

Structures of Quaternary Ru and Sb Oxides by Computer Simulation

Peter D. Battle,[†] Timothy S. Bush,^{†,‡} and C. Richard A. Catlow^{*,‡}

Contribution from Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K., and Davy-Faraday Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London W1X 4BS, U.K.

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Abstract: Pair potentials which facilitate the modeling of mixed metal oxides containing Ru⁵⁺, Sb⁵⁺, and Ru⁴⁺ have been derived. It is shown that these potentials are consistent with the structural differences observed between apparently analogous Sb and Ru compounds and that they can account for the complex crystal structure of Ba₄NaRu₃O₁₂. A prediction is made about the structural stability of some as yet unknown quaternary oxides of Ru.

Introduction

Computer modeling of the structures, energies, and properties of both perfect and defective crystals is now an integral part of solid state chemistry.^{1,2} Although the use of quantum mechanical techniques continues to grow, there remain many systems and problems for which, owing to their size and complexity, models based on interatomic potentials are the only feasible approach. In modeling ionic systems in which cohesion is dominated by the Coulomb forces, simulations relying on Born model potentials have enjoyed considerable success. The reliability of the results of such calculations is of course determined by the quality of such interatomic potentials. These have generally been derived from studies of binary oxides and transferred to more complex systems.³ Although this procedure has proved satisfactory in a number of cases, the extent to which transferability is generally valid is uncertain, and indeed its validity is likely to decrease when the structure under consideration is of greater complexity and lower symmetry than the model compound used in deriving parameters. The use of *ab initio* derived potentials (see *e.g.* ref 2) is a promising approach, but such methods may still not be used routinely for highly complex materials. These questions are of growing importance as simulation methods are used increasingly to examine subtle problems in increasingly complex systems. Indeed the aim of this paper is to extend their application to quaternary oxides of a complexity that has hitherto not been studied.

We recently developed⁴ a set of self-consistent potentials for Mⁿ⁺-O²⁻ and O²⁻-O²⁻ interactions by simultaneously fitting the crystal properties (*e.g.* unit cell parameters, dielectric constants, elastic constants) of a wide range of binary metal oxides (*e.g.* Nd₂O₃, Fe₂O₃), using a single, shared O²⁻-O²⁻ potential, the parameters of which were included in the minimization process. We have thus produced a set of potentials which are inherently transferable, rather than being optimized for one particular compound. The resulting potentials were able to reproduce the crystal properties of appropriate ternary oxides

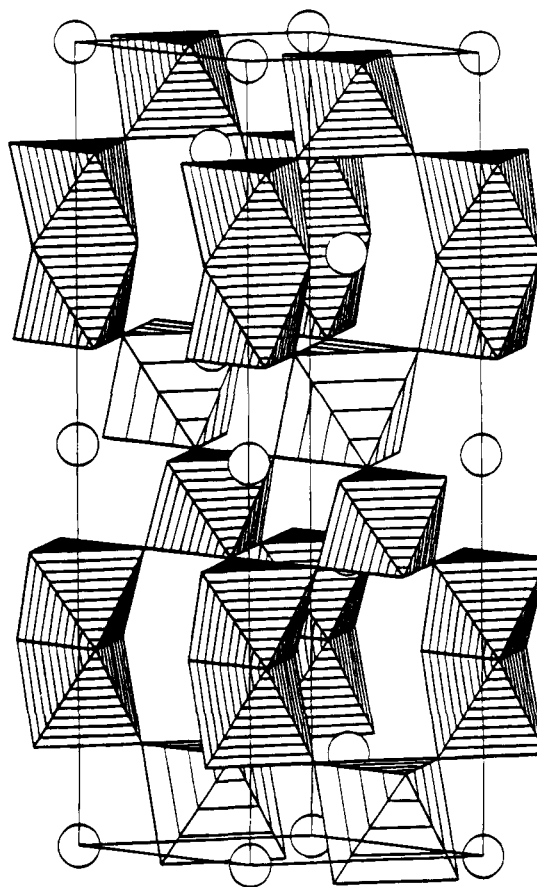


Figure 1. The crystal structure of 8H Ba₄NaRu₃O₁₂. Open circles represent Ba atoms, lightly hatched octahedra contain Na atoms, and densely hatched octahedra contain Ru atoms.

(*e.g.* NdFeO₃) to an accuracy of ~1%. Transition metal cations with electron configurations other than d⁰, d⁵, and d¹⁰ were deliberately omitted from the calculations described above, and this obviously prevents the application of our results to many systems. Indeed, it could be argued that it excludes the most interesting transition metal compounds from consideration. In the present paper we aim to rectify this deficiency by describing the development of the method to include the d³ species Ru(V) and other related cations. We thus demonstrate that the method can be applied to cations with partially filled d shells which

* Author to whom correspondence should be addressed.

[†] Inorganic Chemistry Laboratory.

[‡] The Royal Institution of Great Britain.

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(1) Harding, J. H. *Rep. Prog. Phys.* **1990**, *53*, 1403.

(2) Catlow, C. R. A.; Bell, R. G.; Gale, J. D. *J. Mater. Chem.* **1994**, *4*, 781.

(3) Lewis, G. V.; Catlow, C. R. A. *J. Phys. C* **1985**, *18*, 1149.

(4) Bush, T. S.; Gale, J. D.; Catlow, C. R. A.; Battle, P. D. *J. Mater. Chem.* **1994**, *4*, 831.

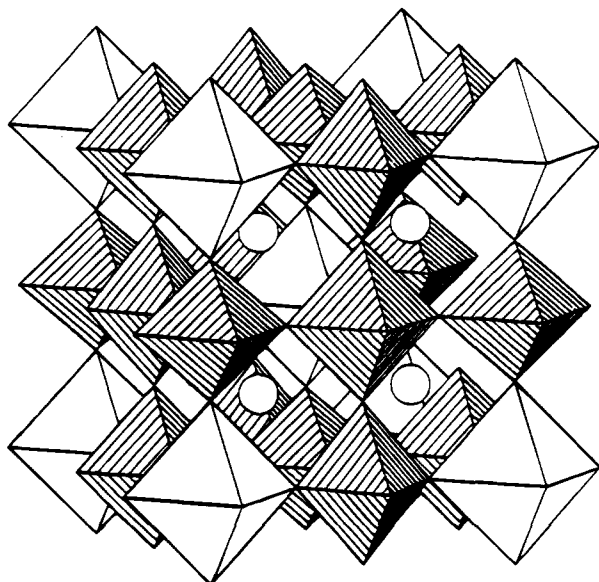


Figure 2. The crystal structure of $\text{Ba}_4\text{Sb}_3\text{MO}_{12}$, showing a 3:1 ordered arrangement of Sb and M atoms. Open octahedra contain M atoms and hatched octahedra contain Sb atoms. Open circles represent Ba atoms.

occur in structures of a complexity previously beyond the scope of modeling techniques.

The particular focus of this paper is the quaternary oxides of Ru and Sb where we shall try to rationalize the similarities and differences in the structural chemistry of Ru(V) and Sb(V). The similarities are evidenced by the fact that $\text{Ba}_3\text{NiRu}_2\text{O}_9$ and $\text{Ba}_3\text{-NiSb}_2\text{O}_9$ both adopt the same 6H perovskite structure, and the intermediate compound $\text{Ba}_3\text{NiRuSbO}_6$ can be prepared;⁵ the three pseudocubic perovskites $\text{Ba}_2\text{LaRuO}_6$, $\text{Ba}_2\text{LaSbO}_6$, and $\text{Ba}_2\text{-LaSb}_{0.5}\text{Ru}_{0.5}\text{O}_6$ show the same effect.⁶ The differences are evident in $\text{Ba}_4\text{NaRu}_3\text{O}_{12}$ which adopts⁷ an 8H hexagonal perovskite structure (Figure 1) whereas $\text{Ba}_4\text{NaSb}_3\text{O}_{12}$ adopts⁸ a pseudocubic perovskite structure with a 3:1 pattern of cation ordering over the six-coordinate sites (Figure 2).

Our interest in these compounds originates in the electronic properties of mixed metal oxides of Ru, which often lie close to the metal-insulator transition. Although SrRuO_3 is a ferromagnetic metal, a combination of properties that indicates that the intraatomic and interatomic electronic interactions are of comparable strength, all oxides of Ru(V) prepared to date have been insulators, often ordering antiferromagnetically at low temperatures. We believe that a cubic mixed-valence compound $\text{Ba}_4\text{MRu}_3\text{O}_{12}$ is likely to be metallic, if it can be prepared. We describe below the development of Ru-O and Sb-O potentials based on a number of structurally characterized oxides, e.g. $\text{Sr}_2\text{-YRuO}_6$.⁹ The majority of the other relevant pair potentials (e.g. $\text{Sr}^{2+}-\text{O}^{2-}$) were derived in our previous work.⁴ We then show that these potentials account for the structural differences between $\text{Ba}_4\text{NaRu}_3\text{O}_{12}$ and $\text{Ba}_4\text{NaSb}_3\text{O}_{12}$, and we go on to consider the likelihood of preparing a compound $\text{Ba}_4\text{MRu}_3\text{O}_{12}$ (where M is divalent or trivalent) that will adopt an ordered pseudocubic structure rather than take a hexagonal form.

Method

All calculations performed in this study employed the static lattice computer code GULP 0.8,¹⁰ which is based on the Born model of the ionic lattice, and from which the structure, crystal properties (for example, elastic constants), and phonon modes of a compound may be calculated. Under this implementation of the Born model, the ionic lattice is represented as an infinite array of point charges using periodic boundary conditions. The lattice energy, which with its derivatives with respect to atomic coordinates allows the calculation of the above lattice properties, is calculated from the sum of the Coulombic interactions and the other interatomic potential energies. The former are represented using an integer point charge model with charges conforming to formal oxidation state and the latter by simple analytical functions which describe both the Pauli repulsions between the closed shell ionic species at small interatomic separations and the attractive dispersion forces at larger separations. Due to the conditional convergence of the Coulombic sum for infinite systems, the Ewald procedure is used for the electrostatic terms, the remaining potential terms being summed pairwise within a chosen radius (typically 12 Å). The non-Coulombic interactions were represented by the Buckingham potential

$$\varphi_{ij}(r) = A_{ij} \exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6}$$

where A_{ij} , ρ_{ij} , and C_{ij} are parameters to be fitted. In order to allow the modeling of dielectric properties and the long-range polarization energy for defects, a dipolar shell model¹¹ was included for most ions. $E_{(\text{core-shell})} = \frac{1}{2}k_{(\text{core-shell})}r^2$ yielding an ion polarizability (α_i) of $q_{\text{shell}}^2/[k_{(\text{core-shell})} + f_{\text{shell}}]$ where q_{shell} is the shell charge, $k_{\text{core-shell}}$ represents the restoring force between the core and shell, and f_{shell} represents the competing distorting forces due to the presence of the surrounding ions; r is the core-shell separation. A more complete account of our general methodology has been given previously.⁴

In the present study we needed initially to derive potentials for $\text{Ru}^{5+}-\text{O}^{2-}$ and $\text{Sb}^{5+}-\text{O}^{2-}$ interactions by fitting to compounds in which this was the only unknown metal oxide potential. In order to increase the number of compounds that could be included in this step we first derived $\text{Er}^{3+}-\text{O}^{2-}$, $\text{Lu}^{3+}-\text{O}^{2-}$, and $\text{Ni}^{2+}-\text{O}^{2-}$ potentials by fitting the structural parameters of Er_2O_3 , Lu_2O_3 , and NiO , respectively; the $\text{O}^{2-}-\text{O}^{2-}$ potential reported recently⁴ was used in these calculations. We then proceeded to fit potentials for the two pentavalent cations. Seven compounds, some having symmetry as low as monoclinic or triclinic, were modeled simultaneously in an attempt to derive a $\text{Ru}^{5+}-\text{O}^{2-}$ potential with a high degree of transferability. The parameters describing the Buckingham potential and the polarizability of the pentavalent cation were varied using a multiple relaxed-fitting approach⁴ whereby a series of experimental structures are relaxed to an energy minimum using a set of starting potentials, and the potential parameters are then refined to optimize the agreement between observed and calculated lattice parameters; this sequence is repeated until convergence is achieved. All other interatomic potentials were held at the values determined in the previous study of binary and ternary oxide systems. Finally, the phonon frequency spectra were calculated after energy minimization using the refined potential parameters in order to verify that a true minimum had been reached.

These calculations did not initially converge to a well-determined set of parameters, and in order to make progress it was necessary to recognize that the compounds under consideration each contained only one of two distinct types of RuO_6 octahedral linkage. In $\text{Ba}_3\text{CaRu}_2\text{O}_9$ ¹² and $\text{Ba}_3\text{SrRu}_2\text{O}_9$ ¹³ the octahedra share a common face, whereas in $\text{Sr}_2\text{-YRuO}_6$,⁹ $\text{Sr}_2\text{LuRuO}_6$, Ba_2YRuO_6 ,¹⁴ $\text{Sr}_2\text{ErRuO}_6$,¹⁵ and $\text{Ba}_2\text{LaRuO}_6$ ¹⁶ the

(10) Gale, J. D. GULP (General Utility Lattice Program), Royal Institution of Great Britain, 1994.

(11) Dick, B. G.; Overhauser, A. W. *Phys. Rev.* **1958**, *112*, 90.

(12) Darriet, J.; Soubeyroux, J. L.; Murani, A. P. *J. Phys. Chem. Solids* **1983**, *44*, 269.

(13) Zandbergen, H. W.; Ijdo, D. J. W. *Acta Crystallogr.* **1984**, *C40*, 919.

(14) Battle, P. D.; Jones, C. W. *J. Solid State Chem.* **1989**, *78*, 108.

(15) Battle, P. D.; Jones, C. W.; Studer, F. *J. Solid State Chem.* **1991**, *90*, 302.

(5) Lightfoot, P.; Battle, P. D. *Mater. Res. Bull.* **1990**, *25*, 89.

(6) Almaer, S. A.; Battle, P. D.; Lightfoot, P.; Mellen, R. S.; Powell, A. V. *J. Solid State Chem.* **1993**, *102*, 375.

(7) Battle, P. D.; Kim, S. H.; Powell, A. V. *J. Solid State Chem.* **1992**, *101*, 161.

(8) Alonso, J. A.; Mzayek, E.; Rasines, I. *Mater. Res. Bull.* **1987**, *22*, 69.

(9) Battle, P. D.; Macklin, W. J. *J. Solid State Chem.* **1984**, *52*, 138.

Table 1. Metal Oxide Potentials and Polarizability Parameters Derived from Lu₂O₃, Er₂O₃, and NiO

	A (eV)	ρ (Å)	C (eV Å ⁻⁶)	q_{core} (e ⁻)	q_{shell} (e ⁻)	k (eV Å ⁻²)	a_{obs}^a (Å)	a_{calc}^a (Å)
Lu ³⁺ -O ²⁻	1007.60	0.3526	0.0	-0.277	3.227	308.91	10.3700	10.3699
Er ³⁺ -O ²⁻	767.147	0.3791	0.0	-0.990	3.990	304.88	9.387	9.387
Ni ²⁺ -O ²⁻	2057.23	0.2670	2.198	2.00			4.1771	4.1771
O ²⁻ -O ²⁻	25.41	0.6937	32.32	0.513	-2.513	20.53		

^a The observed unit cell parameter and the value calculated using these potentials.

Table 2. Ru⁵⁺-O²⁻ and Sb⁵⁺-O²⁻ Potential and Polarizability Parameters Derived from Simultaneous Fitting to a Number of Mixed Metal Oxides

	A (eV)	ρ (Å)	C (eV Å ⁻⁶)	q_{core} (e ⁻)	q_{shell} (e ⁻)	k (eV Å ⁻²)
Ru ⁵⁺ -O ²⁻ (corner-sharing)	17048.85	0.2219	0.0	4.617	0.343	446.3
Ru ⁵⁺ -O ²⁻ (face-sharing)	10041.77	0.2217	0.0	4.617	0.343	446.3
Sb ⁵⁺ -O ²⁻ (corner-sharing)	18752.22	0.2219	0.0	2.105	2.895	101.2
Sb ⁵⁺ -O ²⁻ (face-sharing)	10904.71	0.2273	0.0	2.105	2.895	101.2

octahedra are linked to their neighbors by vertex sharing. Further calculations in which the Ru⁵⁺-O²⁻ potentials in these two cases were allowed to differ were performed and a set of satisfactory parameters was obtained for each geometry. A similar strategy was adopted in deriving Sb⁵⁺-O²⁻ potentials. The ordered perovskites Ba₄NaSb₃O₁₂,⁸ Ba₄LiSb₃O₁₂,¹⁷ and Sr₄NaSb₃O₁₂,¹⁸ the latter being monoclinic and the others cubic, were modeled simultaneously in order to derive a potential which is valid when the SbO₆ octahedra are linked by corner-sharing, and the 6H hexagonal perovskite Ba₃NiSb₂O₉¹⁹ was used as a model for those compounds in which the octahedra are linked through a common face.

In order to test these new pentavalent-cation-oxygen potentials we attempted to model the 8H hexagonal perovskite Ba₄NaRu₃O₁₂, which contains⁷ both face-sharing and vertex-sharing RuO₆ groups. Furthermore, we investigated whether this compound might also be stable in the 3:1 ordered cubic structure adopted by Ba₄NaSb₃O₁₂ and whether the Sb compounds might have an 8H hexagonal phase. We also investigated whether any mixed-valence Ru⁵⁺/Ru⁴⁺ compounds having the general formula Ba₄MRu₃O₁₂ (M = M²⁺ or M³⁺) might adopt the cubic structure. A Ru⁴⁺-O²⁻ potential was developed for this study, as discussed below.

Results

The refined parameters which best describe the Buckingham potential for M-O²⁻ interactions and the cation and oxygen polarizabilities for M = Lu³⁺, Er³⁺, or Ni²⁺ are listed in Table 1. No cation polarizability was included in modeling the Ni²⁺-O²⁻ interaction, and inclusion of dispersion forces was not found to be important in describing the interactions of the lanthanide cations. The parameters subsequently deduced for Ru⁵⁺-O²⁻ and Sb⁵⁺-O²⁻ interactions are listed in Table 2. Again, it was not necessary to consider cation-oxygen dispersion forces. Once the need to use different potentials in different geometries had been recognized, the optimization of the Ru⁵⁺-O²⁻ potentials proceeded smoothly, as did the refinement of the parameters describing corner-sharing Sb⁵⁺-O²⁻ units. The unit cell parameters obtained using these potentials are listed in Table 3, along with the corresponding experimental values.

In order to demonstrate the quality of these potentials, a number of monoclinic compounds, chosen for computational convenience, were modeled without any symmetry constraints, that is they were treated as if they were triclinic. Thus although Ba₂YRuO₆, Ba₃CaRu₂O₉, and Ba₃SrRu₂O₉ were constrained to retain their observed cubic, hexagonal, and monoclinic symmetries, the monoclinic compounds Sr₂MRuO₆ (M = Y, Lu,

Er) were modeled in triclinic symmetry, as was Ba₂LaRuO₆ (which is truly triclinic). The unit cell angles α and γ listed for these Sr-containing compounds in Table 3 thus had the opportunity to distort from 90°, but did not do so. Similarly, Ba₄MSb₃O₁₂ (M = Li, Na) was constrained to be cubic, but monoclinic Sr₄NaSb₃O₁₂ was left unconstrained. As in the case of the monoclinic Ru compounds, the unit cell parameters α and γ did not deviate significantly from 90°.

It was not so straightforward to obtain parameters which adequately describe the Sb⁵⁺-O²⁻ potential in face-sharing SbO₆ octahedra. The values listed in Table 2 are those which best fit the hexagonal structure of Ba₃NiSb₂O₉ as described by Jacobson and Calvert.¹⁹ However, when the structure was allowed to relax to an energy minimum under the influence of this potential, modes with imaginary frequencies appeared in the calculated phonon spectrum, indicating that the structure was unstable. Energy minimization without the constraints imposed by hexagonal symmetry produced a structure that was stable, but with a marked deviation from the higher symmetry unit cell parameters (Table 3), a point to which we return below.

The two Ru-O potentials described above were used simultaneously in the calculation of the unit cell parameters of the 8H perovskite Ba₄NaRu₃O₁₂. The lattice symmetry was initially constrained to be hexagonal, and the calculated unit cell parameters were $a = 5.8558$ Å and $c = 19.425$ Å, in excellent agreement with the experimental values of $a = 5.8142$ Å and $c = 19.264$ Å. There was no significant change in the theoretical values when the calculation was repeated in the absence of symmetry constraints. Attempts to model this compound in the cubic structure adopted by the Sb analogue did not result in a stable structure, nor did attempts to model the Sb compounds as 8H hexagonal perovskites although a structurally similar phase having lower symmetry was found to be stable.

In order to consider the possibility of preparing a cubic mixed-valence compound Ba₄MRu₃O₁₂, the structures of RuO₂ and SrRuO₃²⁰ were modelled simultaneously in order to develop a Ru⁴⁺-O²⁻ potential. Although the linkage of the RuO₆ groups is different in these two compounds (mixed-edge and corner-sharing vs corner-sharing only), it was found that one potential (Table 4) could model both compounds in a satisfactory way, even without any allowance for the polarizability of the Ru⁴⁺ cation (Table 5). This potential was then used along with the other appropriate potentials (including Ru⁵⁺-O²⁻) to assess the likely stability of Ba₄MRu₃O₁₂ in a cubic structure with M = Ca, Sr, Ni, or a rare earth. (It has already been shown that the phase has a 6H perovskite structure for M = Mg and Zn.⁷) There

(16) Battle, P. D.; Goodenough, J. B.; Price, R. J. *Solid State Chem.* **1983**, *46*, 234.

(17) Jacobson, A. J.; Collins, B. M.; Fender, B. E. F. *Acta Crystallogr.* **1974**, *B30*, 1705.

(18) Alonso, J. A.; Mzayek, E.; Rasines, I. J. *Solid State Chem.* **1990**, *84*, 16.

(19) Jacobson, A. J.; Calvert, A. J. *J. Inorg. Nucl. Chem.* **1978**, *40*, 447.

(20) Jones, C. W.; Battle, P. D.; Lightfoot, P.; Harrison, W. T. A. *Acta Crystallogr.* **1989**, *C45*, 365.

Table 3. Observed and Calculated Unit Cell Parameters^a and Calculated Lattice Energies for Compounds Used in the Derivation of Ru⁵⁺-O²⁻ and Sb⁵⁺-O²⁻ Potentials

oxide	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (deg)	β (deg)	γ (deg)	vol (Å ³)	<i>E</i> _{lat} (eV)
Sr ₂ YRuO ₆	5.7690	5.7777	8.1592	90	90.23	90	271.96	-636.06
	5.7922	5.7973	8.1984	90.00	90.01	90.00	275.30	
	0.4	0.34	0.48	0.0	-0.24	0.0	1.23	
Ba ₂ YRuO ₆	8.3198						575.89	-315.79
	8.3331						578.65	
	0.16						0.48	
Sr ₂ ErRuO ₆	5.7500	5.7636	8.1354	90	90.22	90	269.61	-631.21
	5.8198	5.8307	8.2531	90.00	90.03	90.00	280.06	
	1.21	1.16	1.45	0.0	-0.22	0.0	3.87	
Sr ₂ LuRuO ₆	5.7130	5.7180	8.0762	90	90.22	90	263.82	-635.10
	5.7851	5.7889	8.1915	90.00	90.01	89.99	274.31	
	1.26	1.24	1.43	0.0	-0.23	0.01	3.98	
Ba ₂ LaRuO ₆	6.0225	6.0355	6.0759	120.51	119.95	89.79	155.34	-312.31
	6.0658	6.0599	6.0599	119.51	119.95	90.03	157.71	
	0.71	0.4	0.26	0.8	0.0	0.3	1.5	
Ba ₃ CaRu ₂ O ₉	5.891		14.571				437.92	-1057.28
	5.9385		14.3627				438.64	
	0.81		-1.43				0.16	
Ba ₃ SrRu ₂ O ₉	5.9548	10.2740	15.0329		91.69		918.09	-1053.00
	6.0071	10.4047	14.5953		90.00		912.25	
	0.88	1.27	-2.78		-1.84		-0.64	
Ba ₄ NaSb ₃ O ₁₂	8.2806						567.79	-1347.25
	8.2699						565.60	
	-0.13						-0.38	
Ba ₄ LiSb ₃ O ₁₂	8.2170						554.80	-1351.09
	8.2048						552.34	
	-0.15						-0.44	
Sr ₄ NaSb ₃ O ₁₂	8.0913	8.0871	8.0918	90	89.953	90	529.48	-1357.29
	8.1135	8.1146	8.1351	90.063	90.302	89.992	535.59	
	0.27	0.34	0.54	0.07	0.39	0.01	1.15	
Ba ₃ NiSb ₂ O ₉	5.818	5.818	14.360	90	90	120	420.95	-1031.37
	5.960	5.960	14.444	90.00	89.99	120.00	444.29	
	2.43	2.43	0.59	0.0	0.0	0.0	5.54	

^a The data presented are, in descending order, the observed value, the calculated value, and their percentage difference.

Table 4. Ru⁴⁺-O²⁻ Potential Parameters

	<i>A</i> (eV)	ρ (Å)	<i>C</i> (eV Å ⁻⁶)	<i>q</i> _{core} (e ⁻)	<i>q</i> _{shell} (e ⁻)	<i>k</i> (eV Å ⁻²)
Ru ⁴⁺ -O ²⁻	13733.4	0.2259	0.49	4.0		

is an inherent difficulty with this approach as it assumes an ordered arrangement of cations having localized electrons in a compound which is expected to be metallic. Such calculations are, however, still of considerable value, particularly since the compounds used to derive the Ru⁴⁺-O²⁻ potential are both metallic. Our calculations failed to find a stable cubic phase in those cases where M is a divalent cation, but they enabled us to predict that Ba₄MRu₃O₁₂, with a 2:1 ratio of Ru⁴⁺:Ru⁵⁺, will be a cubic or pseudocubic perovskite when M is a trivalent lanthanide. Experiments to establish the validity of this prediction are currently in progress.

Discussion

The calculations described above have shown that the methods used to model the crystal structures and properties of relatively simple binary and ternary solids can also be applied to complex mixed-metal oxides. We have been able to calculate unit cell parameters to better than 1.5% for a wide range of materials, and to ~0.5% in many cases. This latter value is certainly low enough to be used as a starting value in the interpretation of a powder diffraction pattern and the higher value is likely to lead to a predicted pattern which is close enough to the observed pattern to be recognizable and subsequently refined. The need to use coordination-dependent potentials for Ru⁵⁺-O²⁻ interactions highlights the pitfalls of assuming that these potentials are always freely transferable,

but the excellent agreement between the observed and calculated unit cell parameters of Ba₄NaRu₃O₁₂ demonstrates that a set of transferable potentials can be developed once the importance of the coordination differences has been recognized. However, the inadequacy of a single potential means that more than one permutation may have to be tried in any attempt to use the potentials in ab-initio structure determination. The need to use geometry-dependent potentials (to account for variations in cation radius) has been recognized previously.³ In this particular case it is likely that the need to use a different potential in the case of face-sharing octahedra is due to the presence of a strong interaction between the half-filled t_{2g} orbitals on a pair of Ru⁵⁺ cations which are only ~2.5 Å apart. It is interesting to note that the interactions between the cations in neighboring edge-sharing sites (~3.1 Å apart) in RuO₂ are not sufficiently different from those between the corner-sharing sites (~3.9 Å apart) in SrRuO₃ to require the use of a different potential. It would be interesting to investigate whether the same potential could model an insulating oxide of Ru⁴⁺.

The difficulties experienced in modeling Ba₃NiSb₂O₉ are interesting, particularly in view of the previous history of this structure. Jacobson and Calvert¹⁹ showed quite clearly that their sample adopted the 6H hexagonal perovskite structure with Sb occupying the face-sharing cation sites, to form Sb₂O₉ dimers, and Ni occupying the single, corner-sharing cation site. However, a single-crystal X-ray diffraction study by Köhl and Reinen²¹ was equally clear in showing that the dimers have the composition SbNiO₉, and that the single octahedra are occupied by Sb. The results of our own work²² were in agreement with those of Jacobson and Calvert, but we were able to stabilize

(21) Köhl, P.; Reinen, D. Z. Anorg. Allg. Chem. 1977, 433, 81.

(22) Battle, P. D.; Jones, C. W.; Lightfoot, P.; Strange, R. J. Solid State Chem. 1990, 85, 144.

Table 5. Observed and Calculated Unit Cell Parameters^a for RuO₂ and SrRuO₃

oxide	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (deg)	β (deg)	γ (deg)	vol (Å ³)	<i>E</i> _{lat} (eV)
RuO ₂	4.4919		3.1066	90	90	90	62.68	-243.39
	4.5134		3.1069				63.28	
	0.47		0.01				0.96	
SrRuO ₃	5.5304	7.8446	5.5670	90	90	90	241.52	-627.72
	5.5803	7.8917	5.5803				245.75	
	0.90	0.60	0.24				1.75	

^a See Table 3, footnote *a*.

the Köhl–Reinen structure under high pressure. It may be the case that the difficulties experienced in modeling this structure are symptomatic of the close proximity of a phase transition under ambient conditions. Unfortunately, no other Sb compound containing the appropriate structural units has been characterized sufficiently well for us to use it as an alternative source of a potential. It is likely that in the case of these antimony compounds we are working on phases which are close to instability, and that we are thus at the limit of the applicability range of the simple dipolar shell model.

We believe that the successful modeling of Ba₄NaRu₃O₁₂ demonstrates the considerable promise for the application of this computational technique to the solid state chemistry of complex mixed-metal oxides. We were able to differentiate

between two possible structure types for this material, and its Sb analogues, and then to calculate the unit cell parameters to better than 1%. Moreover, we correctly show that the Sb compound is unstable in the hexagonal structure adopted by the Ru compound. However, the challenge for the future is to predict new structures rather than confirm existing knowledge. We therefore look forward with interest to the results of our experiments on Ba₄MRu₃O₁₂.

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