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Samarium Titanates, Strontium Samarium Titanates, and the Question of the Existence of Divalent Samarium in Oxides

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Two of the oxide systems most likely to contain Sm^{2+} as a major constituent have been examined. A phase equilibrium study of the system Sm–Ti–O yielded only three ternary compounds, $Sm_2Ti_2O_7$, Sm_2TiO_5, and $SmTiO_3$. In each of these compounds the samarium is trivalent. For substitutions of samarium into $SrTiO_3$ the valence state of samarium is shown to be trivalent from cell parameter and spectroscopic considerations. The possibility of finding other Sm^{2+} oxides is discussed.

I. Introduction

The existence of lower oxides of samarium has recently been questioned by Felmlee and Eyring.[1] They found that what had been previously reported as Sm_2O[2] and SmO[2–4] were actually SmH_2 and $SmN_{1-x}O_x$. Aside from the silicates ($SmSiO_3$ and Sm_2SiO_4) reported by Bondar, *et al.*,[5] these were the only examples of divalent samarium in single or mixed oxides.

Recent efforts by Brauer, *et al.*,[6] to prepare SmO by reduction of samarium oxyhalides with LiH between 500 and 800° and by careful oxidation of the metal were unsuccessful. Their attempts to stabilize Sm^{2+} in a matrix of SrO or CaO were also unsuccessful. On the basis of thermodynamic calculations utilizing recent data, they indicated that SmO should not be a stable phase at low temperatures but proposed that it may become stable at temperatures above 800°.

In order to investigate this question further two systems which would be likely to form Sm^{2+} oxides were investigated at 1400°.

II. The System Sm–Ti–O

In a recent study of Eu^{2+} compounds McCarthy, White, and Roy[7] used titanium as a reducing agent to prepare Eu_2TiO_4, $Eu_3Ti_2O_7$, $EuTiO_{3-x}$, and a tentative $EuTi_{12}O_{19}$. In addition, EuO and Eu_3O_4 were noted in a number of equilibrium-phase assemblages of the 1400° isotherm of the system Eu–Ti–O. A systematic study of the system Sm–Ti–O at 1400° was undertaken to try to prepare the analogous Sm^{2+} phases.

Experimental Work

The procedures used in this study are described in detail elsewhere,[7,8] and only a brief summary will be given here.

Bulk starting materials were prepared by weighing TiO_2 (99.9%, National Lead Co.), Ti metal (99.5%, A. D. Mackay, Inc.), and Sm_2O_3 (99.9%, Research Chemicals) in the appropriate proportions for a desired composition and grinding this mixture under CCl_4 in an agate mortar. The starting materials were pressed into pellets and heated at 1400° in a tantalum container for 24–36 hr. Argon, purified by passing over titanium metal at 900°, was the furnace atmosphere. Samples were cooled by raising them into a cold part of the furnace.

Both optical examination and X-ray techniques were utilized for phase identification. Silver γ (TiO_{1-y}), silver to gold TiO solid solution, and blue-red Ti_2O_3 could be distinguished readily in the phase assemblages. Except for gray-white Sm_2O_3, the other phases present were fine grained and black.

X-Ray data were collected with nickel-filtered Cu Kα (λ 1.5418 Å) radiation on a diffractometer calibrated with a high-purity silicon standard ($a_0 = 5.4301$ Å). Integrated intensities were measured with a planimeter and cell parameters were refined by the least-squares program of Appleman, Handwerker, and Evans.[9]

In spite of all precautions, some oxygen leaked into the furnace and the original composition of the products had to be corrected for this stray oxygen pickup. It was first necessary to show that the Sm:Ti ratio had not changed and that oxygen was the only component added to or subtracted from the bulk composition. Since oxidation by heating in air of any composition in the ternary isotherm shifts the composition of the solid phases to the join Sm_2O_3–TiO_2, a comparison of the relative amounts of the phases along this join in the oxidized product to those in the oxidized starting mixture indicated whether the Sm:Ti ratio had changed. If the Sm:Ti ratio remained constant, it was necessary only to adjust the bulk composition in the direction of the oxygen apex. This was done by measuring the weight gain on oxidizing the product by heating it in air. In a portion of the phase diagram the Sm:Ti ratio was found to change considerably owing to loss of samarium.

Results

The following are the only ternary compounds which were found in the system Sm–Ti–O at 1400°.

$Sm_2Ti_2O_7$.—This crystallizes in the pyrochlore structure with $a_0 = 10.211$ Å.[10]

Sm_2TiO_5.—Waring and Schneider[11] proposed the existence of this compound although they did not recognize it as belonging to any known structure type. The X-ray diffraction powder data, listed in Table I, were indexed on an orthorhombic cell of $a_0 = 10.59$ Å, $b_0 = 3.792$ Å, and $c_0 = 11.35$ Å, by analogy to the recently elucidated structure of Y_2TiO_5.[12] In this

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[1] T. L. Felmlee and L. Eyring, *Inorg. Chem.*, **7**, 660 (1968).

[2] H. A. Eick, N. C. Baenziger, and L. Eyring, *J. Am. Chem. Soc.*, **78**, 5147 (1956).

[3] F. H. Ellinger and W. H. Zachariasen, *ibid.*, **75**, 5650 (1953).

[4] J. C. Achard, *Compt. Rend.*, **245**, 1064 (1957).

[5] I. A. Bondar, N. A. Toropov, and L. N. Koroleva, *Izv. Akad. Nauk SSSR, Neorgan. Materialy*, **1**, 561 (1965).

[6] G. Brauer, H. Bärnighausen, and N. Schultz, *Z. Anorg. Allgem. Chem.*, **356**, 46 (1968).

[7] G. J. McCarthy, W. B. White, and R. Roy, *J. Inorg. Nucl. Chem.*, **31**, 329 (1969).

[8] G. J. McCarthy, W. B. White, and R. Roy, *J. Am. Ceram, Soc.*, in press.

[9] D. E. Appleman, D. S. Handwerker, and H. T. Evans, Jr., Annual Meeting of the American Crystallographic Association, Cambridge, Mass., 1963, Program pp 42–43.

[10] L. H. Brixner, *Inorg. Chem.*, **3**, 1065 (1964).

[11] J. L. Waring and J. S. Schneider, *J. Res. Natl. Bur. Std.*, **69A**, 225 (1965).

[12] W. G. Mumme and A. D. Wadsley, *Acta Cryst.*, **B24**, 1327 (1968).

TABLE I

X-RAY DIFFRACTION POWDER DATA ON Sm_2TiO_5[a]

d, Å			
Obsd	Calcd	I/I_1[b]	hkl
7.76	7.74	4	101
5.30	5.31	1	200
4.998	5.000	3	102
4.796	4.797	4	201
3.871	3.870	1	202
3.596	3.596	3	011
3.558	3.561	12	103
3.404	3.405	5	111
3.370	3.370	2	301
3.084	3.082	100	210
3.075	3.077	80	203
3.021	3.021	5	112
2.997	2.997	11	302
2.739	2.740	2	104
2.679	2.678	27	013
2.649	2.647	10	400
2.595	2.596	10	113
2.578	2.578	11	401
2.520	2.519	3	311
2.352	2.351	9	312
2.214	2.211	5	304
2.133	2.133 2.132	14	313 411
2.086	2.086 2.087	7	214 205
2.079	2.081	6	501
2.028	2.027	6	412
1.984	1.984	2	502
1.936	1.935	1	404
1.914	1.915	5	115
1.909	1.910 1.909	7	314 305
1.896	1.896	23	020
1.892	1.891	3	006
1.882	1.882	47	413
1.859	1.861	14	106
1.848	1.847	5	503
1.842	1.841	4	121
1.826	1.828 1.825	5	215 511
1.759	1.758	7	512
1.723	1.724 1.723	2	414 405
1.704	1.705 1.703	6	315 222
1.698	1.697	2	504
1.686	1.685	3	602
1.674	1.674	5	123
1.670	1.671	8	116
1.668	1.667	17	306
1.662	1.661	4	513
1.613	1.614 1.612	28	223 216
1.602	1.602 1.602	18	107 322
1.585	1.584	7	611
1.540	1.540 1.539	12	612 406
1.527	1.528 1.527 1.526	13	323 421 316

[a] Orthorhombic cell, $a_0 = 10.59$ Å, $b_0 = 3.792$ Å, $c_0 = 11.35$ Å; space group D_{2h}^{16} (Pnma); Y_2TiO_5 structure. [b] Integrated intensity.

TABLE II

X-RAY DIFFRACTION POWDER DATA ON $SmTiO_3$[a]

d, Å			
Obsd	Calcd	I/I_1[b]	hkl
4.467	4.466	1	101
3.937	3.934	25	110
3.871	3.868	11	002
3.509	3.507	21	111
2.834	2.833	19	020
2.759	2.758	100	112
2.733	2.734	60	200
2.660	2.660	29	021
2.347	2.346	10	211
2.287	2.285	7	022
2.233	2.233	14	202
2.158	2.157	20	113
2.110	2.109	2	122
2.079	2.077	1	212
1.967	1.967	21	220
1.934	1.934	15	004
1.906	1.906 1.905	22	221 023
1.780	1.781 1.774	4	213 301
1.751	1.753	10	222
1.738	1.739 1.736 1.735	56	131 114 310
1.694	1.693	3	311
1.621	1.621	6	132
1.598	1.597	17	024
1.585	1.583	74	312
1.564	1.564	7	223
1.468	1.468	14	133
1.443	1.442	3	232
1.393	1.393	8	041
1.379	1.379	20	224
1.367	1.367	3	400
1.356	1.356	2	025
1.312	1.318 1.312 1.311	4	323 134 330
1.294	1.293	18	331
1.229	1.231 1.225	19	420 116

[a] Orthorhombic cell, $a_0 = 5.468$ Å, $b_0 = 5.665$ Å, $c_0 = 7.737$ Å; space group D_{2h}^{16} (Pbnm); $GdFeO_3$ structure. [b] Integrated intensity.

unusual structure the Sm is seven-coordinated while the Ti is five-coordinated.

$SmTiO_3$.—This was first prepared by Holzapfel and Sieler,[13] who recognized it to be a $Sm^{3+}Ti^{3+}$ distorted perovskite although they did not assign it a unit cell. The X-ray data, listed in Table II, were indexed on an orthorhombic cell of $a_0 = 5.468$ Å, $b_0 = 5.665$ Å, and $c_0 = 7.737$ Å. It appears to crystallize in the $GdFeO_3$ structure.[14]

A portion of the 1400° isotherm is given as Figure 1.

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[13] H. Holzapfel and J. Sieler, *Z. Anorg. Allgem. Chem.*, **343**, 174 (1966).

[14] S. Geller and E. A. Wood, *Acta Cryst.*, **9**, 563 (1956).

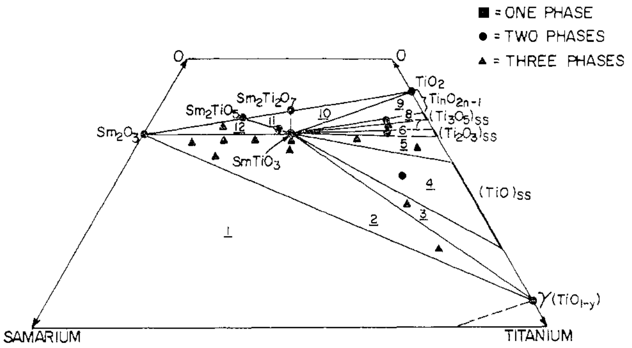

Figure 1.—Phase diagram for a portion of the 1400° isotherm of the system Sm–Ti–O (the portion shown is from 30 to 70 mol % oxygen).

In order to keep the diagram as uncluttered as possible, the phase assemblages are numbered and listed separately in Table III. The diagram is seen to consist of three-phase triangles and two-phase areas connecting the compounds and solid solutions. The runs used to establish these boundaries are also shown. Heavier lines were utilized to indicate the extent of solid solution. Data on the Ti–O binary were taken from Porter[15] and Wahlbeck and Gilles.[16] Also because of space considerations, the dozen or so boundaries connecting the Magneli phase (Ti_nO_{2n-1}) and $SmTiO_3$ were omitted.

Table III

Phase Assemblages in Figure 1

No.	Phase assemblage[a]
1[b]	Sm_2O_3 + SmRV + γ (TiO_{1-y})
2	Sm_2O_3 + γ (TiO_{1-y}) + $SmTiO_3$
3	γ (TiO_{1-y}) + $SmTiO_3$ + (TiO)ss
4	$SmTiO_3$ + (TiO)ss
5	$SmTiO_3$ + (TiO)ss + (Ti_2O_3)ss
6	$SmTiO_3$ + (Ti_2O_3)ss
7	$SmTiO_3$ + (Ti_2O_3)ss + (Ti_3O_5)ss
8	$SmTiO_3$ + (Ti_3O_5)ss
9[c]	$SmTiO_3$ + Ti_nO_{2n-1} and $SmTiO_3$ + Ti_nO_{2n-1} + $Ti_{n+1}O_{2n+1}$
10	$SmTiO_3$ + TiO_2 + $Sm_2Ti_2O_7$
11	$SmTiO_3$ + $Sm_2Ti_2O_7$ + Sm_2TiO_5
12	$SmTiO_3$ + Sm_2TiO_5 + Sm_2O_3

[a] Each phase assemblage is also in equilibrium with a vapor phase whose oxygen fugacity is fixed by each bulk composition. [b] SmRV = samarium metal rich volatile species. [c] This single triangle is actually filled with two- and three-phase assemblages involving Magneli phases, for example, $SmTiO_3$ + Ti_4O_7 and $SmTiO_3$ + Ti_4O_7 + Ti_5O_9.

It should be noted that outside of the region bounded by Sm_2O_3–TiO_2–γ no runs are plotted. (γ is one of the ordered solutions of oxygen in Ti metal. At 1400° it extends from approximately $TiO_{0.47}$ to $TiO_{0.52}$ (*i.e.*, $\sim Ti_2O$).) Bulk compositions in this region exhibited large changes in the Sm:Ti ratio when heated. By comparing the initial and final bulk compositions it was deduced that the component lost was mainly samarium metal. The metal melts at 1060° and has such a large vapor pressure at 1400° that it boils off during the run. After a run of bulk compositions in this region, cold parts of the furnace tube were coated with an amorphous powder. This behavior was also encountered in previous investigations of the Sr–Ti–O[8] and Eu–Ti–O[7] systems and is discussed in greater detail in these publications.

Discussion

No Sm^{2+} titanates were found in this system. In addition, the phase assemblage Sm_2O_3 + $SmTiO_3$ + γ rules out the existence of Sm_3O_4 and SmO at 1400°. If these did exist, phase assemblages such as SmO + $SmTiO_3$, SmO + Sm_3O_4 + $SmTiO_3$, and Sm_3O_4 + $SmTiO_3$ would have been located in the region taken up by Sm_2O_3 + $SmTiO_3$ + γ. This confirms the results of Brauer, *et al.*, and shows that SmO and Sm_3O_4 are not stable phases up to 1400°.

If $Sm^{3+}Ti^{3+}O_3$ could be reduced, some of the Sm^{3+} would have to be converted to Sm^{2+} (there is no "Ti^{2+} ion"—the only example of "divalent titanium" is TiO and that compound is actually metallic). Several runs just below $SmTiO_3$ in oxygen content indicated that no reduction is possible. Instead, even a slight reduction of $SmTiO_3$ caused the separation into three coexisting phases (Sm_2O_3 + $SmTiO_3$ + γ) rather than producing a single reduced $SmTiO_{3-x}$ phase.

III. The System $SmTiO_3$–$SrTiO_3$

Divalent strontium has an ionic radius similar to that expected of divalent samarium in oxides (1.17 Å) and it was thought that small substitutions of Sm into a matrix of the cubic perovskite $SrTiO_3$ might stabilize Sm^{2+}.

Experimental Work

The $SrTiO_3$ was prepared by heating the appropriate amounts of $SrCO_3$ (Baker, 99.5%) and TiO_2 in air at 1400°. An equimolar mixture of Sm_2O_3 and Ti_2O_3 was heated in an evacuated, sealed silica capsule at 1200° to produce $SmTiO_3$.

The mixing, pelletizing, and heating procedures were the same as those described above.

Phase identification was carried out by X-ray techniques.

Cell parameter measurements on the cubic perovskite phase were obtained by repeatedly scanning and measuring the (321) reflection along with a high-purity silicon internal standard.

Diffuse reflectance spectra were obtained on a Beckmann Model DK-2A spectrophotometer equipped with a MgO-coated integrating-sphere reflectance attachment. MgO was used in the reference beam. The specular component was removed from the beam.

Results and Discussion

At 1400° two solid solutions with a miscibility gap between them were found. Orthorhombic $SmTiO_3$ accepts approximately 10 mol % $SrTiO_3$ while cubic $SrTiO_3$ accepts 36 mol % $SmTiO_3$. The solid solutions have a miscibility gap from 10 to 64 mol % $SrTiO_3$. There is a small but definite cell parameter change in the cubic solid solution with $SmTiO_3$ content and this is shown in Figure 2. The shrinking of the cell with increasing $SmTiO_3$ implies that the Sm substituting for Sr is in the trivalent state, as little change would be expected from Sm^{2+} substitution. The positive deviation

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(15) V. Porter, Ph.D. Dissertation, The Pennsylvania State University, 1965.

(16) P. G. Wahlbeck and P. W. Gilles, *J. Am. Ceram. Soc.*, **49**, 180 (1966).

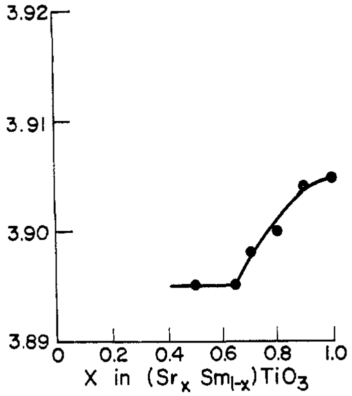

Figure 2.—Variation of the cubic cell edge with composition for $(Sr_xSm_{1-x})TiO_3$.

from linear cell parameter change (Vegard's law) could be due to the fact that actually two substitutions are being made and with opposite effects. With increasing $SmTiO_3$, a larger Ti^{3+} is substituting for Ti^{4+} for each smaller Sm^{3+} which substitutes for Sr^{2+}. The ~0.01-Å change is about that expected from ionic radii differences ($\Delta r_{Ti^{4+}Ti^{3+}} = 0.08$ Å, $\Delta r_{Sr^{2+}Sm^{3+}} = -0.12$ Å) for 36 mol % substitution of $SmTiO_3$ into $SrTiO_3$.

It was felt that another test of valence states was necessary before a definite assignment could be made. A test was available for the presence of Ti^{3+} (and thus Sm^{3+}). Porter[15] and Porter, White, and Roy[17] found that when Ti^{3+} was substituted for Ti^{4+} in the Magneli phases (in this case, Ti_nO_{2n-1} with n decreasing), a broad maximum was noted in the diffuse reflectance spectrum of the powder. This maximum shifted to lower wavelengths as the Ti^{3+}:Ti^{4+} ratio was increased. This maximum has also been found in the Ti^{3+} for Ti^{4+} substitutions in $SrTiO_{3-x}$.[8,18] This test is valid only when Ti^{3+} is the only ion present which is capable of producing spectra in the region scanned (500–2650 nm). In the case of $SrTiO_3$–$SmTiO_3$, Sr^{2+} and Ti^{4+} have rare gas electronic configurations. Trivalent samarium and divalent samarium (equivalent in electronic configuration to Eu^{3+}) do exhibit spectral features in the region scanned[19] but these are weak and would be obscured by the larger absorption features of the blue-black powders.

The broad maximum typical of Ti^{3+} was found for the cubic solid solution. A typical spectrum is shown in Figure 3. The shift in the maximum with increasing Ti^{3+} (and thus Sm^{3+}) is plotted in Figure 4.

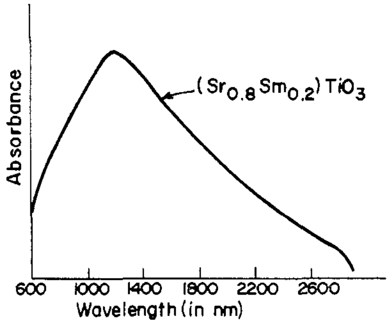

Figure 3.—Typical diffuse reflectance spectrum for $(Sr_xSm_{1-x})TiO_3$.

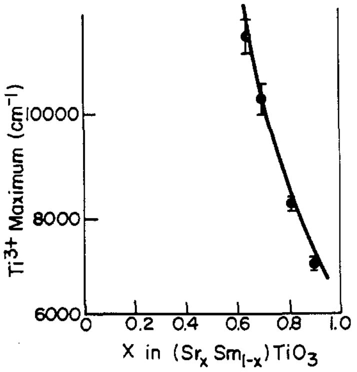

Figure 4.—Variation of the broad maximum in the diffuse reflectance spectrum of $(Sr_xSm_{1-x})TiO_3$ with composition.

According to this test the samarium valence state in $(Sr_xSm_{1-x})TiO_3$ is trivalent. The possibility that a large portion of the samarium is divalent and the rest is trivalent could be raised, but this was discounted owing to the absence of the highly absorbing Sm^{2+}–Sm^{3+} intervalence transfer bands which would be expected in the spectral region examined.

IV. General Discussion

None of the Sm^{2+} titanates proposed by analogy to Eu^{2+} titanates could be prepared. It is thus very unlikely that any other Sm^{2+} mixed oxides in which the bonding is largely ionic (vanadates, molybdates, zirconates, tantalates, etc.) including the silicates of Bondar, *et al.*, can be prepared if the titanates were not, first, because titanium and its lower oxides are among the best reducing agents known and, second, because none of the common oxide crystal structures is likely to be able to supply the apparently vast amount of energy needed to stabilize Sm^{2+} instead of Sm^{3+}. Efforts to reproduce the divalent samarium silicate preparations in our laboratories have been unsuccessful.

Acknowledgment.—This work was supported by U. S. Army Electronics Command Contract No. DA 28-043 AMC 01304(E).

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(17) V. Porter, W. B. White, and R. Roy, to be submitted for publication.

(18) P. P. J. Van Engelen and J. C. M. Henning, *Phys. Letters*, **25A**, 733 (1967).

(19) W. B. White, *Appl. Spectry.*, **21**, 167 (1967).