BaCO₃, 0.452 g (3.40 mmol) RuO₂, and 0.313 g (1.30 mmol) Co₃O₄. After addition of BaCl₂ this mixture was treated in the identical manner as described for the Fe compound.

Structure determination

For X-ray diffraction intensity data collection small black crystals with the shape of hexagonal platelets were selected. The measurements were performed on an Oxford Xcalibur diffractometer equipped with a graphite monochromator and a Sapphire CCD area detector at ambient temperature using MoK α radiation [scans: Fe: φ (360 images, $\Delta\varphi = 1.0^\circ$, 5 s), ω (416 images, $\Delta\omega = 1.0^\circ$, 5 s), Co: φ (180 images, $\Delta\varphi = 2.0^\circ$, 30 s), ω (208 images, $\Delta\omega = 2.0^\circ$, 30 s)]. The crystal of the Fe phase was additionally measured at 150 K to track a possible displacive phase transition to a non-centrosymmetric crystal structure. After empirical absorption correction, the structures were successfully solved with Direct Methods in space group *P6₃/mmc* (No. 194, centrosymmetric, program SHELXS-97-2 [10]). In the refinement procedure oxygen atoms were chosen to be treated with isotropic displacement parameters due to the limited number of unique intensity data (SHELXL-97-2 [11]). Selected information on the data collections, structure determinations and refinements is presented in Table 1. Table 2 gives positional parameters, site occupation numbers and displacement parameters.

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-417626 and CSD-417627.

Chemical composition determination

Chemical μ -probe analyses (JEOL 5900LV operating at 20 kV and equipped with a LINK AN 10000 detector system for EDX analysis) resulted in very stable compositions both for several different points on every investigated crystal and for different crystals with the exact ratio $n(M)/n(\text{Ba}) = 6.0$ for every single measurement (average of 47 atom% Ru, 39 atom% Fe and 14 atom% Ba for the Fe compound; 60 atom% Ru, 26 atom% Co and 14 atom% Ba for the Co compound, respectively). This result also applies for the very crystals measured on the diffractometer. No reliable quantification of the oxygen content is possible with this technique. No further elements were detected.

Magnetic susceptibility and electric conductivity measurements

The magnetic susceptibility $\chi(T)$ of orientated single crystals was measured between 2 K and 500 K in fields up to 5 T in a commercial SQUID magnetometer (Quantum Design). The electrical resistivity of the samples was measured in the temperature range 1.8 K–300 K by using the four-probe dc method.

Acknowledgements

We thank Dr. Stephan D. Hoffmann for initial introduction and help at the diffractometer software, Ingrid Werner for performing the μ -probe measurements and Vinobalan Durairaj for support in electrical resistivity measurements. This work was in part supported by NSF grant DMR-0552267, DoE Grant DOE-FGØ2-97ER45653 and the Elitenetzwerk Bayern within the Advanced Materials Science program.

-
- | | |
|--|--|
| <p>[1] Hk. Müller-Buschbaum, <i>Z. Anorg. Allg. Chem.</i> 2006, 632, 1625–1659.</p> <p>[2] D. Verdoes, H. W. Zandbergen, D. J. W. Ijdo, <i>Mater. Res. Bull.</i> 1987, 22, 1–10.</p> <p>[3] M. L. Foo, Q. Huang, J. W. Lynn, W.-L. Lee, T. Klimczuk, I. S. Hagemann, N. P. Ong, R. J. Cava, <i>J. Solid State Chem.</i> 2006, 179, 563–572.</p> <p>[4] M. C. Cadée, D. J. W. Ijdo, <i>J. Solid State Chem.</i> 1984, 52, 302–312.</p> <p>[5] O. Mentre, F. Abraham, <i>J. Solid State Chem.</i> 1996, 125, 91–101.</p> <p>[6] H. Kato, M. Kato, K. Yoshimura, K. Kosuge, <i>J. Phys.: Condens. Matter</i> 2001, 13, 9311–9333.</p> | <p>[7] R. D. Shannon, <i>Acta Crystallogr.</i> 1976, A32, 751–767.</p> <p>[8] B. Schüpp, L. Shlyk, Y. Prots, I. Bäcker, G. Krabbes, <i>J. Solid State Chem.</i> 2004, 177, 1393–1400.</p> <p>[9] B. Schüpp-Niewa, L. Shlyk, Y. Prots, G. Krabbes, <i>J. Alloys Compd.</i> 2006, 414, 269–275.</p> <p>[10] G. M. Sheldrick, SHELXS-97-2, Program for the Solution of Crystal Structures, Universität Göttingen, Göttingen (Germany) 1997.</p> <p>[11] G. M. Sheldrick, SHELXL-97-2, Program for the Refinement of Crystal Structures, Universität Göttingen, Göttingen (Germany) 1997.</p> |
|--|--|