Preparation, thermal stability and crystal structure of a new ruthenium(V) oxide containing peroxide ions: $Ba_5Ru_2O_9(O_2)$. Structural relationships to the hexagonal-type perovskite

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The compound $Ba_5Ru_2O_{11}$ has been synthesized by solid state reactions at 980 °C and 1 atm oxygen pressure. The crystal structure has been determined on a single crystal ($R_1=0.027$, $wR_2=0.058$). The symmetry is hexagonal ($P6_3/mmc$) with the cell parameters $a=5.9470(5)$ Å, $c=18.0428(10)$ Å, $Z=2$. Perpendicular to the c-axis, the structure is built up by the periodic stacking of three hexagonal close packed [BaO_3] layers separated by a layer of composition [Ba_2O_2] containing $(O_2)^{2-}$ peroxide ions. The detailed formula is then $Ba_5Ru_2O_9(O_2)$ if we emphasize the formation of peroxide ions in the phase. The ruthenium(V) ions occupy the octahedral sites formed between the [BaO_3] layers (hexagonal perovskite slabs) and then constitute isolated [Ru_2O_9] pairs. $Ba_5Ru_2O_9(O_2)$ belongs to a new family of compounds, generically formulated as $[A_2(O_2)][A_nB_{n-1}O_{3n}]$ where n represents the number of [AO_3] successive layers in the hexagonal perovskite slabs. Each member of the series is an intergrowth of [$A_2(O_2)$] and hexagonal perovskite layers; $n=3$ corresponds to $Ba_5Ru_2O_9(O_2)$. The isostructural phase has been observed when ruthenium is replaced by niobium. The $n=4$ member and the intergrowth between the $n=3$ and $n=4$ members of this family has been observed in the Ba–Nb(Ta)–S ternary systems. The former proposed formula for the ternary barium sulfides is discussed in the light of the framework of this new family.

Compounds whose structures are built up by the stacking of layers derived from ABO_3 perovskites have been widely studied and structural relationships between them have been recently reported.[1] The hexagonal perovskite structure is often thought of as a hexagonal close packed (hcp) stacking of AO_3 layers (A is usually an alkaline earth element) with transition metal cations B occupying octahedral sites between the layers to give the stoichiometry ABO_3. It has now been recognized that the structures of many oxides, the stoichiometries of which are not obviously related to that of perovskite, can be considered within the same structural framework if we allow for the inclusion of modified layer types within the stacking sequence. One example is the $A_{3n+3}A'_nB_{3+n}O_{9+6n}$ series[1] where the stacking corresponds to mixed A_3O_9 and $A_3A'O_6$ layers and n represents the number of successive $A_3A'O_6$ layers in the sequence. $n=\infty$ corresponds to the well known structure of Sr_4PtO_6[2] (K_4CdCl_6 type[3]). A large number of oxides containing 4d and 5d elements crystallize in this structural type.[4–8] $Ba_6Ni_5O_{15}$[9] and $Sr_6Co_5O_{15}$[10] are the $n=1$ members of the series with A = Ba(Sr) and A′ = Ni(Co). $Sr_4Ni_3O_9$[11] (A′ = Ni) and $Sr_4Ru_2O_9$[12] (A′ = vacancies) corresponds to $n=3$. The crystal structure of $Sr_9Ni_{6.64}O_{21}$,[13] which is the $n=2$ member of this series, has recently been reported. In line with this principle of structural approach, a similar model has been proposed for the structure of the ruthenate(V) $Ba_5Ru_2O_{10}$.[14] The structure results from the periodic stacking of three hcp BaO_3 layers and one Ba_2O layer. The model results from structural considerations and refinements from X-ray powder data using the Rietveld method. This paper is devoted to the determination of the crystal structure of this phase on a single crystal. The comparison with the previous results is discussed as well as the structural relationships with similar phases in the ternary Ba–Nb(Ta)–S systems.

Experimental

Polycrystalline samples were synthesized from spectroscopic-grade powders of barium carbonate and ruthenium oxide. The stoichiometric mixture was mixed in an agate mortar and heated in a gold crucible at 700 °C for 24 h and at 980 °C for 2 d with intermediate grindings. The preparation was carried out under a flow of oxygen. After the final heating, the powder was cooled slowly to room temperature. The progress of the reaction was monitored using X-ray powder diffraction (XRD), and they were deemed to be complete when the diffraction pattern did not change on heating the sample further. A mixture in the ratio $6BaCO_3:3RuO_2$ contained in an alumina crucible was heated at 1200 °C for 10 d under flowing oxygen and slowly cooled to room temperature (10 °C h^{-1}). The reaction product showed well formed, black plate-like crystals.

Weissenberg and precession photographs of a single crystal showed the diffraction symmetry of this phase to be $6/mmm$ with systematic absence hhl: $l=2n+1$, consistent with space groups $P6_3/mmc$, $P6_3mc$ and $P\bar{6}2c$. The unit-cell parameters $a\approx 5.95$ Å and $c\approx 18.05$ Å allowed the indexing of the X-ray powder diffraction.

A selected single crystal was mounted on a four-circle automatic diffractometer CAD4 (Enraf Nonius) and data were collected using graphite-monochromated Mo-Kα radiation. Crystal data are given in Table 1. Intensities were corrected for Lorentz and polarization effects and empirical absorption corrections were made using the psi-scan technique. Calculations were performed using the SHELXL93[15] program. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/43.

Powder X-ray diffraction (XRD) profiles were recorded on a Philips PW1710 diffractometer, using Cu-Kα radiation. Data of sufficient quality for structure refinements were collected over $5\leqslant 2\theta/\text{degrees}\leqslant 100$, in 0.02 steps, with integration times of 10 s. The Rietveld[16] refinements were performed with the FULLPROF program package.[17] The peak shape was described by a pseudo-Voigt function and the background level was defined by a polynomial function. For each diffraction pattern, a scale factor, a counter zero point, the peak asym-

Table 1 Crystal data and structure refinement parameters of $Ba_{4.9}Ru_2O_{10.8}$ ($\approx Ba_5Ru_2O_{11}$)

formula	$Ba_{4.9}Ru_2O_{10.8}$
M_w	1047.9
wavelength/Å	0.710 73
crystal system	hexagonal
space group	$P63/mmc$ (no. 194)
unit-cell dimensions/Å	$a = 5.9470(5)$ $c = 18.043(1)$
volume/Å^3	552.61
Z	2
D_c/g cm^{-3}	6.30
absorption coefficient/mm^{-1}	20.22
$F(000)$	912.0
crystal size/mm^3	$0.15 \times 0.40 \times 0.15$
θ range for data collection/degrees	3.95–40
index ranges	$0 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 9$, $-32 \leqslant l \leqslant 0$
reflections collected	999 [783 with $I > 3\sigma(I)$]
independent reflections	443 [$R(\text{int}) = 0.0387$]
refinement method	full-matrix least-squares on F^2
data; restraints; parameters	443; 0; 38
final R indices [$I > 3\sigma(I)$]	$R_1 = 0.0267$, $wR_2 = 0.0582$
goodness S	1.158
largest diff. peak and hole/e A^{-3}	2.33 and -1.50

metry and the unit-cell parameters were refined in addition to the atomic parameters.

Thermogravimetry (TG) was performed on a MTB10-8 SETARAM balance with an accuracy $\Delta m = 0.01$ mg. Experiments were carried out under Ar or Ar–5% H_2 atmospheres up to 950 °C.

Results

The unit-cell parameters $a = 5.9470(5)$ Å and $c = 18.0428(10)$ Å, refined with 25 reflections for $21 < \theta$/degrees< 31.5, confirmed the proposed XRD indexation in ref. 14. The structural refinements were carried out in the space group $P6_3/mmc$ (no. 194). Calculations performed with the other possible space groups ($P\bar{6}2c$ and $P6_3mc$) did not improve the final results.

The proposed model in ref. 14 has served as a starting model for the refinements. The formula corresponds to $Ba_5Ru_2O_{10}$ ($Z = 2$) with all the positions fully occupied: Ba(1) in the 4e position (0, 0, 0.139), Ba(2) in the 2c position (1/3, 2/3, 1/4), Ba(3) in the 4f position (1/3, 2/3, 0.016), Ru in the 4f position (1/3, 2/3, 0.674), O(1) in the 6h position (x, $2x$, 3/4 with $x = 0.183$), O(2) in the 12k position (x, $2x$, z with $x = 0.487$ and $z = 0.619$) and O(3) in the 2a position (0, 0, 0). The calculation with isotropic thermal displacement parameters gives R-values $R_1 = 0.0703$ (based on F_o) and $wR_2 = 0.2609$ (based on $F_o{}^2$). The results show that the U_{iso} of oxygen O(3) is high (0.102 Å^2) compared to those of O(1) (0.011 Å^2) and O(2) (0.020 Å^2). Furthermore the isotropic thermal displacement corresponding to Ba(3) is twice as high as those of Ba(1) and Ba(2). Besides, the difference Fourier synthesis showed maxima near the Ba(3) and O(3) positions in the 12k positions (x, $2x$, z) with $x \approx 0.37$, $z \approx 0.01$ close to Ba(3) and $x \approx 0.07$, $z \approx 0.004$ near O(3). Refinements were carried out by considering the same U-values for Ba(3) and the new position Ba(3′) with a repartition of four barium atoms onto these two positions. The occupancy factor was fixed to one sixth for the O(3) oxygen and then the formula unit corresponds to $Ba_5Ru_2O_{10}$ ($Z = 2$). The R-values decrease to $R_1 = 0.0445$ and $wR_2 = 0.1612$ with the isotropic model for the thermal parameters. The occupancy rate of the Ba(3) and Ba(3′) positions stabilizes to *ca.* 2/1 with $U_{Ba(3)} = U_{Ba(3')} = U_{Ba(3')} = 0.010$ Å^2. The most important feature is that the U factor of oxygen O(3) is not defined (<0), indicating missing electron density. At this stage of the refinement, the occupancy factor of this position was refined. Owing to the high correlations between the occupancy and the thermal displacement factor, simultaneous refinements were difficult and therefore the calculations were carried out step by step. The O(3) site occupancy stabilizes near one third which corresponds to the unit formula $Ba_5Ru_2O_{11}$. The corresponding R-values are $R_1 = 0.0437$ and $wR_2 = 0.1514$ with $U_{O(3)} = 0.025$ Å^2. The refinement in the isotropic model of the different site occupancies of Ba(3), Ba(3′) and O(3) positions led to $R_1 = 0.0388$ and $R_2 = 0.1315$. The global composition corresponds to $Ba_{4.87}Ru_2O_{10.8}$ which is close to the stoichiometric formula $Ba_5Ru_2O_{11}$. The final refinements by considering anisotropic thermal displacement factors for all the atoms led to $R_1 = 0.0267$ and $wR_2 = 0.0582$ with $w = 1/[\sigma^2 F_o{}^2 + (0.021)P^2]$ ($P = [\max.(F_o{}^2) + 2F_c{}^2]/3$). Results of the refinements are given in Table 1, structural parameters and interatomic distances are listed in Tables 2 and 3. For comparison, the R-values are $R_1 = 0.0289$ and $wR_2 = 0.0671$ when one considers the stoichiometric composition $Ba_5Ru_2O_{11}$. There is no important variation of the structural parameters except the anisotropic U-values of the O(3) oxygen which became too high [$U_{11} = 0.2112(537)$]. We are therefore inclined to consider that the studied crystal is non-stoichiometric.

In order to confirm this result, Rietveld refinements were carried out on the powder sample prepared at 980 °C, using the previous structural results as a starting model. If one considers a delocalisation of the barium in the Ba(3) and Ba(3′) positions, there is a huge variation in the Ba(3′) position and the refinement diverges. The Ba(3) position is definitively fully occupied by barium atoms. Different models have been tested where the oxygen O(3) is located in the 12k or 2a positions with site occupancies corresponding to $Ba_5Ru_2O_{10}$ and $Ba_5Ru_2O_{11}$. As is shown in Table 4, the best result based on the agreement indices and on the isotropic thermal factor values for O(3) is clearly observed when the oxygen O(3) is in 12k point symmetry with a site occupancy of one third which corresponds to the global composition $Ba_5Ru_2O_{11}$ ($Z = 2$). The refined atomic positions and isotropic thermal parameters are listed in Table 5. The observed, calculated and difference X-ray diffraction profiles are shown in Fig. 1.

TG experiments under Ar–5% H_2 up to 950 °C were performed with a slope of 100 °C h^{-1} (Fig. 2) with a starting mass of *ca.* 100 mg. The observed mass loss (9.03%) agrees very well with the $Ba_5Ru_2O_{11}$ formula (9.02%). The reduction corresponds to the formation of Ru metal which is observed on the X-ray spectra after the experiments. Below 200 °C an uptake is observed (Fig. 2) which can be attributed to physical (or chemical) absorption of hydrogen. Further experiments are in progress in order to clarify this result. However, similar TG experiments under the same conditions but under pure argon did not show similar behaviour (Fig. 3). A monotonic mass loss is observed with increasing the temperature up to 850 °C. Above this temperature a large plateau is observed in the curve (Fig. 3) which corresponds to a mass loss of one oxygen and then to a global composition $Ba_5Ru_2O_{10}$. The corresponding X-ray diffraction pattern of the product shows clearly that it is a unique phase. All the peaks have been indexed as for $Ba_5Ru_2O_{11}$ in hexagonal symmetry with $a = 5.95 \pm 0.01$ Å and $c = 17.9 \pm 0.01$ Å. Parts of the X-ray spectra of the two phases between $28 \leqslant 2\theta$/degrees$\leqslant 57$ are given in Fig. 4 where the decrease of the c-parameter for $Ba_5Ru_2O_{10}$ can be seen.

Table 2 Atomic coordinates for $Ba_{4.9}Ru_2O_{10.8}$ ($\approx Ba_5Ru_2O_{11}$)

atom	site	x	y	z	B_{eq}/Å^2
Ba(1)	4e	0	0	0.1392(1)	0.0094(1)
Ba(2)	2c	1/3	2/3	1/4	0.0109(2)
Ba(3)	4f (56%)	1/3	2/3	0.0155(3)	0.010(1)
Ba(3′)	12k (13%)	0.3611(61)	$2x$	0.0150(5)	0.041(5)
Ru	4f	1/3	2/3	0.6738(1)	0.0072(2)
O(1)	6h	0.1832(7)	$2x$	3/4	0.011(1)
O(2)	12k	0.4884(5)	$2x$	0.6181(3)	0.017(1)
O(3)	12k (30%)	0.0677(24)	$2x$	0.0037(22)	0.034(9)

Table 3 Selected bond lengths (Å) for $Ba_{4.9}Ru_2O_{10.8}$ ($\approx Ba_5Ru_2O_{11}$)

3 × Ru—O(1)	2.069(5)	2 × Ba(1)—O(3)	2.670(35)	6 × Ba(2)—O(2)	3.006(5)
3 × Ru—O(2)	1.888(5)	6 × Ba(1)—O(2)	3.001(1)	3 × Ba(3)—O(2)	2.608(6)
Ru—Ru	2.748(2)	O(3)—O(3)	1.402(46)	3 × Ba(3)—O(3)	2.745(23)
3 × Ba(1)—O(1)	2.749(5)	6 × Ba(2)—O(1)	2.980(1)	3 × Ba(3)—O(2)	2.891(6)

Table 4 *R* factors for different O(3) positions and corresponding isotropic thermal factors

position	occupancy	$B/\text{Å}^2$	R_I	R_p	R_{wp}
12k	1/3	2.14	3.49	6.06	9.21
12k	1/6	−5.56	4.01	6.64	9.92
2a	1	4.22	4.59	6.89	10.10

Table 5 Atomic coordinates and thermal parameters in $Ba_5Ru_2O_{11}$ from Rietveld refinement

atom	*x*	*y*	*z*	$B/\text{Å}^2$
Ba(1)	0	0	0.1392(3)	0.71(18)
Ba(2)	1/3	2/3	1/4	0.46(12)
Ba(3)	1/3	2/3	0.0156(3)	0.93(15)
Ru	1/3	2/3	0.6741(3)	0.45(15)
O(1)	0.1879(60)	2*x*	3/4	0.34(31)
O(2)	0.4847(60)	2*x*	0.6192(15)	0.91(22)
O(3)	0.0754(47)	2*x*	−0.0003(40)	2.14(93)

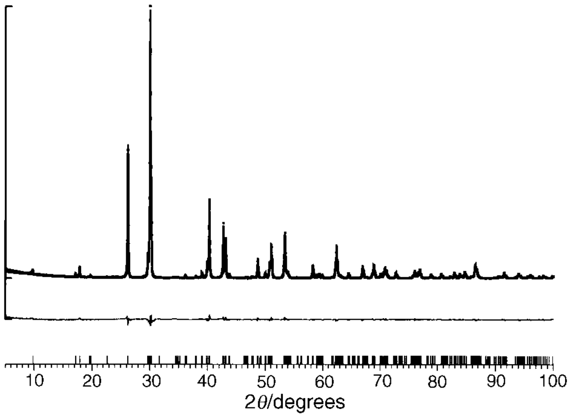

Fig. 1 Observed (dots), calculated (full line) and difference X-ray powder diffraction profiles of $Ba_5Ru_2O_{11}$

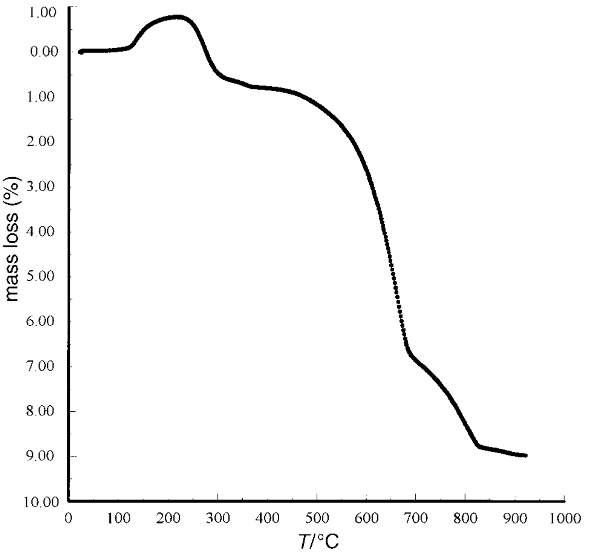

Fig. 2 TG (under Ar–5% H_2 atmosphere) of $Ba_5Ru_2O_{11}$

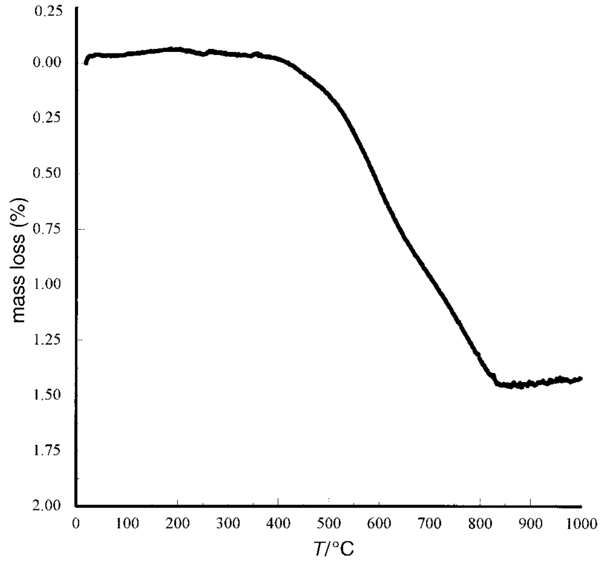

Fig. 3 TG (under Ar atmosphere) of $Ba_5Ru_2O_{11}$

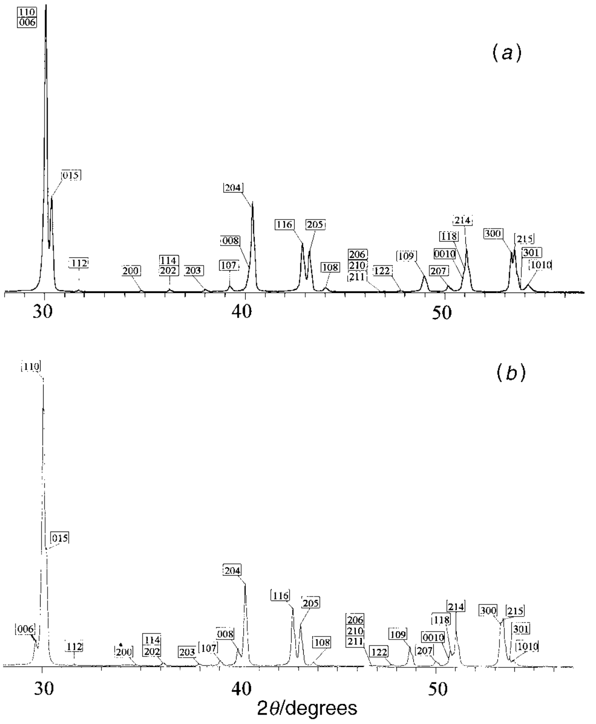

Fig. 4 X-Ray diffraction profiles of (*a*) $Ba_5Ru_2O_{10}$ and (*b*) $Ba_5Ru_2O_{11}$ from 28° to 57°

Discussion

Perpendicular to the *c*-axis, the structure of $Ba_5Ru_2O_{11}$ can be described as resulting from the stacking of three BaO_3 layers and one layer with the nominal composition Ba_2O_2 (Fig. 5). The sequence of BaO_3 layers is hexagonal close packing like in the 2H-hexagonal perovskites. Then the ruthenium atoms occupy face-sharing oxygen octahedra grouped in pairs

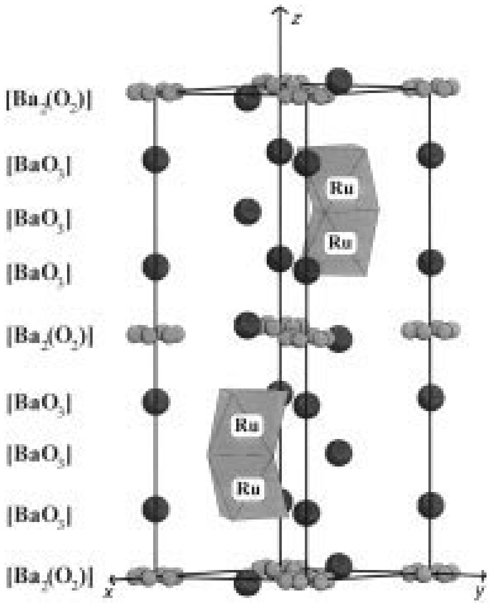

Fig. 5 Representation of the $Ba_5Ru_2O_9(O_2)$ structure

(Fig. 5). The Ru^V—O bond distances ($1.888 < d/\text{Å} < 2.069$) are in good agreement with those found in the literature[18] for analogous compounds of pentavalent Ru. The assumption that ruthenium is in a pentavalent state has been confirmed by a valence bond calculation. The most commonly adopted empirical expression for the variation of the length d_{ij} of a bond with valence is $v_{ij} = \exp[(R_{ij} - d_{ij})/0.37]$.[19] The calculation yields 4.84 (for the single crystal) with the parameter $R_{ij} = 1.888$.

The slabs of hexagonal perovskite are separated by Ba_2O_2 layers (Fig. 5). The non-stoichiometry observed in the single crystal studied can be explained by the experimental thermal conditions used to prepare them. To clarify the following discussion we will consider the exact stoichiometry Ba_2O_2 for the layer. The oxygen atoms are grouped in pairs with a bond distance of 1.402 Å (single crystal) or 1.554 Å (powder refinement) which is characteristic of peroxide ions $(O_2)^{2-}$ with an O—O single bond. For comparison the length of the O—O bond is 1.49 Å in BaO_2[20] and 1.47 Å in H_2O_2.[21] The oxygens are delocalized in the 12k position (near the 2a position) with an occupancy factor of 1/3 and then there are three possibilities of orientation of the peroxide ions in the structure, as shown in Fig. 6. The main difference between the single crystal and powder refinements is the delocalization of the barium atoms of the Ba_2O_2 layer in two positions in the former case (Table 2). This result can also be explained by the method of preparation of the single crystals which have been obtained at higher temperature. The Ba(1) atom is surrounded by eleven oxygens with bond distances ranging between 2.542 Å [or 2.670 Å depending on the orientation of the $(O_2)^{2-}$ pair] and 3.001 Å (Table 3; Fig. 7). The environment of Ba(2) is a trigonal prism [6 × Ba(2)—O = 3.006 Å] capped by six oxygens forming a hexagon [6 × Ba(2)—O = 2.980 Å] in the middle plane (Fig. 7). If one considers the 4f position for Ba(3), the environment is a trigonal prism [3 × Ba(3)—O = 2.608 Å and 3 × Ba(3)—O = 2.891 Å] capped by three oxygen atoms in the middle plane at 2.745 Å (Fig. 7).

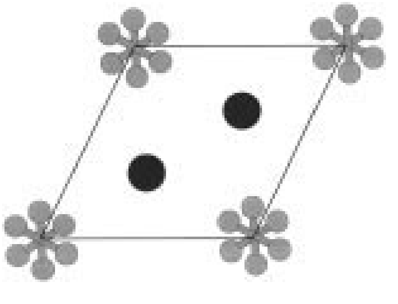

Fig. 6 Representation of the $[Ba_2(O_2)]$ layers

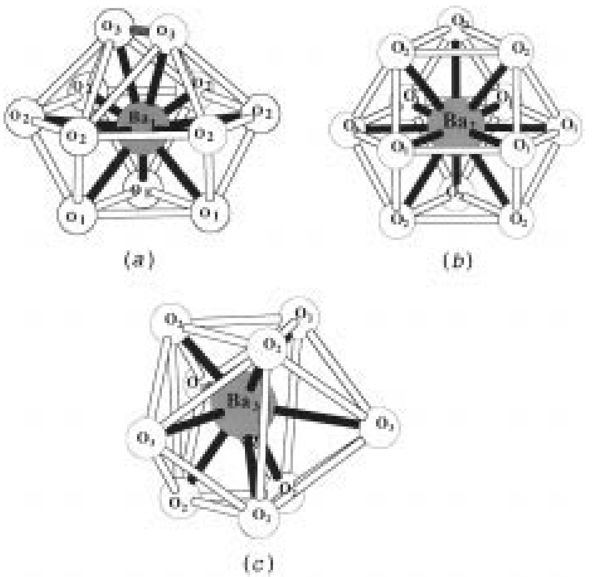

Fig. 7 Representation of the environments of the barium atoms

The main observation in the structure of $Ba_5Ru_2O_{11}$ is the formation of peroxide ions in the Ba_2O_2 layers which is to our knowledge the first time that such a feature has been observed. The structure can then be described as a layered compound where the framework is constituted by slabs of hexagonal perovskite separated by layers of composition Ba_2O_2. One can imagine a new series of compounds built up from such a framework of BaO_3 and Ba_2O_2 mixed layers but with various thicknesses of the hexagonal perovskite slabs. The general formula is $[A_2(O_2)][A_nB_{n-1}O_{3n}]$ where n represents the number of hexagonal BaO_3 layers in the sequence. $Ba_5Ru_2O_{11}$ corresponds to $n = 3$ and can be formulated as $Ba_5Ru_2O_9(O_2)$. One can postulate that the loss of one oxygen observed by TG corresponds to one oxygen in the Ba_2O_2 layer. We shall pursue this point in order to try to confirm the structural model proposed in ref. 14.

We noted in the literature a paper[22] in which a new barium niobate with a composition close to 5.5BaO–1Nb_2O_5 was reported. The X-ray powder data were indexed in hexagonal symmetry with cell parameters ($a = 6.046$ Å, $c = 18.33$ Å) close to those of $Ba_5Ru_2O_{11}$ but without any information on the crystal structure. One can postulate that this niobate is isostructural with $Ba_5Ru_2O_{11}$ or $Ba_5Ru_2O_{10}$. The outstanding question is the exact stoichiometry in oxygen of the phase in line with our results on the corresponding ruthenate. A structural investigation is in progress in order to confirm the oxygen content of this barium niobate, with the hypothesis that it corresponds to the $n = 3$ member of the $[A_2(O_2)][A_nB_{n-1}O_{3n}]$ general new series.

As is well known, $(S_2)^{2-}$ ions are frequently encountered in solid state compounds and we pointed out the structural investigations on the Ba–Nb(Ta)–S ternary systems.[23–28] A review of the literature shows that the stoichiometries and the crystal structures of the different phases are very uncertain. For example, Swinnea *et al.*[23] reported the single crystal structure of $Ba_{16.5}Nb_9S_{42}$ ($Z = 1$) which appears to them an unlikely composition. They proposed instead the most likely composition $Ba_{18}Nb_9S_{40.5}$ ($Z = 1$). The symmetry is rhombohedral ($R\bar{3}m$) with the cell constants $a = 6.877$ Å, $c = 41.84$ Å.

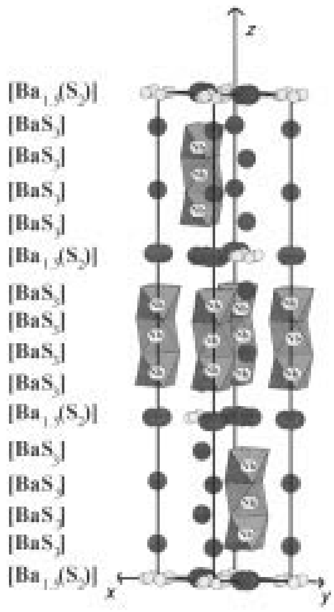

Fig. 8 Representation of the $Ba_{16.5}Nb_9S_{42}$ structure ($n=4$)

A representation of the structure is given in Fig. 8 using the positional parameters from ref. 23. It appears clearly that the crystal structure corresponds to the $n=4$ member of the previous proposed series if the oxygens are replaced by sulfurs. The structure is now based on the stacking of four hexagonal BaS_3 layers separated by a layer of $Ba_{1.5}S_2$ composition. The two sulfur atoms constitute characteristic disulfide ions with an S—S bond distance of 2.12 Å. The barium position is partially occupied which confirms the tendency of this type of layer to be non-stoichiometric, as was observed for the ruthenate. The detailed formula can be expressed as $3[Ba_4Nb_3S_{12}][Ba_{1.5}(S_2)]$, or $Ba_{16.5}Nb_9S_{36}(S_2)_3$ to emphasize the existence of disulfide ions in the structure. As can be checked from the formula, the niobium is in a pentavalent state. A similar phase has been reported for tantalum[24] with the formula $Ba_{16.5}Ta_9S_{39}$. The authors proposed this chemical composition from the experimental results of a powder X-ray refinement and the chemical analysis. They postulated that the anions are only sulfides with a formal charge (+5) of the tantalum ions. If one considers now the formula $Ba_{16.5}Ta_9S_{36}(S_2)_3$, as we expected, the comparison between the experimental and theoretical analysis appears to be better. The experimental results from ref. 24 are: Ba(mass%) = 42.9, Ta(mass%) = 31.2, S(mass%) = 25.3 and the calculated values for $Ba_{16.5}Ta_9S_{42}$: Ba(mass%) = 43.2, Ta(mass%) = 31.1, S(mass%) = 25.7. For the proposed formula $Ba_{16.5}Ta_9S_{39}$, the corresponding results are: Ba(mass%) = 44.0, Ta(mass%) = 31.6 and S(mass%) = 24.3.

Two other phases have been reported in the Ba–Nb(Ta)–S ternary systems[25–28] which correspond respectively to the $n=3$ member and the intergrowth between the $n=3$ and $n=4$ members of the proposed series. As previously, the proposed formula seems to be doubtful and a complete reinvestigation of these systems is in progress. Preliminary experimental results seem to confirm this assumption. It seems to us that the contradictory results published until now on these systems arise from the fact that the different authors did not consider the possibility of the coexistence of sulfide and disulfide ions in the structures. This point is imaginable if one describes the structures in terms of hexagonal perovskite slabs with different thicknesses separated by $A_2(X_2)$ layers where (X_2) are peroxide or disulfide ions. The non-stoichiometry observed in the $A_2(X_2)$ layer can be explained more by a charge balance than a stereochemistry problem.

To conclude, a new route is open in the synthesis of new compounds belonging to the new series $[A_2(X_2)][A_nB_{n-1}X_{3n}]$ where X can be oxygen or sulfur for example, A an alkaline earth element and B a transition metal. The main characteristic of the structures is that a part of the anions are grouped in pairs forming $A_2(X_2)$ layers. In the general formula n represents the number of close-packed AX_3 layers constituting the hexagonal perovskite slabs. To our knowledge, $Ba_5Ru_2O_9(O_2)$ represents the first example of an oxide with this type of structure. The original chemical behaviour of this phase observed under hydrogen or argon atmosphere is relatively encouraging for the pursuit of further investigations in this way.

References

1 J. Darriet and M. A. Subramanian, *J. Mater. Chem.*, 1995, **5**, 543.
2 J. J. Randal and L. Katz, *Acta Crystallogr.*, 1959, **12**, 519.
3 G. Bergerhoff and O. Schimtz-Dumont, *Z. Anorg. Allg. Chem.*, 1956, **284**, 10.
4 J. Darriet, F. Grasset and P. D. Battle, *Mater. Res. Bull.*, to be published.
5 A. P. Wilkinson, A. K. Cheetham, W. Kunman and Å. Kvick, *Eur. J. Solid State Inorg. Chem.*, 1991, **28**, 453.
6 A. W. Powell, P. D. Battle and J. G. Gore, *Acta Crystallogr., Sect. C*, 1993, **49**, 852.
7 J. F. Vente, J. K. Lear and P. D. Battle, *J. Mater. Chem.*, 1995, **11**, 1785.
8 C. Lampe-Önnerud and H. C. zur Loye, *Inorg. Chem.*, 1996, **35**, 2155.
9 J. A. Campa, E. Gutierrez-Puebla, M. A. Monge, I. Rasines and C. Ruiz-Valero, *J. Solid State Chem.*, 1994, **108**, 230.
10 W. T. A. Harrison, S. L. Hegwood and A. J. Jacobson, *J. Chem. Soc., Chem. Commun.*, 1995, 1953.
11 F. Abraham, S. Minaud and C. Renard, *J. Mater. Chem.*, 1994, **4**, 1763.
12 C. Dussarrat, J. Fompeyrine and J. Darriet, *Eur. J. Solid State Inorg. Chem.*, 1995, **32**, 3.
13 J. A. Campa, E. Gutierrez-Puebla, M. A. Monge, I. Rasines and C. Ruiz-Valero, *J. Solid State Chem.*, 1996, **126**, 27.
14 C. Dussarrat, J. Fompeyrine and J. Darriet, *Eur. J. Solid State Inorg. Chem.*, 1994, **31**, 289.
15 G. M. Sheldrick, SHELXL93, A Program for Refinement of Crystal Structure, University of Göttingen, Germany, 1993.
16 H. M. Rietveld, *J. Appl. Crystallogr.*, 1969, **2**, 65.
17 J. Rodriguez-Carvajal, FULLPROF, ver. 3.1, 1995, LLB.CE, Saclay, France.
18 S. Frenzen and Hk. Müller-Buschbaum, *Z. Naturforsch., B*, 1995, **50**, 581.
19 N. E. Brese and M. O'Keefe, *Acta Crystallogr., Sect. B*, 1991, **47**, 192.
20 S. C. Abrahams and J. Kalnajs, *Acta Crystallogr.*, 1954, **7**, 838.
21 W. R. Busing and A. H. Levy, *J. Chem. Phys.*, 1965, **42**, 3054.
22 P. P. Leshchenko, L. N. Lykova, L. M. Kovba and E. A. Ippolitova, *Russ. J. Inorg. Chem.*, 1982, **27**, 721.
23 J. S. Swinnea, H. Steinfink, L. E. Rendon-Diazmiron and M. Gomezdaza, *J. Solid State Chem.*, 1995, **117**, 300.
24 M. Saeki and M. Onoda, *Mater. Res. Bull.*, 1989, **24**, 1491.
25 M. Saeki and M. Onoda, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 2923.
26 M. Saeki and M. Onoda, *Mater. Res. Bull.*, 1989, **24**, 41.
27 M. Saeki and M. Onoda, *Mater. Res. Bull.*, 1990, **25**, 723.
28 J. S. Swinnea, H. Steinfink, L. E. Rendon-Diazmiron and M. Gomezdaza, *J. Solid State Chem.*, 1985, **56**, 249.

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