A New Family of Manganese(II,III)−Rare Earth Pyrochlores

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Polycrystalline samples of a new family of blackish brown pyrochlores of composition $Mn_2R_2[MnSb_3]O_{14}$ (R = Y, In, La, Pr, Nd, Sm−Lu), with two Mn^{2+} and one Mn^{3+} per formula, have been prepared by heating mixtures of reagent grade MnO_2, R_2O_3, and Sb_2O_3 to 1280 or 1300 °C in stoichiometric molar ratios. The composition was established by chemical analysis and confirmed by X-ray powder diffraction methods, neutron powder diffraction data for the Y and Ho compounds, and magnetization measurements. These pyrochlores crystallize in the $Fd\bar{3}m$ space group (no. 227) with $Z = 4$. All of the atoms are in special positions and show only one variable position parameter, u. The unit-cell dimensions, a (Å), range from 10.1227(8) (R = In), to 10.347(2), (R = La). The oxygen positional u parameters were determined from X-ray powder diffraction data for 2Mn+2R at (c) sites, Mn+3Sb at (d) positions, and the origin at the inversion center; and vary from $u = 0.420$ (R = Y) to $u = 0.429$ (R = Pr). Neutron diffraction data for R = Y and Ho gave $u = 0.42167(7)$ and $u = 0.42162(9)$, respectively. Interatomic distances are given. Magnetization measurements from 4 to 350 K are consistent with high spin Mn^{2+} and high spin Mn^{3+} at (c) and (d) positions, respectively. The possibility of predicting u parameters in pyrochlores from a values and ionic radii is discussed.

Introduction

A large number of materials with a wide diversity of properties show the crystal structure of the mineral pyrochlore.[2] Among these materials, the oxides, of which there are examples of various compositions, often show the stoichiometry $A_2B_2O_7$, and crystallize in the $Fd\bar{3}m$ space group (no. 227) with $Z = 8$ and all the atoms in special positions, giving rise to scalenohedral or distorted cubic AO_8 polyhedra, and corner-sharing trigonal antiprismatic or distorted octahedral BO_6 groups. The attention raised by the magnetic properties of pyrochlores containing manganese and rare earths,[3−4] has recently been enhanced by the discovery[5] of colossal magnetoresistance in one of them, $Tl_2Mn_2O_7$, which has attracted considerable interest[6−9] in fundamental physics and potential technological applications of manganese containing pyrochlores.

After describing various pyrochlores, some of the authors tried to search for similar compounds in which 3d−4f interactions could be present, and chose the system Mn−R−Sb (R = rare earth) years before giant magnetoresistance was described[5] in $Tl_2Mn_2O_7$. They observed that mixtures of Mn, R, and Sb oxides in various molar ratios led to crystalline samples of a new family of pyrochlores. Part of the dissertation[10] of one of the authors consisted of the determination of the stoichiometry of these pyrochlores and their study by X-ray powder diffraction (XRD). At present chemical analyses, neutron powder diffraction (NPD) Rietveld refinements, and magnetization measurements confirmed unpublished previous results. This article describes the new family and shows evidence for the occurrence of high-spin Mn^{2+} and high-spin Mn^{3+} cations at the A and B positions, respectively, of the pyrochlore structure.

Experimental Details

Preparation. Mixtures of reagent-grade MnO_2, R_2O_3 (R = Y, In, La, Pr, Nd, Sm−Lu), and Sb_2O_3 at molar ratios Mn:R:Sb = 3:2:3 with 5−10% excess of Sb_2O_3 were heated at 680, 880, 1080, and 1280 °C. Some of them were also heated to 1300

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Table 1. Composition (weight percent) of Mn−Rare Earth Antimonates(V)[a]

		Mn		R		Sb	
no.	R	calc	obs	calc	obs	calc	obs
1	Y	17.7	17.5	19.1	18.9	39.2	38.8
2	La	16.0	16.1	26.9	26.7	35.4	35.1
3	Gd	15.4	15.4	29.4	29.2	34.2	33.9

[a] Calculated values for $Mn_3R_2Sb_3O_{14}$.

°C. After each thermal treatment, which lasted 24 h, the products were weighed and thoroughly ground.

Chemical Analyses. Three 500-mg samples (R = Y, La, Gd) were fused with 5 g of Spectroflux No. 100 (Johnson Matthey) and analyzed (Mn, R, Sb) using a Perkin-Elmer Plasma 40 emission spectrometer.

X-ray Diffraction Studies. The *d*-spacing measurements were made at room temperature with Cu Kα radiation, $\lambda = 1.540598$ Å, at a scan rate of 0.1 °(2θ) min^{-1} from 14° to 156° (2θ) using W metal, $a = 3.16524(4)$ Å, as an internal standard. Additional experimental details on instrumental conditions and measurement of I_o' intensities by step scanning can be seen elsewhere.[11] Unit-cell parameters were refined from the 2θ values of eight from the last 12 reflections. The calculation of the intensities was performed[12] in the space group (S.G.) $Fd\bar{3}m$ (no. 227), taking the origin at the inversion center, ($\bar{3}m$), assuming $Mn_2R_2[MnSb_3]O_{14}$ stoichiometry; $Z = 4$; A cations, Mn^{2+} and R^{3+}, at 16(c) sites, (0,0,0); smaller B cations, Mn^{3+} and $3Sb^{5+}$, at 16(d), ($^1/_2$ $^1/_2$ $^1/_2$); two types of oxygen, O(1) and O(2), at 8a, ($^1/_8$ $^1/_8$ $^1/_8$), and 48(f), (u $^1/_8$ $^1/_8$), respectively; and arbitrarily chosen thermal factors of 0.80 Å^2 for oxygen, 0.30 Å^2 for the most heavy atom, and the thermal factors obtained from these two values by interpolation of the respective atomic masses. The intensities were calculated[12] for u values of 0.415, 0.416, ..., 0.435, and the chosen value was that leading to the smallest R factor, $R = (\sum|I_o^{1/2} - I_c^{1/2}|)/\sum I_o^{1/2}$, where $I_o = kI_o'$, and $k = \sum I_c/\sum I_o$.

Neutron Powder Diffraction Experiments. NPD patterns were collected at room temperature at the D2B high-resolution neutron diffractometer of the Institut Laue Langevin, Grenoble. The high-flux mode was used; a wavelength of 1.594 Å was selected from a Ge monochromator. The collection time was 3 h. The NPD data were treated by the Rietveld method[13] using the FULLPROF refinement program.[14] A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. No regions were excluded in the refinement, and the background was refined to a fifth-degree polynomial, taking as coherent scattering lengths for Ho, Sb, Y, Mn, and O 8.01, 5.57, 7.75, −3.73, and 5.805 fm, respectively. In the final run the following parameters were refined: scale factor, six background coefficients, zero-point error, unit-cell parameters, pseudo-Voigt corrected for asymmetry parameters, u positional coordinate for O(2), relative occupancy factors for (Mn, Ho) at (c) positions, and (Mn, Sb) at 16(d) sites, and isotropic thermal factors.

Magnetization Measurements. A SQUID magnetometer (Quantum Design) operating from 350 to 4 K was used in magnetization measurements. The applied field was between 1 and 5 kOe, and the expected magnetic susceptibility sensitivity 1×10^8 emu units.

Results

XRD Studies. The products of thermal treatments were blackish brown in color and showed XRD patterns[2] typical of $A_2B_2O_7$ cubic pyrochlores exempt from impurities, S.G. $Fd\bar{3}m$ (no. 227), $Z = 8$. Table 1 contains the results of chemical analyses for R = Y, La, Gd that correspond to $Mn_2R_2[MnSb_3]O_{14}$ stoichiometry. Table 2 includes XRD data. The small R_d discrepancy factors confirm the assumed model too, particularly the presence of the R^{3+} cations at (c) sites, as in all known rare earth pyrochlores.[15]

In the cubic $A_2B_2O_7$ pyrochlores, there are some significant distances: eight A−O, two d_1 and six d_2 (average, d_3); six B−O, d_4; one distance between cations, d_5; and two O−O distances, d_6 and d_7. All of these are functions of a and u, the unit-cell dimension and the oxygen positional parameter, respectively:

$$d_1 = \text{A}-\text{O(1)} = (a3^{1/2})/8 \tag{1}$$

$$d_2 = \text{A}-\text{O(2)} = a[(u - {}^1/_4)^2 + {}^1/_{32}]^{1/2} \tag{2}$$

$$d_3 = \text{A}-\text{O} = (d_1 + 3d_2)/4 \tag{3}$$

$$d_4 = \text{B}-\text{O} = a[({}^1/_2 - u)^2 + {}^1/_{32}]^{1/2} \tag{4}$$

$$d_5 = \text{A}-\text{A} = \text{B}-\text{B} = \text{A}-\text{B} = (a2^{1/2})/4 \tag{5}$$

$$d_6 = \text{O(2)}-\text{O(2)} = a2^{1/2}({}^5/_8 - u) \tag{6}$$

$$d_7 = \text{O(1)}-\text{O(2)} = a(u - {}^1/_8) \tag{7}$$

These distances for the members of the new family are listed in Table 2. In particular d_3 decreases rather smoothly along the series. The fact that Pr, Eu, and Tb fit into the trends observed for the rest of the lanthanides is an indication that these elements are trivalent too. The difference of d_4 with respect to the calculated distance, 1.991 Å, increases gradually from 0.4% (R = La) to 2.9% (R = Lu). With the exception of Eu and Yb, which show anomalous atomic radii, the deviations of d_5 with respect to $2r_R$ are small, ranging from −2.6 to 3.3% for R = La and R = Lu, respectively.

Refinement of the Structure from NPD Data. All the reflections present in the NPD pattern of the samples (R = Y, Ho) could be indexed in a cubic unit cell. As in XRD data, no impurity phases were detected. The $Fd\bar{3}m$ symmetry was confirmed since no additional superstructure reflections or splitting of the peaks were detected. The crystal structure was refined in this space group, with only one variable positional parameter corresponding to O(2). The results of the refinement are summarized in Table 3. The goodness of the fit is shown in Figure 1. Table 4 lists the main interatomic distances and angles.

The crystallographic compositions obtained after the NDP data refinements (Table 3) show that the composition assumed for this family of pyrochlores is globally correct and can be written as $Mn_2R_2[MnSb_3]O_{14}$, containing Mn at both A and B sublattices of the pyrochlore structure. This crystallographic formula implies oxidation states of Mn^{2+} for 16(c) positions and Mn^{3+} for 16-(d) positions, which is sound from the chemical or crystallochemical point of view.

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Table 2. XRD Powder Data and Interatomic Distances (Å) for $Mn_2R_2[MnSb_3]O_{14}$ Pyrochlores (Space Group $Fd\bar{3}m$ (No. 227), $Z = 4$)[a]

R	a, Å	V, Å^3	D_c, g cm^{-3}	10^3u_0	10^2R_d	d_1	d_2	d_3	d_4	d_5	$2r_R$	d_6	d_7
Y	10.1715(6)	1052.3	5.88	420	4.3	2.202	2.495	2.422	1.974	3.596	3.620	2.949	3.001
In	10.1227(8)	1037.4	6.30	425	3.7	2.192	2.518	2.436	1.944	3.579	3.252	2.863	3.037
La	10.347(2)	1108.1	6.18	426	4.1	2.240	2.581	2.496	1.983	3.658	3.754	2.912	3.114
Pr	10.3014(6)	1093.1	6.29	429	3.4	2.230	2.592	2.501	1.962	3.642	3.656	2.855	3.132
Nd	10.2809(4)	1086.7	6.37	428	3.3	2.226	2.579	2.491	1.962	3.635	3.642	2.864	3.115
Sm	10.2459(6)	1075.6	6.51	428	4.1	2.218	2.570	2.482	1.956	3.622	3.604	2.855	3.105
Eu	10.2297(4)	1070.5	6.56	428	5.7	2.215	2.566	2.478	1.953	3.617	4.084	2.850	3.100
Gd	10.2190(5)	1067.2	6.65	428	2.9	2.212	2.564	2.476	1.951	3.613	3.604	2.847	3.096
Tb	10.2083(6)	1063.8	6.69	426	5.3	2.210	2.546	2.462	1.956	3.609	3.564	2.873	3.073
Dy	10.1871(6)	1057.2	6.78	427	2.8	2.206	2.548	2.463	1.948	3.602	3.546	2.853	3.077
Ho	10.1714(6)	1052.3	6.84	426	2.8	2.202	2.537	2.453	1.949	3.596	3.532	2.863	3.062
Er	10.1591(6)	1048.5	6.90	428	2.5	2.200	2.549	2.461	1.939	3.592	3.514	2.830	3.078
Tm	10.1515(7)	1046.1	6.93	428	4.0	2.198	2.547	2.459	1.938	3.589	3.452	2.828	3.076
Yb	10.1386(8)	1044.2	7.00	428	5.1	2.195	2.543	2.456	1.935	3.585	3.880	2.825	3.072
Lu	10.1316(5)	1040.0	7.05	428	3.0	2.194	2.542	2.455	1.934	3.582	3.468	2.823	3.070

[a] $R_d = (\Sigma|I_o{}^{1/2} - I_c{}^{1}/{}_{2}|)/\Sigma I_o{}^{1/2}$; d_1 = A−(O)1; d_2 = A−O(2); d_3 = A−O; d_4 = B−O; d_5 = A−A = B−B = A−B; d_6 = O(2)−O(2); d_7 = O(1)−O(2).

Table 3. Structural Data for $Mn_2R_2[MnSb_3]O_{14}$ (R = Y, Ho), after the Rietveld Refinement of NPD Data at Room Temperature (Space Group $Fd\bar{3}m$ (No. 227), $Z = 4$)

parameter			R = Y	R = Ho
A, Å			10.17596(7)	10.17913(8)
V, Å^3			1053.72(1)	1054.71(2)
	R,Mn(1)	16c (0 0 0)		
B, Å^2			0.17(7)	0.11(8)
f_{occ}(R)			0.498(6)	0.528(9)
	Sb,Mn(2)	16d ($^1/_2$ $^1/_2$ $^1/_2$)		
B, Å^2			0.21(6)	0.29(7)
f_{occ}(Sb)			0.72(2)	0.73(2)
	O(1)	8a ($^1/_8$ $^1/_8$ $^1/_8$)		
B, Å^2			0.96(6)	0.99(7)
f_{occ}			0.978(6)	0.97(1)
	O(2)	48f (u $^1/_8$ $^1/_8$)		
u			0.42167(7)	0.42162(9)
B, Å^2			0.96(1)	0.99(2)
crystal formula			$Y_{1.98(2)}Mn_{2.02(2)}[Sb_{2.88(6)}Mn_{1.12(6)}]O_{13.96(2)}$	$Ho_{2.12(4)}Mn_{1.88(4)}[Sb_{2.92(4)}Mn_{1.08(8)}]O_{13.94(2)}$
reliability factors (%)]				
χ^2			5.27	3.99
R_p			4.69	4.40
R_{wp}			5.79	5.71
R_{exp}			2.60	2.86
R_I			6.19	7.44

A view of the structure is illustrated in Figure 2, where A cations, i.e., Mn(1) and Ho, are coordinated to two O(1) and six O(2) oxygens placed in the corners of scalenohedra or distorted cubes. The oxygen coordination polyhedra of B cations, Mn(2) and Sb, are trigonal BO_6 antiprims in a three-dimensional array with B−O−B angles of 132°.

Magnetization Measurements. Table 4 includes the results of fitting the magnetic susceptibilities for $Mn_2R_2[MnSb_3]O_{14}$ pyrochlores to a $\chi^{-1} = C(T + \theta_W)$ law in various temperature ranges. The observed effective magnetic moment was determined as $\mu_o = 2.828C^{1/2}$. The expected magnetic moment, μ_c, equals $\mu_c = [2(\mu_1)^2 + 2(\mu_2)^2 + (\mu_3)^2]^{1/2}$, where μ_1 is the magnetic moment for the R^{3+} cations;[17] and μ_2 and μ_3 those for high spin Mn^{2+}, 5.91 Bohr magnetons (μ_B), and high spin Mn^{3+}, 4.89 μ_B. In general, an acceptable agreement between μ_o and μ_c is observed. As Table 5 shows, the samples with R = Nd, Dy, Ho, and Er deviate from the Curie−Weiss law at a much higher temperature than the other compounds. Figure 3 illustrates how the dc magnetic susceptibility varies at lower temperatures for these four compounds.

Discussion

Six pyrochlores formulated[18,19] as $RMn[MnSb]O_6$ (R = Y, Eu, Gd, Dy, Ho, Yb), with Mn^{2+} at (c) and (d) sites and unit-cell a (Å) parameters from 10.27 (R = Eu) to 10.14 (R = Yb), were probably a mixture of the compounds described here accompanied by some impurities, since the authors mention that their samples were not single phase. On the other hand, Mn^{2+} could hardly occupy small (d) sites, and the $A_2B_2O_6$ defect pyrochlores[2] use to contain A cations such as Ag^+ or cations with one nonbonding electron pair, Tl^+, Pb^{2+}, Bi^{3+}.

In principle, the u parameter can be predicted from [2] or [4] equalizing d_2 or d_4 to the sum of the A or B radii[20] respectively, assuming high spin both Mn^{2+} and

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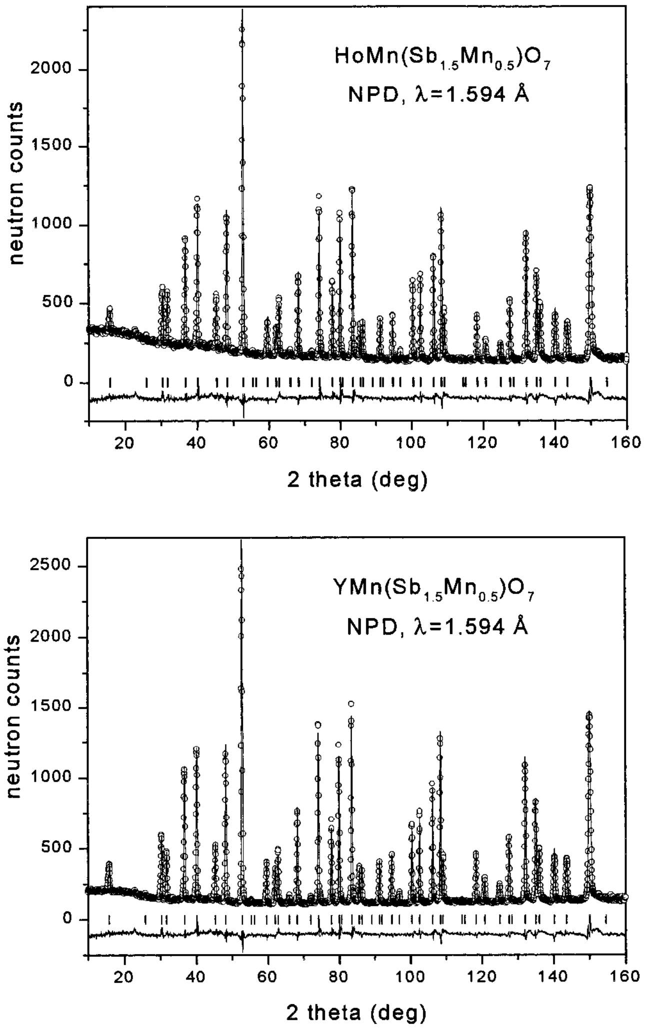

Figure 1. Observed (circles), calculated (solid line), and difference (at the bottom) NDP profiles for $Mn_2R_2[MnSb_3]O_{14}$ (R = Y, Ho) at 298 K. The tick marks indicate the positions of the allowed Bragg reflections.

Table 4. Main Interatomic Bond Distances (Å) and Angles (deg) from Neutron Powder Diffraction Data for $Mn_2R_2[MnSb_3]O_{14}$ (R = Y, Ho)

		R = Y	R = Ho
[R,Mn(1)]O_8 Scalenohedra			
[R,Mn(1)]−O(1)	(×2)	2.2032(1)	2.2038(1)
[R,Mn(1)]−O(2)	(×6)	2.5075(5)	2.5079(6)
[R,Mn(1)]−O	(×8)	2.4314(5)	2.4319(6)
[Sb,Mn(2)]O_6 Trigonal Antiprisms			
[Sb,Mn(2))−O(1)	(×6)	1.9676(4)	1.9684(6)
[Sb,Mn(2)]−O(1)−[Sb,Mn(2)]		132.20(1)	132.18(2)

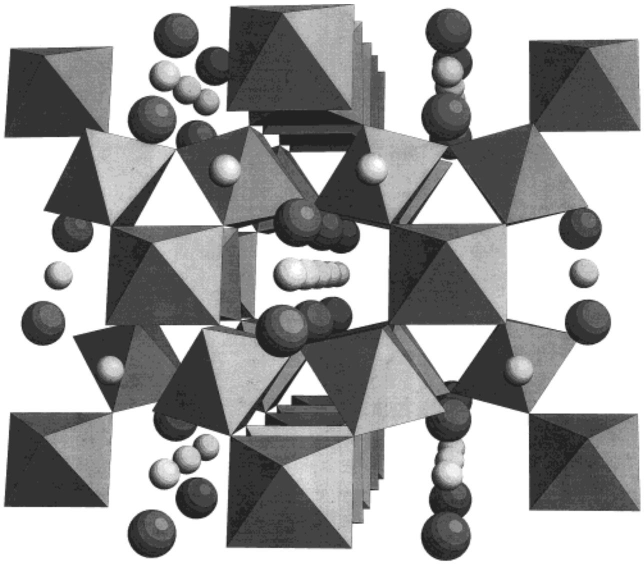

Figure 2. View of the $Mn_2R_2[MnSb_3]O_{14}$ structure, emphasizing the three-dimensional arrangement of the $(Mn^{3+},Sb^{5+})O_6$ trigonal antiprisms. Small and large circles represent A cations, Mn^{2+} and Ho^{3+}, and oxygen atoms, respectively.

Table 5. Fitting of Paramagnetic Susceptibilities for $Mn_2R_2[MnSb_3]O_{14}$ Pyrochlores to a $\chi^{-1} = C(T+\theta_W)$ Law at Various $T_1 - T_2$ (K) Ranges, and Comparison of Observed, μ_o, and Calculated, μ_c, Magnetic Moments (μ_B)

R	T_1	T_2	10^5r^a	C	θ_W	μ_R[17]	μ_c	μ_o
Y	35	350	99 993	11.41	34.6		9.70	9.55
In	20	300	99 991	11.81	29.3		9.70	9.72
La	30	300	99 999	9.87	36.0		9.70	8.89
Pr	50	300	99 998	11.91	36.5	3.5	10.89	11.91
Nd	150	350	99 999	13.59	42.0	3.5	10.89	10.43
Sm	20	350	99 962	12.42	42.5	1.50	9.92	9.97
Eu	50	290	99 987	15.41	50.0	3.4	10.82	11.10
Gd	50	300	99 998	26.21	7.85	8.0	14.90	14.48
Dy	180	300	99 984	44.53	48.6	10.6	17.85	18.87
Ho	100	225	99 991	37.78	17.6	10.4	17.62	17.38
Er	150	280	99 946	35.28	33.4	9.5	16.57	16.80
Tm	50	345	99 992	26.18	40.3	7.3	14.16	14.47
Yb	40	300	99 961	15.66	36.6	4.5	11.60	11.19
Lu	50	345	99 992	10.97	36.7		9.70	9.37

[a] Correlation coefficient.

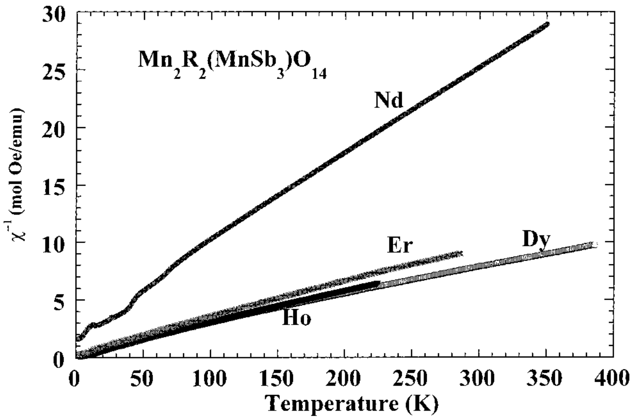

Figure 3. Reciprocal of the dc mass susceptibility, H/M, for the pyrochlores $Mn_2R_2[MnSb_3]O_{14}$ (R = Nd, Dy, Ho, Er).

Mn^{3+} like in all Mn oxocompounds. The result of the calculations is shown in Table 6, columns u_1 and u_2, together with the deviations, δ_1 and δ_2, with respect to the observed, u_o, values. The sum of the deviations for the 15 members of this family, $\sum\delta$, is much larger when the u values are calculated from r_A, suggesting that the u value depends more on the size of the hexacoordinated cations.

Columns u_3 and u_4 of Table 6 have been calculated by two other methods.[21,22] After deducing from [1] and [2] that $d_1 < d_2$ for $u > 0.375$, like in all the pyrochlores whose u positional parameter is known, the first method[20] assumes that

$$d_1 = r_A + r_O \quad d_4 \le r_B + r_O \quad d_6 \ge 2r_O \quad d_7 \ge 2r_O \qquad (8)$$

where r_A, r_B, and r_O are the respective radii[12] for A, B,

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Table 6. Comparison between Observed and Calculated Positional Oxygen Parameters, $10^{-3}u_n$, for $Mn_2R_2[MnSb_3]O_{14}$ Pyrochlores

R	u_o	r_1	u_1	δ_1	u_2	δ_2	u_3	δ_3	u_4	δ_4
Y	420	0.990	402	18	416	4	425	5	413	7
In	425	0.940	396	29	414	11	423	2	408	17
La	426	1.060	406	20	424	2	430	4	420	6
Pr	429	1.043	405	24	422	7	429		418	11
Nd	428	1.035	405	23	421	7	428		417	11
Sm	428	1.020	404	24	419	9	427	1	416	12
Eu	428	1.013	403	25	419	9	427	1	415	13
Gd	428	1.007	403	25	418	10	426	2	415	13
Tb	426	1.000	402	24	418	8	426		414	12
Dy	427	0.994	402	25	417	10	425	2	413	14
Ho	426	0.988	401	25	416	10	425	1	413	13
Er	428	0.982	401	27	415	13	424	4	412	16
Tm	428	0.977	401	27	415	13	424	4	412	16
Yb	428	0.973	400	28	414	14	424	4	411	17
Lu	428	0.969	400	28	414	14	423	5	411	17
$\Sigma\delta$				372		141		35		195

[a] $r_1 = r_A$ for CN 8 and HS Mn^{2+}; $r_2 = r_B$ for CN 6 and HS Mn^{3+} = 0.611 Å; r_O = 1.38 Å. u_n values were calculated from: (u_1) [2], r_1; (u_2) [4], r_2; (u_3) [8], r_1, r_2; (u_4) [9], r_1, r_2. $\delta_n = |u_n - u_O|$.

and oxygen ions. From these assumptions two inequalities can be drawn:

$$^5/_8 - (2^{1/2}r_O)/a \geq u_3 \geq (2r_O)/a + {}^1/_8, \qquad (9a)$$

and

$$^1/_2 - {}^1/_8\{3[(r_B + r_O))/(r_A + r_O)]^2 - 2\}^{1/2} \geq u_3 \geq {}^1/_2 - \{[(r_B + r_O)/a]^2 - {}^1/_{32}\}^{1/2} \qquad (9b)$$

Equations 9a and 9b are valid for the origin at the center and allow calculations[21] of u_3 from a and the ionic radii[20] r_O, r_A, and r_B. The estimation of u_3 by this method leads to two inequalities, i.e., to four values. For example, for R = Pr it leads to 433 > u_3 > 396 and 457 > u_3 > 425, which can be written as 433 > u > 425. The chosen value is 429, the average of 433 and 425.

The second method[22] does not use the a value because it consists of solving the equation in u obtained after equalizing r, ratio of the average A−O to the B−O distances, with the quotient between the sums of the ionic radii, $r = d_3/d_4 = (r_A + r_O)/(r_B + r_O)$. The solution of this equation is given by the best-fit polynomial as shown by eq 10:

$$u = -0.751846 + 3.63005r - 5.03230r^2 + 3.57083r^3 - 1.09316r^4 + 0.051435r^6 \qquad (10)$$

which from[20] r_O, r_A, and r_B leads to column u_4 of Table 6. The best calculation of the u parameters results from the application of the system of unequalities [9], which leads to an average deviation of two units in 10^3u_n. This gives estimated deviations of 0.01 Å for d_1−d_4 and d_6 distances of Table 2, and 0.015 Å for d_5 and d_7.

Calculated values of u = 0.425 from eq 9 for R = Y and Ho assuming high-spin Mn^{2+} and high-spin Mn^{3+} at (c) and (d) positions respectively, only deviate less than 1% from the u parameters of 0.42167(7) and 0.42162(9), respectively, determinated from NPD data.

Conclusions

Chemical analyses and XRD powder data were used to establish the composition, $Mn_2R_2[MnSb_3]O_{14}$, of a new family of oxide pyrochlores, in which two Mn^{2+} and two R^{3+} cations occupy at random the A positions of the $A_2B_2O_7$ pyrochlore structure, whereas one Mn^{3+} and three Sb^{5+} are also random at the B sites. NPD studies of the Y and Ho compounds confirm this composition. Magnetization measurements are consistent with the presence of two high-spin Mn^{2+} and one high-spin Mn^{3+} at A and B positions, respectively, showing the paramagnetic behavior of these materials in various temperature intervals. To the best of our knowledge, this is the first example of a pyrochlore-like compound with the presence of Mn^{2+} cations at the A positions of the structure confirmed by neutron diffraction data and magnetization measurements. The prediction of the positional u parameter of oxygen atoms from ionic radii considerations leads to acceptable results for the whole family.

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Supporting Information Available: X-ray powder diffraction patterns for $Mn_2R_2[MnSb_3]O_{14}$ (R = Y, In, La, Pr, Nd, Sm−Lu) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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