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Nonstoichiometric Phases in the Sn–Nb–O and Sn–Ta–O Systems Having Pyrochlore-Related Structures

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Phases in the Sn–Nb–O and Sn–Ta–O systems with cubic pyrochlore related structures have been synthesized and characterized by X-ray diffraction, tin Mössbauer, density determinations, and chemical analyses. All data fit the general formula $Sn^{2+}_{2-x}(M_{2-y}Sn^{4+}_{y})O_{7-x-y/2}$, where M is Nb^{5+} or Ta^{5+}. Thus, there are generally both cation and anion vacancies. The cubic cell increases with increasing x and with increasing y. The observed range in a was 10.55–10.61 Å for both the Nb and Ta systems. Mössbauer data indicate that Sn^{2+} is actually not at the $\bar{3}m$ site of the ideal pyrochlore structure. The structure of $Sn^{2+}_{1.76}Ta_{1.56}Sn^{4+}_{0.44}O_{6.54}$ was refined to an R of 1.6 using 46 independent observations. Sn^{2+} was found to be displaced from the $\bar{3}m$ position by 0.38 ± 0.02 Å. These static displacements are apparently somewhat cooperative, since none of these phases is centric; thus, they do not belong to the space group $Fd\bar{3}m$ of the ideal pyrochlore structure.

Introduction

Very little is known about ternary oxides of divalent tin. Tungsten bronzes of the type $Sn^{2+}_{x}WO_3$ are known (*1*), and two forms of $Sn^{2+}WO_4$ have recently been prepared and characterized (*2, 3*).

Phases have been reported in the Sn–Nb–O and Sn–Ta–O systems with pyrochlore-type structures (*4–6*). Since the ideal formula for the pyrochlore structure is $A_2M_2O_7$, these phases might be expected to be $Sn^{2+}_{2}Nb_2O_7$ and $Sn^{2+}_{2}Ta_2O_7$. However, it has been shown (*5, 6*) that these phases are nonstoichiometric, and the formula $Sn^{2+}_{2+x}M_2O_{7+x}$ has been proposed where M is Nb or Ta. Bodiot (*6*) reports an upper limit of 0.74 for x while Trunov *et al.* (*5*) indicate an upper limit of 1.0. This formulation seems unreasonable for the pyrochlore structure since it implies interstitial Sn^{2+} and O or even more unlikely situations. A more plausible mechanism for nonstoichiometry would be $Sn^{2+}_{2-x}M_2O_{7-x}$ since A cation and oxygen deficiencies are known for the pyrochlore structure. However, this mechanism appears to be inconsistent with the data of Bodiot (*6*) and Trunov *et al.* (*5*). Thus, a primary objective of our investigation was to determine the actual mechanism for nonstoichiometry in these systems.

Divalent tin in oxides has been found only in very asymmetric environments typical of lone-pair cations. There are two short bonds on one side as in α-$SnWO_4$ (*3*), or three short bonds on one side as in $SnSO_4$ (*7*) and β-$SnWO_4$ (*2*), or four short bonds on one side as in SnO (*8*). In all these cases of course, tin is not at a center of symmetry. In the pyrochlore structure the A cation site is a center of

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symmetry. There are two short bonds, but they are directly opposite each other. Thus, there would be no obvious place to accommodate the lone pair of a divalent tin at this site. The 5*s* electrons would then presumably occupy a spherical orbital about the tin, giving rise to a high *s* density at the tin nucleus, and this would result in a very high Mössbauer chemical isomer shift. A second objective of our study was to investigate this possibility.

During the course of our work, a Mössbauer study of partially oxidized $Sn_2Nb_2O_7$ and $Sn_2Ta_2O_7$ was published by Stewart *et al.* (*9*). However, whereas their study was restricted to phases where the tin to niobium or tantalum ratio was one, our study includes phases where this ratio is less than and greater than one. Furthermore, our characterization is more extensive, and includes a complete structure determination of one of these phases for the first time.

Experimental

The reactants were reagent grade SnO (Baker and Adamson) and Matthey "Specpure" Nb_2O_5 and Ta_2O_5. Various ratios of SnO to Nb_2O_5 or SnO to Ta_2O_5 were intimated mixed by grinding together. These reactants were sealed in silica ampoules under vacuum. The ampoules were heated at 900°C for about 10 hr. All products were examined optically and by X-ray diffraction. Only very rarely were the products single phase. However, it was found possible to use ractant ratios which produced only tin metal as a second phase. These samples could then easily be purified by washing with acid. All experiments described in this paper were performed on samples judged to be single-phase by optical and X-ray examination. Samples were accurately weighed before and after washing so that the tin loss could be used as a check on the final compositions.

The TGA experiments were carried out in air and in an H_2/Ar mixture. Samples were heated to 900°C and held until constant weight was achieved. Heating in air results in the oxidation of the Sn^{2+} to Sn^{4+}; thus, the weight gain can be related to the Sn^{2+} content. Heating in the H_2/Ar mixture results in the reduction of all tin to tin metal. Ta^{5+} is not reduced by the H_2/Ar mixture, but Nb^{5+} is reduced to Nb^{4+}, i.e., NbO_2. Oxygen analyses were carried out by the inert gas fusion method. Densities were determined by standard procedures using a pycnometer. X-ray powder patterns were obtained at 25°C using a Hägg–Guiner camera with $CuK_{\alpha 1}$ radiation and an internal standard of high-purity KCl ($a = 6.2931$ Å at 25°C).

X-ray intensity data were collected on a Picker automatic powder diffractometer using $CuK\alpha$ radiation and a graphite monochromator. The sample was ground and passed though a 400-mesh screen. This powder was packed into a sample holder which was sufficiently large to intercept all X-rays over the entire theta range scanned. The sample was also thick enough to absorb essentially all X-rays. The pattern was step scanned from 10° to 164° 2θ. The stepping increments were 0.01° in the region of peaks and 0.05° in background regions. The counting time at each step was 3.6 sec. Of the 51 possible peaks which could have been observed, 46 were judged to be observed. Resolution problems were not encountered since the structure of the sample was cubic. Background corrections were made by linear interpolation between regions judged to be true background.

Least-squares refinement of the intensity data used the full matrix program (*10*), SFLS6, adapted for powders. Sigma values were taken to be $(I_0)^{1/2} + 200$, the function $w(I_o - I_c)^2$ was minimized, and R is defined as $\sum |I_o - I_c| / \sum I_o$. The unobserved reflections were not used in the refinement, but their intensities were calculated. Atomic scattering factors were taken from Cromer and Waber (*11*). Real and imaginary anomalous dispersion corrections were made using Cromer's (*12*) values.

Mössbauer spectra were recorded on a spectrometer which has already been described (*13*). The $BaSnO_3$ source was at room temperature while the sample temperature was varied from 295–4°K by means of an Air Products Cryotip system. Samples were prepared by intimately mixing the finely ground compound with Apiezon grease and placing between aluminum foil in a copper holder which

TABLE I

ANALYTICAL RESULTS FOR $Sn^{2+}_{2-x}M^{5+}_{2-y}Sn^{4+}_{y}O_{7-x-y/2}$ PHASES

Composition	SnO:$MO_{2.5}$[a]	a, Å[b]	d_c[c]	d_o	%O_c[d]	%O_o	Weight[e] loss, c	Weight loss, o	Weight[f] gain, c	Weight gain, o	Sn loss[g]	Sn loss
$Sn^{2+}_{1.55}Nb_{1.80}Sn^{4+}_{0.20}O_{6.45}$	1:1	10.5881 (4)	5.35	5.33	21.58	21.5	9.54	9.5	5.19	5.2	1.24	1.4
$Sn^{2+}_{1.52}Nb_{1.59}Sn^{4+}_{0.41}O_{6.32}$	3:2	10.6130 (5)	5.31	5.30	21.16	21.0	10.50	10.5	5.09	5.1	11.3	11.4
$Sn^{2+}_{1.80}Ta_{1.90}Sn^{4+}_{0.10}O_{6.75}$	1:1	10.5617 (8)	7.64	7.23	15.94	15.7	4.72	4.7	4.25	4.2	0.0	0.0
$Sn^{2+}_{1.76}Ta_{1.56}Sn^{4+}_{0.44}O_{6.54}$	3:2	10.5907 (5)	7.25	7.18	16.15	16.2	6.52	6.4	4.35	4.4	2.56	2.8

[a] Reactant ratios.

[b] Cubic cell edge; numbers in parentheses are the standard deviations in the last significant figure.

[c] Density in g/cc.

[d] Total oxygen.

[e] Weight loss under H_2/Ar mixture.

[f] Weight gain in air.

[g] % tin metal washed from product.

was attached to the Cryotip unit. The samples contained 5 mg Sn/cm^2 and satisfied the thin absorber requirement. All spectra were fitted to Lorentzian line shapes using the computer program of Stone (*14*) which had been modified by Dr. H. D. Grundy of the Geology Department, McMaster University. No constraints were imposed on the positions, widths or intensities of the lines and all fits gave satisfactory χ^2 values. In all cases, an asymmetry was observed in the quadrupole split doublet arising from the Sn^{2+} site which became less pronounced as the temperature was lowered. This behavior is indicative of asymmetric bonding to the tin nucleus and is known as the Gol'danskii–Karyagin effect (*15*). Isomer shifts are measured relative to SnO_2 at room temperature and are accurate to 0.05 mm/sec.

Results

All our results are consistent with the formulation $Sn^{2+}_{2-x}M_{2-y}Sn^{4+}_{y}O_{7-x-y/2}$ where M is Ta or Nb. The determination of the limits of x and y in these two systems would be a very ambitious undertaking, particularly since achieving equilibrium often appears difficult. Consequently, we restricted our detailed studies to four compositions which could establish the structural basis for the nonstoichiometry of these pyrochlore phases.

The results on the four phases studied are summarized in Table I. The various analytical data agree well with the compositions given. Errors in x and y are estimated to be ± 0.01. The tantalum containing phases are white, whereas the niobium containing phases are yellow.

All products were polycrystalline with no crystals large enough for single crystal X-ray diffraction. However, the powder diffraction data were consistent with the space group *Fd*3*m* which is the space group of the ideal pyrochlore structure. No reflections were observed for any sample which violated this space group, and in no case was there any evidence of line splitting indicative of noncubicity. Nonetheless, a second-order harmonic test (*16*) was positive for all samples of Table I. The strength of the second harmonic signal was about two to three times that of quartz for the niobium compounds and about 18 times that of quartz for the tantalum compounds. Thus, these phases are definitely not centrosymmetric, and the true space group cannot be *Fd*3*m*.

Structural Analysis

One of the four compositions in Table I was chosen for detailed structural analysis using X-ray diffraction data. A phase with Ta rather than Nb was chosen because the difference between the scattering powers of Ta and Sn is greater than in the case of Nb and Sn. Thus, the X-ray data more clearly distinguish between Ta and Sn than between Nb and Sn. The composition $Sn_{1.76}\square_{0.24}Ta_{1.56}Sn_{0.44}O_{6.54}$ was chosen, due to its greater departure from the ideal $Sn_2Ta_2O_7$ stoichiometry; thus, the mechanism for the range of composition might be more definitely established.

The least-squares refinement was initiated in space group *Fd*3*m* according to the analytical composition. Thus, 0.78 Ta and 0.22 Sn were placed in *c* (origin), and oxygen (O) in position *e*, 0.54 oxygen (O′) in position *a*, and 0.88 Sn in position *d*. Refining the scale factor, isotropic *B*'s (except for O′), the oxygen positional parameter, and the occupancy of position *d* lead to an *R* of 0.059 (Table II). The agreement between the occupancy parameter and the analytical data was not exact but was perhaps acceptable. However, the value of *R* and the thermal parameter of Sn^{2+} both seemed too large. In addition, there were a number of discrepancies between observed and calculated intensities that were definitely outside experimental error. A very glaring discrepancy was that a "forbidden" reflection was definitely observed. This was the 442 reflection which, although weak, appeared for all samples examined in both the Nb and Ta systems. This reflection is not forbidden by the space group (*Fd*3*m*) but is forbidden in the sense that isotropic atoms in positions *a*, *b*, *c*, *d*, and *f* will not contribute to it. Thus, it might be regarded as a systematic absence of the pyrochlore structure (*17*). Other forbidden reflections such as the 644 could pre-

TABLE II

CRYSTALLOGRAPHIC PARAMETERS[a] FOR $Sn^{2+}_{1.76}Ta_{1.56}Sn^{4+}_{0.44}O_{6.54}$

	Case 1	Case 2	Case 3
Sn^{2+}:*x*	0.5	0.518 (1)	0.5254 (3)
Sn^{2+}:*y*	0.5	0.518 (1)	0.4746 (3)
Sn^{2+}:*z*	0.5	0.474 (1)	0.5
Sn^{2+}:μ^b	0.94 (3)[a]	0.88 (1)	0.88 (1)
Sn^{2+}:*B*	6.0 (5) Å^2	0.9 (2) Å^2	1.0 (2) Å^2
Ta, Sn^{4+}:*B*	0.49 (8) Å^2	0.54 (2) Å^2	0.54 (2) Å^2
O:*x*	0.312 (5)	0.315 (1)	0.316 (1)
O:*B*	1.8 (11) Å^2	0.8 (2) Å^2	0.9 (3) Å^2
O′:*B*	1.0 Å^2	7 (3) Å^2	7 (3) Å^2
R	5.9	1.6	1.8

[a] Numbers in parentheses are the standard deviations in the last significant figure. Parameters not followed by parentheses were not refined.

[b] Occupancy parameter which is actually multiplied by six for Cases 2 and 3.

sumably have been found with sufficient counting time. These forbidden reflections do, however, become allowed with anisotropic thermal parameters or with isotropic atoms in positions *e*, *g*, *h*, or *i*.

An anisotropic thermal parameter was therefore introduced for Sn^{2+} which, due to the high symmetry, is only one additional parameter. The thermal ellipsoid at position *d* is constrained by symmetry to an ellipsoid of rotation. It can either elongate or flatten along the threefold axis (Fig. 1). In terms of positional displacements (thermal or otherwise), this corresponds to moving toward the two close oxygens (elongation) or toward the six more distant oxygens (flattening). The anisotropic refinement led to some flattening of the thermal ellipsoid. This also occurred for Hg in $Hg_2Nb_2O_7$ (*17*). In fact, elongation can hardly be possible since the bond distances along the threefold axis are so short. However, the *R* only reduced to 0.051, and discrepancies between intensities were still apparent. Thus, it appeared that the displacements of Sn^{2+} could not adequately be described by a thermal ellipsoid.

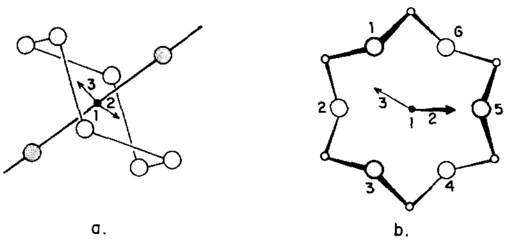

FIG. 1. A 100 perspective is shown in a, and 111 projection in b. The small open circles are Ta and Sn^{4+}. The small solid circle is the ideal ($\bar{3}m$) position for Sn^{2+}. The large circles are oxygen. The shaded circles are the O′ oxygens, and the numbered oxygens in b correspond to those in Table IV. For Case 1, there is no displacement of Sn^{2+}. The displacements for Cases 2 and 3 are indicated by arrows. Of course, there are six equivalent directions for each of these displacements.

Instead of placing Sn^{2+} in position *d*, refinements were carried out using positions *h* and *g*. Position *e* would merely correspond to an elongation of the thermal ellipsoid; thus, it was not considered. It would be structurally impossible for Sn^{2+} to occupy position *f*.

In position *g*, Sn^{2+} moves off the threefold axis and two mirror planes, but remains on one mirror plane. This model (Case 2) refined to give very good agreement between observed and calculated intensities (Tables II and III). Furthermore, the thermal parameters were

TABLE III

OBSERVED AND CALCULATED INTENSITIES

h	k	l	I_0	I_1	I_2	I_3
1	1	1	9110	7078	8897	8829
2	2	0	176	17	156	166
3	1	1	4284	4300	4189	4162
2	2	2	70398	70984	70392	70440
4	0	0	24658	25260	24765	24789
3	1	1	404	372	497	505
4	2	2	252	347	322	304
3	3	3	—	1661	2209	2239
5	1	1	—	613	727	744
			2976	2274	2936	2983
4	4	0	25854	24934	25730	25713
5	3	1	2234	2581	2213	2203
4	4	2	103	0.0	87	95
6	2	0	217	142	282	281
5	3	3	1179	1552	1081	1079
6	2	2	24508	23285	23840	23824
4	4	4	6462	6300	6495	6427
5	5	1	—	1515	2280	2315
7	1	1	—	906	769	751
			3174	2421	3049	3066
6	4	2	—	6	31	35
7	3	1	—	2111	2341	2330
5	5	3	—	637	470	469
			2787	2748	2711	7799
8	0	0	2774	3007	3001	3034
7	3	3	449	311	565	594
6	4	4	—	0.0	23	29
8	2	2	—	80	174	176
6	6	0	—	67	4	3
			158	147	178	179
5	5	5	—	104	194	213
7	5	1	—	1050	571	590
			751	1154	765	803
6	6	2	7571	7433	7687	7601
8	4	0	6642	6510	6655	6647
7	5	3	—	952	657	658
9	1	1	—	562	756	735
			1483	1514	1413	1393
8	4	2	—	0.0	100	101
6	6	4	168	32	178	181
9	3	1	987	1295	1078	1042
8	4	4	4074	4486	4419	4399
7	5	5	—	592	431	438
9	3	3	—	288	165	174
7	7	1	—	427	533	533
			1092	1307	1129	1145
8	6	2	—	6	4	2
10	2	0	—	25	1	1
			—	31	5	3
7	7	3	—	642	1140	1190
9	5	1	—	846	1178	1193
10	2	2	—	3954	3711	3813
6	6	6	—	1318	1357	1331
			7245	6760	7386	7527
9	5	3	824	816	884	860
8	6	4	—	0.0	56	64
7	7	5	—	470	372	367
11	1	1	—	370	329	311
			606	840	701	678
8	8	0	1478	1574	1473	1438
9	5	5	—	542	1124	1175
9	7	1	—	836	556	579
11	3	1	—	935	1231	1150
			2857	2313	2911	2904
10	4	4	—	0.0	6	11
8	8	2	—	0.0	78	75
			—	0.0	84	86
8	6	6	—	3	21	30
10	6	0	—	35	234	220
			227	38	255	250
9	7	3	—	1249	864	902
11	3	3	—	569	922	905
10	6	2	—	6423	6078	6025
			7798	8241	7864	7832
12	0	0	—	672	525	585
8	8	4	—	3620	3835	3715
			4451	4292	4360	4300
7	7	7	—	138	295	320
11	5	1	—	1283	1185	1179
			1429	1421	1480	1499
9	7	5	—	1136	754	753
11	5	3	—	1032	831	790
			1708	2168	1585	1543
12	4	0	3192	3871	3228	3381

TABLE III—*continued*

h k l	I_0	I_1	I_2	I_3
9 9 1	1052	568	992	1040
10 8 2	160	4	70	73
11 5 5	—	550	250	294
13 1 1	—	786	1120	999
9 9 3	—	927	1030	995
11 7 1	—	1388	1837	1822
10 6 6	—	4286	4059	3982
	8282	7937	8296	8092
12 4 4	4259	4687	4090	4220
13 3 1	—	1592	7130	1550
11 7 3	—	1813	3396	3540
9 7 7	—	828	477	512
	5831	4233	5603	5602

now all reasonable, and the occupancy parameter agreed exactly with the analytical data.

In position *h*, Sn^{2+} moves off the threefold axis and all the mirror planes, but it remains on a twofold axis. This model (Case 3) also refined to give excellent agreement between observed and calculated intensities (Tables II and III). Again, the thermal parameters were all reasonable, and again the occupancy parameter agreed exactly with analytical data.

In view of the excellent results obtained with positions *h* and *g*, there appears to be no justification to try the general position (position *i*). Likewise, no additional information would be gained by refining in a noncentric, lower symmetry space group. A lower *R* would not be significant in view of the very low *R*'s already obtained in space group *Fd*3*m* with positions *h* and *g*. Furthermore, the distance between Sn^{2+} described by Case 1 and that described by Case 2 is only 0.2 Å, and the mean square displacement for a *B* of 1.0 Å^2 is 0.1 Å. Thus, in a sense, these positions are overlapped.

In the composition $Sn_{1.76}\square_{0.24}Ta_{1.56}Sn_{0.44}O_{6.54}$ there is inherent disorder in that two kinds of atoms occupy position *c*, and two other positions are only partially occupied. In such an inherently disordered system, one could not hope to choose between positions *i*, *h*, and *g* for Sn^{2+}. Some Sn^{2+} could well be in each position, and some Sn^{2+} in the same position might be described by different positional parameters. In fact, the true Sn^{2+} positions must be described in an acentric space group. Some interaction between the thermal parameter of Sn^{2+} and its positional parameters is unavoidable. More or better data would not necessarily be of much value in this disordered system. We can say, however, that on the average Sn^{2+} is displaced by 0.38 ± 0.02 Å from the centric position in a direction roughly perpendicular to the threefold axis resulting in a toroidal shaped electron density.

The thermal parameter of O′ is high, but not unreasonable in view of its high standard deviation and the disorder in this structure. This high *B* probably reflects static displacements due to the partial occupancy and large displacements at the Sn^{2+} site.

The position occupied by 0.78 Ta and 0.22 Sn^{4+} is essentially octahedral. All six cation–anion distances must be equal. Cases 2 and 3 give the same oxygen positional parameter, and thus the same cation–anion distances for the Ta–Sn^{4+} "atom." This distance, 1.99 ± 0.03 Å, agrees very well with the weighted sum of Shannon and Prewitt (*18*) radii, 2.00 Å. The oxygen–cation–oxygen angles are those of an ideal octahedron within the standard deviations, e.g., 89° ± 4°.

A description of the Sn^{2+} bonding is, of course, complicated by the disorder. If Sn^{2+} were in the ideal position, *d*, and if the O′ site were completely occupied, Sn^{2+} would have two close axial oxygens at 2.293 Å and six more equatorial oxygens at 2.71 Å (Fig. 1). However, the O′ site is only about half occupied, and Sn^{2+} has apparently moved 0.38 Å off the centric site.

The two types of Sn^{2+} displacements according to Case 2 and Case 3 of Table II are indicated in Fig. 1. The resulting interatomic distances are given in Table IV. Averaging the closest six distances gives 2.52 Å for Case 2 and 2.49 Å for Case 3. These seem reasonable since an analogous average is 2.47 Å in α-$SnWO_4$ (*3*) and 2.56 Å in β-$SnWO_4$ (*2*).

The reliability of this refinement might be questioned since it is based on data collected

TABLE IV

Sn^{2+}–O DISTANCES

	Case 1	Case 2	Case 3
O (1)	2.71 Å	2.91 Å	2.39 Å
O (2)	2.71	3.09	2.39
O (3)	2.71	2.91	2.74
O (4)	2.71	2.55	3.05
O (5)	2.71	2.33	3.05
O (6)	2.71	2.55	2.74
O′ (1)	2.29	2.36	2.33
O′ (2)	2.29	2.29	2.33

from powder rather than from a single crystal. However, the important factors in a least-squares refinement are the number of *independent* observations and their accuracy. With Cu radiation the number of independent reflections which could be observed from the powder was 51, and this number would go up to 77 for a single crystal. The only compound with the pyrochlore structure which has been refined from single crystal data is $Cd_2Re_2O_7$, and the number of independent observations was 66 for Mo radiation (*19*). Thus, the number of independent observations using a single crystal only increases by a factor of about 1.5. The accuracy of measuring the intensity of a peak generally depends on the systematic errors since any level of statistical accuracy can, in principle, be obtained with single crystal or powder data. For a material with high X-ray absorption it is entirely possible that the powder intensities will be significantly more accurate than the single crystal intensities. The effect of high absorption on intensities is easily dealt with using a powder diffractometer (*20*). However, for a highly absorbing single crystal, accurate data requires a very accurate measurement and orientation of the crystal, or the crystal must be ground to a nearly perfect sphere. In practice, it may simply not be feasible to obtain a good absorption correction for a highly absorbing single crystal; thus, intensities from the powder may be more accurate. The systematic error which can be a serious problem with powder intensity data is preferred orientation. This can be an especially severe problem with materials having easy cleavage planes. Even in a cubic material it is possible to have preferred orientation; however, we found preferred orientation to be insignificant with our sample preparation technique which included passing the powder through 400-mesh screen.

Only one observed peak was rejected from the least-squares refinement. This is the peak which occurs at the lowest angle where there can be an uncertainty both in the observed and the calculated intensity. The observed intensity can suffer a significant absorption error at low angles because the requirement that the sample surface be flat becomes impossible to achieve as θ approaches zero. The uncertainty in the calculated intensity arises from the effect of assumed oxidation state on form factors. There is little basis to choose atomic, formal ionic, or intermediate form factors, yet the choice will effect the calculated intensity at low angles. At higher angles there is no problem since then the form factors do not vary significantly with choice of oxidation state. Despite these possible sources of discrepancy, the intensity agreement for the 111 reflection is rather good (Table III).

Mössbauer

The spectra obtained for each of the phases studied consisted of three well resolved peaks which can only be analyzed realistically in terms of a doublet, with a chemical isomer shift characteristic of a Sn^{2+} species, and a singlet due to a Sn^{4+} species. The data are summarized in Table V. These data are similar to those reported earlier (*9*) for Nb and Ta phases of similar composition. There are small changes in the parameters with temperature; the increase in I.S. with decreasing temperature could be due to a second order Doppler shift effect. However, it is possible that these changes may be partially due to the fact that the spectra obtained at higher temperatures are not of such good quality as those at 4°K.

The isomer shift of the Sn^{4+} species is little different from that of SnO_2, but the linewidth (0.95 mm/sec) is only marginally wider than the source line width, whereas SnO_2 gives a broadened line (*21*). We conclude that the Sn^{4+} is in fairly regular octahedral site with all six Sn–O distances equal or nearly so.

TABLE V

MÖSSBAUER DATA

		Sn^{2+}		Sn^{4+}		Area ratio Sn^{2+}/Sn^{4+}		
						Mössbauer		
	Temperature	I.S.	Q.S.	I.S.	Q.S.	Measured	Corrected	Analytical
$Sn^{2+}_{1.55}Nb^{5+}_{1.80}Sn^{4+}_{0.20}O_{6.45}$	295	3.30	1.80	0.03	—	2.6		
	77	3.00	1.75	0.09	—	4.4		
	4	3.40	1.86	0.14	—	6.7	7.7	7.75
$Sn^{2+}_{1.52}Nb^{5+}_{1.59}Sn^{4+}_{0.41}O_{6.32}$	295	3.31	1.75	0.04	—	1.4		
	77	3.04	1.63	0.08	—	2.9		
	4	3.39	1.79	0.10	—	3.1	3.5	3.706
$Sn^{2+}_{1.80}Ta^{5+}_{1.90}Sn^{4+}_{0.10}O_{6.75}$	295							
	77	3.48	1.86	0.05	—	3.4		
	4							18.0
$Sn^{2+}_{1.76}Ta^{5+}_{1.56}Sn^{4+}_{0.44}O_{6.54}$	295	2.79	1.50	0.04	—	1.3		
	77	3.05	1.56	0.05	—	2.5		
	4	3.44	1.84	0.09	—	3.3	3.8	4.0

Other pyrochlore type structures $A_2^{3+}Sn_2^{4+}O_7$, where A^{3+} is a rare earth ion, are known to give ^{119}Sn Mössbauer spectra in which the resonance due to the Sn^{4+} is considerably broadened indicating a distorted Sn^{4+} site (*22*). This is consistent with the fact that Brisse and Knop (*23*) find that the O–Sn–O angles depart from 90° by from 6 to 9° for rare earth stannate pyrochlores whereas we find that this angle is significantly closer to 90° for $Sn_{1.76}^{2+}Ta_{1.56}Sn_{0.44}^{4+}O_{6.54}$.

A number of Sn^{2+}–O systems whose structures are reasonably well established have been studied by Mössbauer spectroscopy. The isomer shifts range from 2.71 mm/sec for SnO (black) (*24*) to 3.90 for $SnSO_4$ (*25*), while the quadrupole splittings are 1.45 and 1.00 mm/sec, respectively. Our isomer shifts fall between those values indicating that the *s* electron density is not as great as it is in $SnSO_4$. This suggests that there is a higher percentage of *s* character in the Sn–O bonds in the pyrochlores than in $SnSO_4$. If the Sn^{2+} was at a center of symmetry with the 5*s* electron pair stereochemically inactive, a high *s* electron density would result and an isomer shift $\gg$4 mm/sec would be expected. Furthermore, in such cases one might expect a zero, or small quadrupole splitting, whereas we find a relatively large splitting. These data indicate that the Sn^{2+} is not at a center of symmetry.

A stoichiometric $Sn_2^{2+}M_2^{5+}O_7$ pyrochlore would have only one Sn^{2+} site of symmetry $\bar{3}m$, and this would give rise to a simple quadrupole doublet. Stewart *et al.* (*9*) argue that because those pyrochlores are nonstoichiometric, the Sn^{2+} will be in several environments each with its own Mössbauer parameters, so that the spectrum observed will be the summation of several different I.S. and Q.S. values, and that this explains their line broadening. However, it should be pointed out that line widths of less than 0.9 mm/sec are rarely observed and widths of 1 mm/sec are usual for tin compounds even in cases where there is one unique tin environment. The line widths reported by Stewart and co-workers (0.9–1.1 mm/sec), and which we also find, are therefore not unusual. This would indicate that the sites occupied by the Sn^{2+} are not sufficiently different to have any appreciable effect on the Mössbauer parameters.

It is possible, in theory at least, to obtain the Sn^{2+}/Sn^{4+} ratio by measuring the relative areas of the Sn^{2+} and Sn^{4+} Mössbauer absorption envelopes. Those areas will depend upon the properties of the crystal lattice and upon the temperature. The effect of lowering the temperature upon the area ratios is evident from Table V, but these are not expected to change appreciably on further cooling. However, the ratios so obtained do not agree well with the compositions given in Table I, and this is because no allowance has been made for the differences in lattice vibration for the two sites. Stewart and co-workers (*9*) have made estimates of this difference, and if we use their f_0 ratios, i.e., 0.87 and 0.89 for the niobate and tantalate, respectively, much better agreement with the compositions in Table I is achieved.

Discussion

Our results indicate that the pyrochlore phases in the Sn–Ta–O and Sn–Nb–O systems should be represented by the general formula $Sn_{2-x}^{2+}M_{2-y}^{5+}Sn_y^{4+}O_{7-x-y/2}$, where M^{5+} is Ta or Nb. This general formula has not been proposed before. It suggests that pyrochlore phases are possible with Sn/M^{5+} ratios less than and greater than one; in fact, we have observed both situations. For the ideal stoichiometry, i.e., $Sn_2M_2^{5+}O_7$, both *x* and *y* would be zero; and presumably zero represents the smallest possible value for *x* and *y*. It does not appear that phases have been prepared, by us or others, where both *x* and *y* are zero. This is probably because of the ease with which Sn^{2+} disproportionates under synthesis conditions. Once some Sn^{4+} is formed it substitutes for Nb or Ta rather than going on the Sn^{2+} site. The reaction of such an oxidized phase with tin metal may be very slow.

The range of cell dimensions we observed is not indicated in Table I. In fact, we observed a range of 10.55–10.61 Å in both the Ta and Nb system. This is in reasonable agreement with Trunov *et al.* (*5*), who reported a range of 10.54–10.58 Å in the Ta system and with

Bodiot (*6*) who reported a range of 10.55–10.58 Å in the Ta system and a range of 10.58–10.62 Å in the Nb system.

Comparison of the cell dimensions in Table I indicates increasing size with increasing y. This is to be expected since Sn^{4+} is significantly larger than Ta^{5+} or Nb^{5+}. Furthermore, since a niobate will have essentially the same cell volume as an isostructural analogous tantalate (*18*), the cell edges of niobates vs tantalates in Table I can be used to show that the edges also increase with increasing x. Again, this might be considered the expected trend since it has been observed in oxides that vacancies cause an expansion around the vacant site (*26*) and an overall increase in the cell volume (*27*).

The general formula for compounds with the pyrochlore structure may be written as $A_2O'(MO_3)_2$ to emphasize its framework nature (*17*). The MO_3 network is always intact, but vacancies may occur at both A and O′ sites. The largest departure from the $A_2M_2X_6X'$ formula (X is O or F) is AM_2X_6 (*28*). Large thermal *B*'s are common for the A cation in these grossly defect pyrochlores (*29–33*). The large *B* has been interpreted as static statistical displacements using position *e* which gives rise to forbidden reflections (*33*) just as in the Sn–M^{5+}–O pyrochlores. However, the presence of these forbidden reflections does not prove that the displacements are static rather than thermal. The question of whether the displacements of the A cation in the AM_2X_6 and the Sn–M^{5+}–O pyrochlores are static and statistical or anisotropic thermal motions cannot be answered by ordinary X-ray diffraction methods. It is important to note, however, that the displacement of the A cation in the AM_2X_6 pyrochlores is apparently in an entirely different direction than in the Sn–M^{5+}–O pyrochlores. Position *e*, used for A in the AM_2X_6 pyrochlores, describes displacements along the threefold axis, but Sn^{2+} is displaced perpendicular, or nearly so, to this axis.

A discussion of the Sn^{2+} bonding in the $Sn^{2+}_{2-x}M^{5+}_{2-y}Sn^{4+}_{y}O_{7-x-y/2}$ phases is difficult due to the apparent high degree of disorder. If the Sn^{2+} displacements corresponded to thermal motion, the average environment would be very unusual for Sn^{2+} in that it would have inversion symmetry with two close axial oxygens. Removal of one or both of the close oxygens without Sn^{2+} displacements would lead to an even more unusual bonding situation for Sn^{2+}. However, the positive second harmonic test proves that the Sn^{2+} displacements are static. (Of course, it is possible that at high temperatures there is large thermal motion of Sn^{2+} which becomes static displacements at low temperatures.) If the static displacements of Case 3 are assumed, and if it is assumed that one of the O′ oxygens is missing, the Sn^{2+} environment is similar to that reported for $SnSO_4$ (*7*). The closest distances are 2.34, 2.40, 2.40, 2.92, 2.99, and 2.99 Å in $SnSO_4$; they would be 2.33, 2.39, 2.39, 2.74, 2.74, 3.05, and 3.05 Å in the pyrochlore case. Several other arrangements around Sn^{2+} could be described by assuming different O′ occupancies for Case 2 and 3 situations.

The true space group for the pyrochlores is not known. In view of the second harmonic signal it cannot be $Fd3m$ or any other centric space group. It might be an acentric space group such as $F\bar{4}3m$, or it might even be a noncubic space group. However, the MO_3 part of the structure conforms very well to space group $Fd3m$. The static Sn^{2+} displacements must be cooperative in order to destroy the centricity for a domain large enough to allow a second harmonic signal. It is impossible to comment on the cooperative nature of these displacements, but our discussion regarding the local displacements of Sn^{2+} should nonetheless be valid.

The Mössbauer spectra clearly establish the presence of both Sn^{2+} and Sn^{4+} in these pyrochlores. The data indicate that the Sn^{4+} is in a site of high symmetry and confirms the X-ray data, while the Sn^{2+} has a quite distorted environment. Clearly, the Sn^{2+} cannot be at a center of symmetry with the 5*s* electron pair in a spherical orbital, or a much more positive isomer shift would be observed, and the quadrupole splitting would be zero, or small from a lattice contribution. As it is, the I.S. values are less positive, and the Q.S. larger, than for $SnSO_4$ (*25*) indicating that the Sn^{2+} environment in these pyrochlores is more asymmetric than that found in $SnSO_4$. Furthermore, the observation of a Gol'danskii–Karyagin effect in the Sn^{2+} spectrum means that the bonding to this nucleus is anisotropic. This could arise because of the relatively strong bonds to the two O′ on the threefold axis. The bonding would be weaker at right angles to this axis, where the Sn–O bonds are larger and thermal displacements would therefore be easier in this direction. Oxygen vacancies in a particular direction will of course make thermal motions easier in that direction, but this would presumably be averaged if the vacancies are statistically distributed. These facts are consistent with either Cases 2 or 3 (Fig. 1), but not with Case 1.

The ratios of $Sn^{2+}:Sn^{4+}$ estimated from the Mössbauer data agree well with the analytical and crystallographic data considering the approximations made. Agreement with the $Sn^{2+}_{1.55}Nb_{1.80}Sn^{4+}_{0.20}O_{6.45}$ composition is particularly good, and it is this composition that is closest to that reported by Stewart *et al.* (*9*). For the other compositions agreement between the Mössbauer and X-ray data is not as good, but is still much better than that obtained by the previous workers (*9*) for the tantalate system.

The color of the Sn–Ta–O pyrochlores (white) vs that of the Sn–Nb–O pyrochlores (yellow) has been discussed by Stewart *et al.* (*9*). They suggested that the yellow color of the niobium pyrochlores might be due to the presence of reduced niobium, i.e., Nb^{4+}. However, we consider this very unlikely, especially since $PbTa_2O_6$ is white, whereas $PbNb_2O_6$ is yellow with both being prepared in air. Certainly, Nb^{5+} is easier to reduce than Ta^{5+}, but reduction by Sn^{2+} or Sn^0 should not occur. However, since Nb^{5+} is easier to reduce, an excited charge transfer process with an electron transferring from Sn^{2+} to Nb^{5+} would be at lower energies than the corresponding Sn^{2+} to Ta^{5+} transfer. Thus, this charge transfer band might be in the blue (and near uv) for the niobate but further into the uv for the tantalate. Of course, it is possible that it is some other charge transfer band that has shifted to higher energies on going from the niobate to the tantalate.

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