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STRUCTURE AND SOME PROPERTIES OF THE PREVIOUSLY UNKNOWN YTTERBIUM SILICATE A-Yb_2SiO_5

V. A. Izhevskii

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Nonisothermal oxidation of ytterbium N-woehlerite ($Yb_4Si_2O_7N_2$), also known as the J-phase, has revealed a previously unknown and possibly unstable modification, Yb_2SiO_5. The phase is isostructural with the A type modification $(RE)_2SiO_5$ (RE = rare earth). A new crystallographic description is provided for the detected phase and thermal stability data are compared with such data available for analogous RE compounds. The results indicate that oxidation of RE oxynitrides may produce metastable phases of the type $(RE)_4Al_{2(1-x)}Si_{2x}O_{9+x}$ or phases that cannot be prepared by standard methods because their low-temperature stability range is so narrow.

Work on the synthesis and consolidation of covalent nitrides began at the Materials Science Institute, in the late 1950s and early 1960s [1-3] under the supervision of G. V. Samsonov. Those investigations examined the behavior of systems of refractory nitride(s) and oxides, in particular silicon nitride–oxide systems. This led to the birth of a scientific field which subsequently came to be known as "the technology of nonmetallic nitrides." By the time of the "ceramic boom" in the 1980s and 1990s the Institute had accumulated a wealth of theoretical and practical experience in this area of materials science and the investigations were successfully extended. The work reported here, on the crystallographic description of a RE silicate, is also a development of that field.

Silicates of rare earth elements, namely, compounds of the type $(RE)_2SiO_5$ and $(RE)_2Si_2O_7$ as well as RE oxynitrides [$(RE)_4Si_2O_7N_2$ and $(RE)_2Si_5O_3N_4$], are the compounds most commonly found as part of the intergrain phases of ceramic materials based on Si_3N_4 and SiC, which are obtained by liquid-phase sintering, using RE oxides as activator additives. In studying the processes of phase formation in the $Yb_2O_3-Si_3N_4-SiO_2-(Al_2O_3)$ we made a detailed examination of the properties of a number of $Yb_4Al_4O_3$ solid solutions. Investigation of the behavior of $Yb_4Si_2O_7N_2$, known as N-woehlerite or J-phase, under oxidation in air, showed that the process takes place in at least three stages. A low-temperature modification, Yb_2SiO_5, which had not previously been detected and may possibly be metastable, was found to form in the first stage. This paper gives a complete crystallographic characteristic of that phase. Its stability is discussed in comparison with published data for other known modifications of $(RE)_2SiO_5$.

Specimens of ytterbium N-woehlerite $Yb_4Si_2O_7N_2$ were obtained by sintering in nitrogen under an excess pressure of 0.3 MPa. Mixtures were prepared in accordance with the stoichiometric composition from powders of silicon nitride (more than 98% of the α modification), ytterbium oxide, and high-purity silicon oxide (no more than 0.2 mass% impurities). The sintered specimens were highly homogeneous and single-phase as shown by x-ray phase analysis and scanning electron microscopy. The residual porosity was less than 10%.

The behavior of the material under oxidation was studied by thermogravimetric-differential thermal analysis (TG-DTA) in air. Specimens measuring 3 × 3 × 7 mm and weighing about 500 mg were cut from large sintered specimens by a diamond disk. Alundum crucibles and equipment were used. The experiments were carried out on a Netsch STA 409 apparatus.

Since the preliminary investigations showed that active oxidation begins 700°C, the heating rate was kept the same (2 deg/min) over the entire range of temperatures (20-1500°C). After the nonisothermal stage the specimens were held at 1500°C for 5 h to guarantee complete oxidation. The oxidation rate was 10 deg/min. The oxidation products including intermediate products (the oxidized specimen was rapidly cooled from a certain temperature) were studied by chemical as

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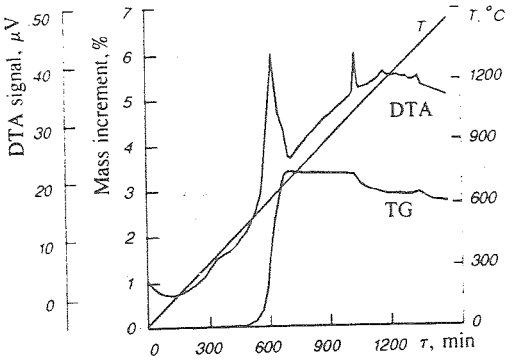

Fig. 1

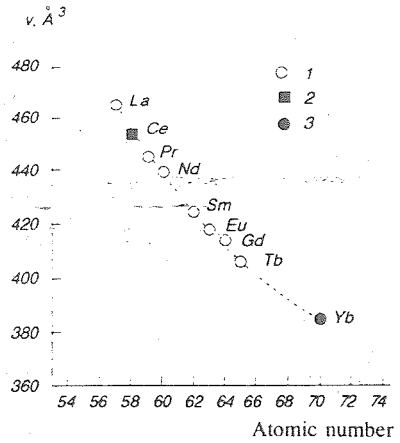

Fig. 2

Fig. 1. DTA and TG curves obtained during oxidation of ytterbium woehlerite $Yb_2Si_2O_7N_2$.

Fig. 2. Comparative data about the unit cell volume of A type RE silicates $(RE)_2SiO_5$. 1) [3], 2) [21], 3) this paper.

well as x-ray methods. The oxygen, nitrogen and silicon contents were determined by methods of analytical chemistry. Single-phase N-woehlerite $Yb_4Si_2O_7N_2$ was used as the reference. In x-ray structural analyses the reference was 99.999% pure silicon. All of the x-ray analyses were done on powder specimens.

The TG and DTA curves shown in Fig. 1 show that $Yb_4Si_2O_7N_2$ is oxidized in at least three stages. Oxidation was seen to begin at 575 ± 10°C. An increment in mass occurs in the first stage (TG) and a broad asymmetry exothermic peak on the DTA corresponds to it. The diffraction pattern obtained after that stage (quenching from 980°C) resembles those of unoxidized $Yb_4Si_2O_7N_2$, but its diffraction reflections are shifted slightly and considerably broader. This indicates that the structure has defects and/or that the oxidation products are possibly inhomogeneous. Chemical analysis showed that the material contains about half the stoichiometric amount of nitrogen that is present in unoxidized material (3.15 mass% N in $Yb_4Si_2O_7N_2$).

A less smeared exothermic peak on the DTA curve at 1025 ± 5°C corresponds to the second transformation. The transformation is accompanied by a loss of mass, which is attributed to the liberation of gaseous nitrogen. The results of x-ray analyses indicate that the modification Yb_2SiO_5 (A-Yb_2SiO_5, according to the Felsche classification of RE silicates [4]) not previously described is formed in that earlier stage. The specimen also contained insignificant amounts (traces) of partially oxidized $Yb_4Si_2O_7N_2$. The formation of the A-Yb_2SiO_5 phase, its crystallographic description, and its possibly being metastable are discussed below.

The results of chemical analysis of that intermediate product of oxidation indicate a further reduction of nitrogen content: 0.98 mass%. That value is in good agreement with the thermogravimetric effect, although the amount of nitrogen is anomalously high. It is extremely unlikely that some nitrogen is dissolved in the A-Yb_2SiO_5 structure and is present in ionic form. Excess nitrogen is more probably present in incompletely oxidized residual $Yb_4Si_2O_7N_2$, traces of which manifest themselves in x-ray analysis. In that case nitrogen can be present in ionic and/or molecular form. A similar phenomenon was observed during oxidation of yttrium oxynitride $Yb_{10}(SiO_4)_6N_2$ [5].

The preferred formation of Yb_2SiO_5 from oxidized $Yb_4Si_2O_7N_2$, instead of another known stable silicate $Yb_2Si_2O_7$ during oxidation, in our opinion is attributable primarily to the fact that in the first case the Yb:Si ratio remains constant during oxidation.

The oxidation of $Yb_4Si_2O_7N_2$ (or $(RE)_4Si_2O_7N_2$ in the general case) can be considered from the standpoint of the structure. Ditetrahedral elements having the composition Si_2O_5N or Si_2O_6N, linking together by N ions [6, 7], are further bound together by polyhedra with the composition $Yb-O_n((RE)O_n)$. During oxidation of the material the nitrogen ions that bind the ditetrahedral elements are also oxidized and possibly remain in the structure as atomic or molecular nitrogen. As the temperature rises nitrogen molecules are liberated and simultaneously the respective positions are occupied by oxygen. That process evidently leads to a regrouping of the structural elements that contain silicon and oxygen and the formation of isolated

TABLE 1. x-Ray Characteristics of A-Yb_2SiO_5*

d_{expt}(E)	I_{expt}	*hkl*	d_{calc}(*E*)	d_{expt}(E)	I_{expt}	*hkl*	d_{calc}(*E*)	d_{calc} (*E*)	I_{expt}	*hkl*	d_{calc}(*E*)
8,64	6	100	8,63	2,613	68	$22\bar{1}$	2,614	1,729(*b*)	10	$51\bar{1}$, 500	1,731, 1,726
5,332	56	110	5,328	2,331(*b*)	4	$31\bar{2}$, 221	2,333, 2,325	1,702(*s*)	11	$32\bar{3}$	1,705
4,633	32	011	4,633	2,216	4	$32\bar{1}$	2,215	1,692(*b*)	16	040, 123	1,694, 1,684
4,313	27	200	4,316	2,181	6	$1\bar{3}0$	2,184	1,667(*b*)	15	$33\bar{2}$ $51\bar{2}$ 140	1,671, 1,667, 1,661
3,788	20	111	3,789	2,167	6	212	2,165	1,641	6	331, $10\bar{4}$	1,642, 1,641
3,639	14	210	3,639	2,128	12	031	2,127	1,596(*b*)	15	402, $11\bar{4}$	1,599, 1,595
3,511	7	$21\bar{1}$	3,515	2,054(*b*)	21	410, $40\bar{2}$	2,056, 2,056	1,583(*b*)	19	141, $43\bar{1}$, $52\bar{1}$	1,588, 1,587, 1,583
3,274	31	$10\bar{2}$	3,275	2,041	21	$21\bar{3}$	2,039	1,572(*b*)	17	240, $1\,33$	1,576, 1,574
2,987	79	021	2,988	2,026(*b*)	11	131, 013	2,024, 2,021	1,563(*b*)	16	$24\bar{1}$, $42\bar{3}$ 430	1,566, 1,564, 1,560
2,962	69	$20\bar{2}$	2,960	1,955	29	321	1,954	1,540(*b*)	10	033, 223, 520	1,544, 1,540, 1,538
2,877	65	300	2,877	1,899(*b*)	3	302, $31\bar{3}$	1,897, 1,894	1,505(*bb*)	4	$51\bar{3}$, $14\bar{2}$, 241	1,515, 1,504, 1,496
2,748(*s*)	54	102	2,754	1,866(*s*)	7	113, $42\bar{1}$	1,866, 1,863	1,468(*b*)	13	133, $24\bar{2}$, $34\bar{1}$	1,472, 1,470, 1,466
2,720	100	121	2,721	1,842(*b*)	54	231, $12\bar{3}$, 032	1,844, 1,842, 1,840	1,455(*b*)	14	114, $61\bar{1}$, 332	1,458, 1,456, 1,452
2,646(*s*)	22	310	2,648	1,789(*b*)	14	$23\bar{2}$, $33\bar{1}$, 023	1,795, 1,788, 1,776	1,445(*b*)	15	422, $41\bar{4}$, 142	1,446, 1,446, 1,442

*The measurements were made by the x-ray diffraction method, using powder specimens (Siemens D5000, CuK_α radiation); s, shoulder, b, broad, bb, very broad. Indexed for the $P2_1/c$ space group; a = 8.951(3) Å, b = 6.772(2) Å, c = 6.588(2) Å, β = 105.36(4)°, ν = 385.1(1) $Å^3$.

SiO_4 tetrahedra. In the final account this results in the formation of the silicate A-Yb_2SiO_5, the structure of which consists of isolated SiO_4 tetrahedra and anions of the second type, i.e., oxygen ions which are not bound to silicon and are inside slightly distorted tetrahedra consisting $(Re)^{3+}$ ions [4, 8]. The structure as a whole can thus be considered as a combination of tetrahedral elements of two kinds: SiO_4 and $O-RE_4$ tetrahedra. Although the structure of B-$(RE)_2SiO_5$ is very similar to that described above [4, 9], the results obtained in this study suggest that the formation of A-Yb_2SiO_5 during oxidation of ytterbium woehlerite is preferred because A-Yb_2SiO_5 and partially oxidized $Yb_2Si_2O_7N_2$ are structurally more similar.

The third, weak exothermic effect noticed on the DTA curve at 1150 + 15°C (Fig. 1) was not accompanied by visible changes in mass. According to the x-ray data, as a result of this the low-temperature modification A-Yb_2SiO_5 was transformed into its stable high-temperature analog B−Yb_2SiO_5. Chemical analysis revealed that the nitrogen content in the material decreased further to 0.86 mass %. That value is also anomalously high and can be explained only by the oxidized specimen being slightly inhomogeneous, i.e., by some portions being incompletely oxidized to that time.

The fourth, weakest exothermic effect on the DTA curve involves further loss of nitrogen (liberation of nitrogen from the material): data from chemical analysis showed about 0.3 mass % N. x-Ray analysis did not reveal any further changes in the oxidation product (B-Yb_2SiO_5) as a result of that transformation, before and after prolonged (up to 5 h) further isothermal holding at 1500°C.

The fact that we detected the A-Yb_2SiO_5 phase as the intermediate product of oxidation of $Yb_4Si_2O_7N_2$ requires more detailed discussion of both modifications of the silicates $(RE)_2O_3-SiO_2$ (RE = La−Lu, as well as Y and Sc). Compounds of

the type $(RE)_2Si_2O_5$ (with the molar ratio $(RE)_2O_3$:SiO_2 = 1:1) are stable phases in all systems. Their melting points lie between 1930 and 1980°C. Compounds of the type $(RE)_2Si_2O_5$ form two modifications, which are customarily denoted A and B [4, 10-15]. The modification A-$(RE)_2Si_2O_5$ is known for rare earths with a large ionic radius (La, Tb) and has a monoclinic structure (space group $P2_{1/c}$). The modification B-$(RE)_2Si_2O_5$ was shown to exist for rare earths with a small ionic radius (Tb–Lu), including Y and Sc). That phase also has a monoclinic structure (space group I2/*a*; the space groups B2/b, B2*a*, B2/c, and I2/c previously assigned were found to be wrong). Contrary to the data of [16] and all the doubts, Sc_2SiO_5 forms a B type structure [13, 17, 18]. Moreover, the silicate La_2SiO_5 undoubtedly forms an A-type structure, which was mentioned as unknown in [19]. The hypothesis, advanced in [20], that some sort of third modification exists for the rare earths Gd, Tb, and Dy was refuted unequivocally and it was found that a known A modification forms for those elements [15]. The erroneous interpretation of the x-ray data for the aforementioned RE silicates was in all likelihood due to the preferred orientations in specimens of A modification silicates [10].

These data indicate that Tb is the "boundary" element that divides the series of RE orthosilicates with preferred formation of an A or B modification. Felsche [4] maintains that A-Tb_2SiO_5 is a stable modification, although on the other hand Buisson and Michel [21] report data on obtaining B-Tb_2SiO_5 by melting. Furthermore, the data given by Gentner [14] indicate that the A modification of Tb_2SiO_5 was obtained when a stoichiometric mixture of terbium oxide and silicon oxide was annealed at 1200°C for 30 days (with intermediate pulverization of the specimen), a mixture of A and B modifications of Tb_2SiO_5 was obtained after annealing for 40 days, and single-phase B-Tb_2SiO_5 was obtained after annealing for 80 days. The data of [10] about the existence of an A modification of Dy_2SiO_5 should be assessed critically since the specimens in that case contained 1-2% Nd and because of the difference in the ionic radii of those two rare earths could have led to stabilization of the A-Dy_2SiO_5 that is unstable in other cases.

Table 1 shows the results of x-ray structure analyses of A-Yb_2SiO_5. The structure of the phase in principle is analogous to that of A-Yb_2SiO_5 also known as X_1-Yb_2SiO_5 [13, 22]. The calculated lattice constants of A-Yb_2SiO_5 are: a = 0.8951(3) Å, b = 0.6722(2) Å, c = 0.6588(2) Å, β = 105.36(4)°, ν = 385.1(1) Å^3.

On the basis of published data [4, 23] and the results of this study we obtained a curve of the unit cell volume versus the atomic number of the rare earth for phases of the type A-$(RE)_2SiO_5$ (Fig. 2). The calculated data for A-Yb_2SiO_5 are in good agreement with the general law.

The thermodynamic stability of A-Yb_2SiO_5 was not investigated. Our data on the formation of that phase in the interval 1025-1150°C may indicate that it is thermodynamically stable from room temperature up to 1150°C, i.e., the temperature of the transformation to the high-temperature modification B-Yb_2SiO_5. On the other hand, A-Yb_2SiO_5 may be a metastable phase, the formation of which involves a stage of oxidation of ytterbium oxynitride (J-phase).

At the given stage of the investigations nothing is known about the stability of A-Yb_2SiO_5 at temperatures below 1150°C. The transformation temperature may be the threshold of the thermodynamic stability of the phase. Kinetically induced shifts of the transition temperature to lower values are unlikely because the oxidation products are extremely fine-grained and, therefore, have a high reactivity. Moreover, the heating rate was fairly low (2 deg/min). Although the A → B transformation may be reversible, this is extremely difficult to check since such transformations in all systems with the participation of rare earths proceed by a reconstructive mechanism and hence are extremely long [4, 14, 15, 24, 25]. Long quenches in the temperature range 900-1200°C are planned in order to ascertain whether A-Yb_2SiO_5 is stable.

Of all the RE silicates only Yb_2SiO_5 definitely has two stable modifications, A and B. The low-temperature modification A-Yb_2SiO_5 is gradually transformed into B-Yb_2SiO_5 under heating. The transformation temperature, according to the published data [13, 22], is roughly 1190°C. Since the ionic radius of Yb^{3+} (0.900 Å), the temperature of any thermodynamic transformation of Yb_2SiO_5 should be lower than for Y_2SiO_5. The Yb_2SiO_5 transformation temperature that we observed ($\approx$ 1150°C) agrees well with such a premise.

The results of this investigation indicate that silicates of the type A-$(RE)_2SiO_5$ can be obtained with relative ease for such rare earths as Dy, Ho, Er, Tm, and Lu, which have a temperature range of stability below 1250-1100°C; this is done by air oxidization of the corresponding compounds of the type $(RE)_2Si_2O_7N_2$.

On the basis of the data reported we make the general conclusion that oxidation of RE oxynitrides can be fruitful method of obtaining phases and/or their modifications, which are metastable and are difficult to obtain by ordinary methods (synthesis in the temperature interval of phase stability requires unrealistically long annealing). The structural similarity of the respective oxynitrides and certain products of their oxidation makes it possible to obtain the necessary modifications of silicates in this way. Oxidization of $(Re)_4Si_2O_7N_2$–$(Re)_4Al_2O_9$ solid solutions can produce nitrogen-free solid solutions of the type $(Re)_4Al_{2(1-x)}Si_{2x}O_{9+x}$, which were observed earlier in $(Re)_2O_3$–Al_2O_3–SiO_2 for Gd, Y, and Yb [25, 28, 29].

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