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The Structural and Electronic Properties of the Ru(V) Perovskites $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ and $Ba_2TaRu_{0.5}Na_{0.5}O_6$

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The compounds $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ and $Ba_2TaRu_{0.5}Na_{0.5}O_6$ have been used to study the magnetic properties of Ru(V) when present in low concentrations in a mixed metal oxide. $Ba_2TaRu_{0.5}Na_{0.5}O_6$ is a simple cubic perovskite (a_0 = 4.1321(5) Å) with a random distribution of Ta, Ru, and Na over the six-coordinate sites and a magnetic susceptibility that follows the Curie–Weiss Law (μ_{eff} = 3.44 μ_B, θ = −142 K). Neutron powder diffraction has been used to show that $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ is a distorted perovskite (space group $I\bar{1}$, a = 6.0741(5), b = 6.0895(5), c = 8.6124(9) Å, α = 89.93(1), β = 90.39(1), γ = 89.91(1)°) with a 1 : 1 ordered arrangement of La and Ru/Sb atoms over the six-coordinate sites. Again the magnetic susceptibility follows a Curie–Weiss law (μ_{eff} = 3.78 μ_B, θ = −170 K). These results are considered in the light of the magnetic susceptibility of Ba_2LaRuO_6 (μ_{eff} = 4.00 μ_B, θ = −304 K). © 1993 Academic Press, Inc.

Introduction

The pentavalent cation of the second-row transition metal ruthenium has been found in many pseudo-cubic, perovskite-related oxides (Fig. 1). In most of the compounds studied to date it occupies half of the six-coordinate (B) sites, with the remainder of the octahedra being occupied by a lanthanide (*1*, *2*) or a cation from the first transition series (*3*). Neutron diffraction studies (*4*, *5*) have shown that in the former case Ru(V) and Ln(III) order in a 1 : 1 alternate fashion over the B sites, whereas in the latter case the transition metal cations are randomly distributed over the six-coordinate sites. In both cases the symmetry of the lattice is usually lower than cubic, but the distortions are primarily due to the displacement of the oxide ions away from their ideal positions. It is thus reasonable to think of the Ru(V) cations in, for example, Sr_2FeRuO_6 as occupying 50% of the sites in a primitive cubic array of transition metal cations with a unit cell parameter $a_p \sim 3.9$ Å, whereas those in Ba_2LaRuO_6 fill the sites in a face-centered cubic array with a unit cell parameter $\sim 2a_p$. The magnetic properties of both types of compound have been studied in some detail. The materials containing both a first-row transition metal and Ru(V) often show spin-glass behavior (*5*), whereas those in which Ru(V) is the only magnetic cation generally undergo a transition to an antiferromagnetic

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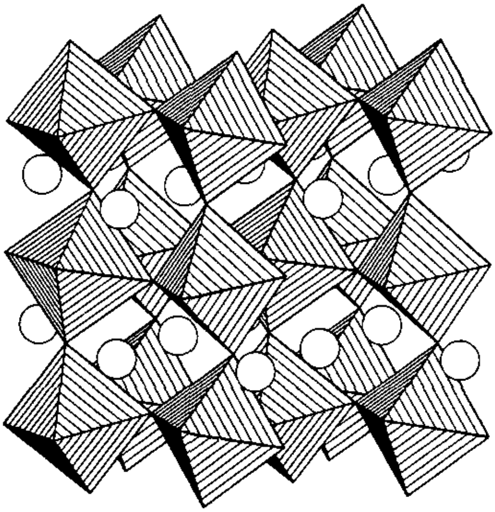

FIG. 1. The structure of a pseudo-cubic perovskite, drawn with all the MO_6 cation octahedra (hatched) equivalent. Unfilled circles are alkaline earth cations.

phase at ~30 K (*4*). However, the magnetic properties of these latter compounds above the Neel temperature are rather unusual, in that the effective magnetic moment, μ_{eff}, and the Weiss constant, θ, are both greater than would be expected for a d^3 electron system with $T_N \sim 30$ K. In the case of Ba_2LaRuO_6, for example, $\mu_{eff} = 4.0\ \mu_B$ and $\theta = -304$ K. The spin-only magnetic moment for a d^3 ion on an octahedral site would be 3.87 μ_B, and any orbital contribution would be expected to reduce, rather than increase, the moment from this value. The ratio $\theta/T_N \sim 10$ is also considerably larger than that usually found in antiferromagnets (~3). We have previously explained these observations (*4*) by assuming that the outer *d* electrons in these compounds cannot be described using localized electron theory, and that a model involving the introduction of some itinerant electron character is more appropriate. This move toward delocalization is caused by intercation interactions, which might be expected to diminish if the concentration of Ru(V) cations in the compound were decreased. No dilute Ru(V) oxides which could be used to test this proposal have been reported previously but we describe below the preparation of two compounds which can be used to establish whether or not localized electron theory is applicable when the Ru(V) content is low. Initially we attempted to use the similarities in the structural chemistries of Ru(V) and the isovalent post-transition metal Sb(V) : $4d^{10}$ to produce diluted ruthenates. This approach met with some success, in that, knowing that $Ba_3NiRu_2O_9$ and $Ba_3NiSb_2O_9$ are isostructural, we were able to prepare $Ba_3NiRuSbO_9$ (*6*). In these three compounds the pentavalent cations lie in M_2O_9 dimers made up from two face-sharing MO_6 octahedra. Pursuing the analogy further, we made the antimony analogues of $BaLaZnRuO_6$ and $BaLaNiRuO_6$, but we were unable to synthesize the corresponding solid solutions, for example $BaLaZnRu_{1-x}Sb_xO_6$, and we were therefore unable to use this system to characterize dilute, paramagnetic Ru(V). We ascribed the failure of our synthesis to the reluctance of RuO_6 and SbO_6 octahedra to link by vertex-sharing, as they would be required to do in a perovskite with a disordered arrangement of six-coordinate cations. In order to demonstrate the validity of this explanation we attempted to prepare $Ba_2LaRu_{0.5}Sb_{0.5}O_6$, believing that the presence of the large lanthanum cations would cause a 1 : 1 ordering of the La and Sb/Ru cations on the six-coordinate sites so that each SbO_6 or RuO_6 octahedron would be vertex-linked only to LaO_6 octahedra, as is the case in Ba_2LaRuO_6 and Ba_2LaSbO_6 (*7*). The structural and magnetic characterization of this compound is described below. Furthermore, in a program to study the effect of magnetic dilution on the hexagonal compound $Ba_2Ru_{1.5}Na_{0.5}O_6$, we have prepared a second dilute Ru(V) system, the cubic phase $Ba_2TaRu_{0.5}Na_{0.5}O_6$, the magnetic properties of which are also described below.

Experimental

A polycrystalline sample of $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ was prepared by firing a pelletized stoichiometric mixture of $BaCO_3$, La_2O_3, Sb_2O_3, and RuO_2 in air at temperatures increasing to 1300°C. The reaction took several days to go to completion and the reactants were ground and repelletized many times during the heating program. The purity of the rust-colored product was assessed by X-ray powder diffraction. $Ba_2TaRu_{0.5}Na_{0.5}O_6$ was prepared in a similar way, but at a maximum temperature of 800°C and using Ta_2O_5 and Na_2CO_3 as appropriate. A slight (~10%) excess of sodium carbonate was found to be necessary to compensate for loss by volatalization during the heating program. The reaction was judged to be complete when the black product gave a monophasic X-ray diffraction pattern. Neutron diffraction data were collected on $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ at room temperature using the powder diffractometer D1a at ILL Grenoble. The instrument was operated with a mean neutron wavelength of 1.9127 Å and a 2θ step size of 0.05°. Data were collected in the angular range $0 < 2\theta < 140°$ over a period of ~12 hr. Magnetic susceptibility data were collected on both compounds in the temperature range from 6 to 296 K using a Cryogenics SCU500 SQUID magnetometer operating at a magnetic field of 5 kG. Data were collected as the sample was warmed after cooling in zero magnetic field (zfc) and also after cooling in the measuring field (fc).

Results

The slightly broadened peaks in the X-ray powder diffraction pattern of $Ba_2TaRu_{0.5}Na_{0.5}O_6$ could be indexed using a primitive cubic unit cell of size 4.132(5) Å. The adoption of this simple unit cell indicates that the Ta, Na, and Ru cations are randomly distributed over the six-coordinate sites in the perovskite structure; the broadening could indicate either a relatively low crystallinity or a small distortion away from cubic symmetry. The corresponding data on $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ were more complex, suggesting that, as proposed above, the lanthanum and the pentavalent cations are ordered in a 1 : 1 fashion over the octahedral sites. This ordering was investigated more fully using the neutron diffraction data, which were analyzed using the Brookhaven version of the Rietveld profile analysis method (*8*, *9*). A pseudo-Voigt peak shape function was used with the background level estimated by interpolation between regions free from Bragg peaks. The structure is highly pseudo-symmetric and, without careful profile analysis, could (almost) be taken to be face-centered cubic. However, attempts to refine the structure in relatively high-symmetry space groups were unsuccessful and we eventually concluded that the lattice is triclinic. The same conclusion was reached previously (*4*) during a structural study of Ba_2LaRuO_6. To facilitate comparison with many other distorted perovskites, our final refinements were carried out in the nonstandard space group $I - 1$ with the unit cell parameters taking the following values: $a = 6.0741(5)$, $b = 6.0895(5)$, $c = 8.6124(9)$ Å, $\alpha = 89.93(1)$, $\beta = 90.39(1)$, and $\gamma = 89.91(1)°$. Refinement of sixteen atomic parameters and the appropriate profile parameters against the intensities of 304 Bragg reflections then resulted in the agreement indices $R_{wpr} = 4.6\%$, $R_I = 1.9\%$. The structural model which gives rise to this excellent level of agreement is essentially a distorted perovskite with the octahedral sites ordered in such a way that half are occupied by La(III) cations and the remainder by a disordered arrangement of Ru(V) and Sb(V), as illustrated in Fig. 2. The corresponding atomic coordinates are presented in Table I and the most important bond lengths and bond angles are listed in Table II. The final observed and calculated diffraction profiles

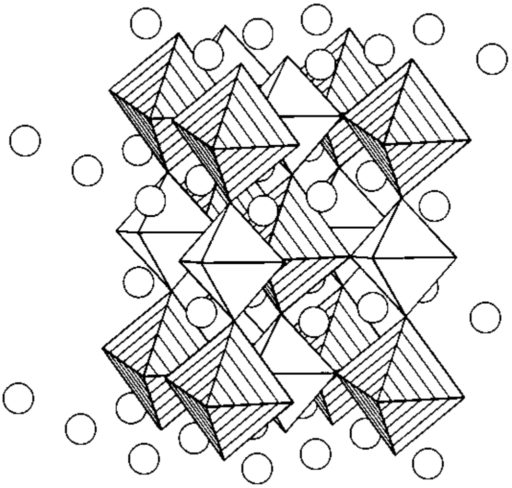

FIG. 2. The crystal structure of $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ showing an ordered arrangement of LaO_6 (hatched) and Ru/SbO_6 (unhatched) octahedra. Ba atoms are represented by unfilled circles.

TABLE II

BOND LENGTHS (IN Å) AND BOND ANGLES (IN DEGREES) FOR $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ AT ROOM TEMPERATURE

La–O1	2.33(1)	O1–La–O2	94.4
La–O2	2.31(1)	O1–La–O3	90.8
La–O3	2.35(1)	O2–La–O3	92.8
Ru/Sb–O1	1.98(1)	O1–Ru/Sb–O2	93.5
Ru/Sb–O2	2.04(1)	O1–Ru/Sb–O3	90.0
Ru/Sb–O3	1.97(1)	O2–Ru/Sb–O3	94.5
Ba–O1	3.18(1)		
	2.90(1)		
	2.93(1)		
	3.21(1)		
Ba–O2	3.01(1)		
	3.08(1)		
	2.66(1)		
Ba–O3	2.95(1)		
	3.16(1)		
	2.94(1)		
	3.16(1)		

are drawn in Fig. 3. The close spacing of the reflection markers gives some indication of the pseudo-symmetry present. The results of our magnetic measurements on $Ba_2TaRu_{0.5}Na_{0.5}O_6$ are plotted in Fig. 4. The fc and zfc data deviate slightly at temperatures below ~100 K, thus suggesting that short-range interactions are causing the formation of spin clusters. However, at higher temperatures the data obey a Curie–Weiss law with $\mu_{eff} = 3.44\ \mu_B$ and $\theta = -142$ K. The data collected on $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ (Fig. 5) also follow a Curie–Weiss law at high temperatures ($\mu_{eff} = 3.78\ \mu_B$, $\theta = -170$ K). The zfc and fc data agree well to the lowest temperature measured, although there is a marked deviation from Curie–Weiss behavior below 50 K. It may well be that a magnetic transition occurs below 6 K, but this has not been explored in the present study.

TABLE I

STRUCTURAL PARAMETERS FOR $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ AT ROOM TEMPERATURE (SPACE GROUP I–1)

Atom	x	y	z	B_{iso} (Å^2)
Ba	0.491(1)	0.512(2)	0.255(1)	0.61(5)
La	0	$\frac{1}{2}$	0	0.21(4)
Ru/Sb	$\frac{1}{2}$	0	0	0.55(5)
O1	0.278(1)	0.237(1)	−0.021(1)	1.28(3)
O2	0.240(1)	0.791(1)	0.025(1)	1.28(3)
O3	0.490(1)	0.029(1)	0.227(1)	1.28(3)

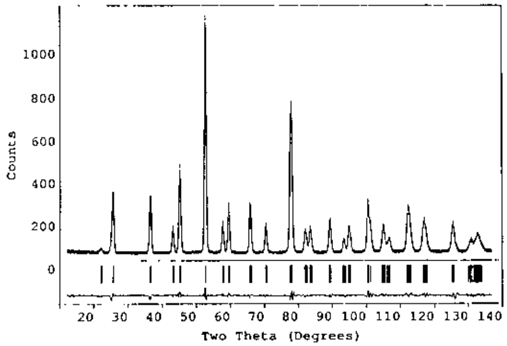

FIG. 3. The observed (. . .), calculated (—), and difference neutron powder diffraction profiles of $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ at room temperature. Reflection positions are marked.

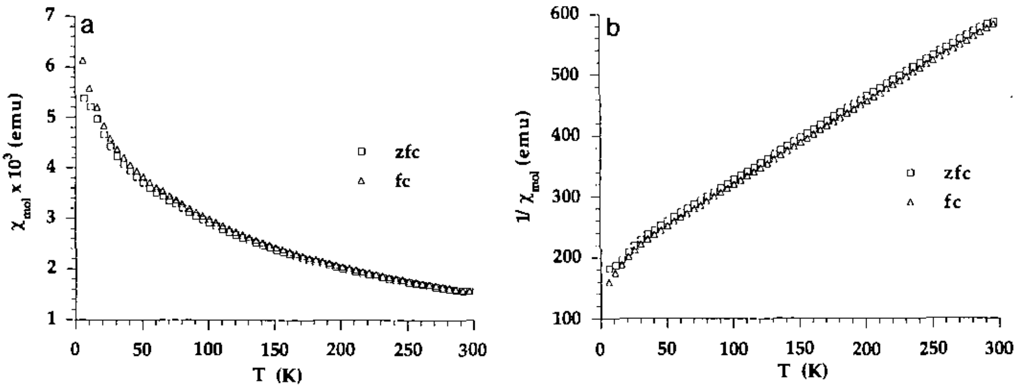

FIG. 4. The temperature dependence of (a) the molar magnetic susceptibility and (b) the inverse susceptibility of $Ba_2TaRu_{0.5}Na_{0.5}O_6$.

Discussion

The adoption by $Ba_2TaRu_{0.5}Na_{0.5}O_6$ of a simple cubic perovskite structure can be contrasted with the structural behavior of other related compounds. $Ba_2Ru_{1.5}Na_{0.5}O_6$ adopts (*10*) an 8H hexagonal perovskite structure in which two-thirds of the Ru(V) cations lie in face-sharing octahedra, thus forming Ru_2O_9 dimers, while the remaining Ru(V) and Na cations occupy corner-sharing octahedra. Partial substitution of tantalum for ruthenium to form $Ba_2Ta_{0.5}RuNa_{0.5}O_6$ leads to the adoption of a distorted 6H–$BaTiO_3$ structure (*11*), and we have now shown that further substitution of Ta(V) for Ru(V) leads to the formation of a cubic structure. This demonstrates the wide range of chemical compositions that can be accommodated in the perovskite structure and the ease with which pentavalent cations can sometimes be interchanged. However, it also emphasizes the difficulty of predicting the detailed structure of a perovskite-like material. In general a hexagonal structure will be increasingly favored for the perovskite ABO_3 as the radius ratio r_A/r_B increases. Thus the transition from cubic $Ba_2TaRu_{0.5}Na_{0.5}O_6$ to 6H $Ba_2Ta_{0.5}RuNa_{0.5}O_6$ can be understood given that $r_{Ta} > r_{Ru}$. However, this argument cannot be used to account for the 8H structure of $Ba_2Ru_{1.5}Na_{0.5}O_6$, which has a lower fraction of face-sharing cation octahedra (the hallmark of hexagonal packing) than the 6H structure. It is clearly invalid to attempt to explain the structural chemistry of perovskites in terms of cation size alone, and it is worth noting that we have been unable to prepare any other compound containing pentavalent cations that is isostructural with 8H $Ba_2Ru_{1.5}Na_{0.5}O_6$. The reasons for this merit further study.

The successful preparation of $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ is in accord with our explanation for the failed synthesis of, for example, $BaLaNiRu_{1-x}Sb_xO_6$. It appears that it is possible to prepare mixed ruthenate/antimonates provided that RuO_6 and SbO_6 octahedra are not required to share corners; in $Ba_3NiRuSbO_9$ they share faces and in $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ they are separated by LaO_6 octahedra. The crystal structure of the latter compound is similar to that of Ba_2LaRuO_6, where the mean La–O and Ru–O distances were 2.34 and 1.96 Å, respectively. The latter, taken together with the mean Sb–O distance of 1.98 Å in $SrLaCuRuO_6$ (*12*), would lead to a predicted mean Sb/Ru–O distance of 1.97 Å, slightly shorter than the observed value of 2.00 Å. It is still not clear why

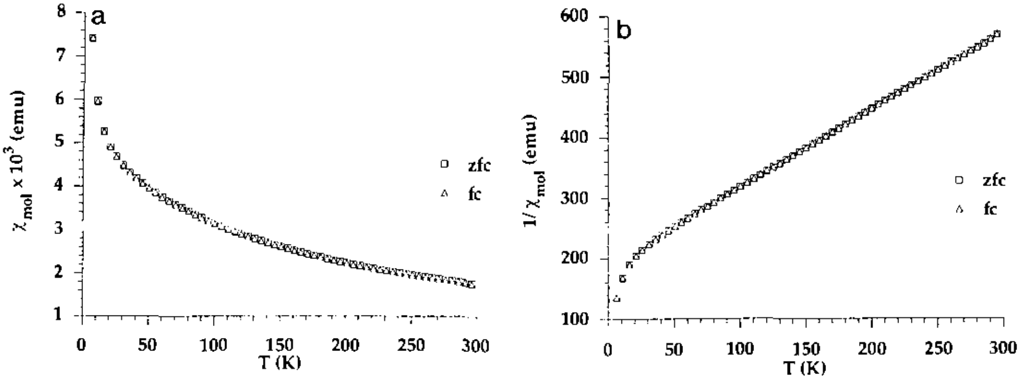

FIG. 5. The temperature dependence of (a) the molar magnetic susceptibility and (b) the inverse susceptibility of $Ba_2LaRu_{0.5}Sb_{0.5}O_6$.

we have been unable to prepare compounds containing corner-sharing RuO_6 and SbO_6 octahedra, but the successful synthesis of related compounds (for example, $Ba_2SbTa_{0.5}Na_{0.5}O_6$ (*11*)) suggests that it is likely to be a consequence of the electronic structures of the cations Ru(V) : $4d^3$ and Sb(V) : $4d^{10}$.

The effective magnetic moment (3.44 μ_B) deduced from the high-temperature magnetic susceptibility of $Ba_2TaRu_{0.5}Na_{0.5}O_6$ is in the range expected for a localized-electron $4d^3 : {}^4A_{1g}$ system and suggests that the Ru(V) cations in this compound can be considered to lie within the localized electron regime. However, the value of θ (~142 K) reported above, although smaller than that of Ba_2LaRuO_6, is still large, particularly for a compound that does not undergo a magnetic phase transition above 6 K. It appears that relatively strong short-range magnetic interactions occur between the transition metal cations even in this dilute system, and it is likely that they are responsible for the low-temperature deviation from Curie–Weiss behavior. The effective magnetic moment of Ru(V) in $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ (3.78 μ_B) is surprisingly close to the spin-only value for a d^3 ion, given that a significant degree of spin-orbit coupling is usually associated with cations from the second transition series. This suggests that, in this second apparently dilute compound, the intercation interactions are again strong enough to cause a significant deviation away from idealized localized-electron behavior, a view which is reinforced by the enhanced value of θ. It would be interesting to study these compounds further at lower temperatures, although the concentration of Ru(V) in $Ba_2TaRu_{0.5}Na_{0.5}O_6$ is below the percolation threshold for a simple cubic lattice and the observation of long-range magnetic ordering would be surprising. However, the 50%-occupied face-centered sublattice in $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ might be expected to show magnetic order at the very lowest temperatures. The observed deviations from localized-electron behavior in these two compounds suggest that the intercation interactions are not negligible despite the low concentration of magnetic cations. This implies that although the Ta(V) and La(III) cations do not contribute any unpaired electrons to the system, they do play a significant role in broadening the energy width of the Ru(V) atomic *d* orbitals to the extent that the electrons associated with the latter cannot be described by Curie–Weiss parameters characteristic of localized electrons.

Thus, although we have succeeded in preparing two compounds that are chemically dilute in Ru(V), they cannot be considered to be magnetically dilute. The influence of the intercation interactions appears to be stronger in $Ba_2LaRu_{0.5}Sb_{0.5}O_6$ than in $Ba_2TaRu_{0.5}Na_{0.5}O_6$; it is, not surprisingly, greatest in the more electron-rich Ba_2LaRuO_6.

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