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Formation and general characterization of a previously unknown ytterbium silicate (A-type Yb_2SiO_5)

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On non-isothermal oxidation of ytterbium nitrogen woehlerite ($Yb_4Si_2O_7N_2$), also known as the J-phase, a previously unknown and possibly metastable modification of Yb_2SiO_5 was detected. It is isostructural with the A-type RE_2SiO_5 modifications (RE = rare-earth element). The crystallographic data and stability of this new modification of Yb_2SiO_5 are discussed and compared with available data on RE_2SiO_5 compounds. The present results suggest that, in general, oxidation of rare-earth oxynitride phases might prove to be a fruitful method to obtain phases that are metastable or cannot be prepared by standard methods since their low-temperature stability range would require unrealistically long firing periods.

1. Introduction

Rare-earth silicates (e.g. RE_2SiO_5 and $RE_2Si_2O_7$) and oxynitrides (e.g., $RE_4Si_2O_7N_2$ and $RE_2Si_3O_3N_4$) are important secondary phases commonly observed in Si_3N_4 and SiC high-performance ceramics sintered with rare-earth oxides as sintering additives. The present authors are currently investigating the physico-chemical properties of members of the solid-solution series $Yb_4Si_2O_7N_2$–$Yb_4Al_2O_9$ [1]. On studying the oxidation of ytterbium nitrogen woehlerite ($Yb_4Si_2O_7N_2$) (also known as the J-phase), a rather complex oxidation behaviour was observed. A previously unknown and possibly metastable low-temperature Yb_2SiO_5 modification was observed during an intermediate oxidation stage. The present paper will give a crystallographic characterization of this remarkable phase. Its stability will be discussed in comparison with available data on the other known RE_2SiO_5 modifications.

Further and more detailed results on the synthesis, some properties, oxidation behaviour and decomposition temperatures of $Yb_4Si_2O_7N_2$ and $Yb_4Si_2O_7N_2$–$Yb_4Al_2O_9$ solid solutions will be published elsewhere [1, 2].

2. Experimental procedure

Ytterbium nitrogen woehlerite ($Yb_4Si_2O_7N_2$) was prepared by sintering stoichiometric mixtures of isostatically pressed powder blends of Yb_2O_3 (99.5% purity; Ventron, Germany), amorphous SiO_2 (Aerosil 2000; greater than 99.8% purity; Degussa, Germany) and Si_3N_4 (greater than 98% α-Si_3N_4; DP 14/13, Starck, Germany). X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) showed the sintered woehlerite samples to be single phase. The residual porosity amounted to about 10%. Rectangular samples with the dimensions 3 mm × 3 mm × 7 mm were diamond cut from a sintered bar and their oxidation behaviour was investigated by simultaneous thermal analysis (STA) (Netzsch, Germany model STA 409 with an upper temperature limit of about 1500 °C) in air using alumina crucibles. The STA samples had a mass of about 500 mg. Since preliminary differential thermal analysis (DTA) runs showed that active oxidation has already occurred below 700 °C, a heating rate of $2\ K\ min^{-1}$ from room temperature to 1500 °C was used. After being held at 1500 °C for 5 h, the samples were cooled to room temperature at the rate of $10\ K\ min^{-1}$. Chemical analyses of the oxidation products at different oxidation stages were performed by carrier-gas hot extraction (N and O) and fluor combustion–Fourier transform infrared spectroscopy (Si), the latter being based on an analysis scheme developed at the present authors' institute. Pure $Yb_4Si_2O_7N_2$ was taken as a standard. Oxidation products were identified by XRD (Siemens D5000 X-ray powder diffractometer with position-sensitive detector; Ni-filtered Cu Kα radiation) in the 2θ range from 10 to 80°. For unit-cell parameter refinement, 99.999% pure silicon was added as internal standard.

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3. Results and discussion

3.1. Oxidation products of $Yb_4Si_2O_7N_2$

Fig. 1 shows the results of a STA measurement in air. The DTA and thermogravimetry (TG) curves illustrate that the oxidation of ytterbium nitrogen woehlerite ($Yb_4Si_2O_7N_2$) proceeds in (at least) three steps.

Oxidation starts at around 575 ± 10 °C (onset temperature). A weight gain is observed which is accompanied by a large and broad exothermic DTA effect with an asymmetric shape. XRD analysis of the oxidation product quenched from temperatures slightly above this first DTA effect gave an X-ray pattern similar to that of unoxidized $Yb_4Si_2O_7N_2$, but characterized by broad and slightly shifted X-ray reflections (full width at half-maximum (FWHM), $2\theta \approx 0.45$–$0.60°$). This indicates some structural imperfections and/or inhomogeneities in the oxidation product. Chemical analysis shows that about 1.4 mass% nitrogen is retained in the structure, i.e. about half of the nitrogen has been lost when compared with unoxidized $Yb_4Si_2O_7N_2$ (which contains 3.15 mass% N).

A second, small and sharp DTA effect is observed at 1025 ± 5 °C. It is accompanied by a small weight loss which is attributed to loss of gaseous nitrogen. The X-ray pattern of the resulting oxidation product at this stage was found to be that of a previously unknown Yb_2SiO_5 modification (A-Yb_2SiO_5 according to the rare-earth silicate nomenclature established by Felsche [3]) and, additionally, traces of partly oxidized $Yb_4Si_2O_7N_2$. The occurrence of A-Yb_2SiO_5, its crystallography and possible metastability are discussed in more detail in Section 3.2.

The results of the chemical analysis of this intermediate silicate oxidation product indicates a further lowered nitrogen content (0.98 mass% N) which is consistent with the corresponding effect in the TG curve although the measured absolute nitrogen content is considered to be too high owing to unverified reasons such as oxidation gradients within the sample. It is considered implausible that some nitrogen is dissolved in ionic form in the structure of A-Yb_2SiO_5. It is more probable that there is nitrogen retention in remnants of unoxidized or partly oxidized $Yb_4Si_2O_7N_2$ within the STA sample. The nitrogen may be present in ionic and/or molecular form. Similar processes of nitrogen retention have been reported for the yttrium oxynitride compound $Y_{10}(SiO_4)_6N_2$ [4].

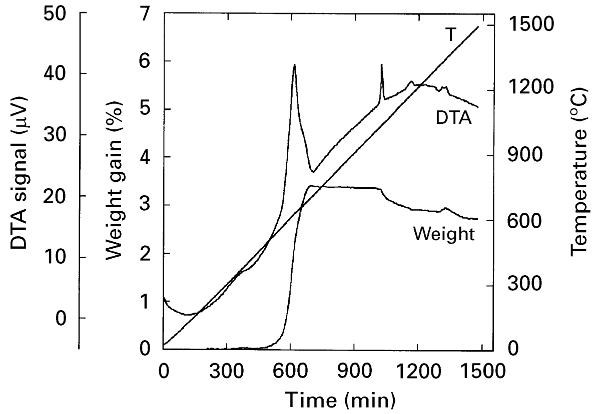

Figure 1 Result of STA measurement of the oxidation of $Yb_4Si_2O_7N_2$. Note the four exothermic effects in the DTA curve. For explanation see text.

The formation of Yb_2SiO_5 (and not that of the other known stable ytterbium silicate, $Yb_2Si_2O_7$) on oxidation of $Yb_4Si_2O_7N_2$ was to be expected since the Yb-to-Si ratio is exactly maintained during the oxidation process.

The oxidation of $Yb_4Si_2O_7N_2$ (or, in general, $RE_4Si_2O_7N_2$) may be discussed in terms of its structure which consists of either Si_2O_5N or Si_2O_6N ditetrahedral units with N ions occupying the bridging position [5, 6]. These units are interconnected by Yb–O_n (RE–O_n) polyhedra. On oxidation the nitrogen ions in the units are oxidized and possibly retained as atomic or molecular nitrogen. With increasing temperature, they evaporate as nitrogen gas with a concomitant replacement of their positions by oxygen ions. This obviously induces a rearrangement of the resulting Si–O units, causing the formation of isolated SiO_4 tetrahedra. As a result the structure of A-RE_2SiO_5 is formed. This structure is described by a three-dimensional network of isolated SiO_4 tetrahedra, extra non-silicon-bonded oxygen and RE^{3+} ions [3, 7]. Although B-RE_2SiO_5 has a very similar but slightly less space-filling structure [3, 8], it may be concluded from our results that formation of A-RE_2SiO_5 is favoured during the second oxidation step, on account of stronger structural similarities between A-RE_2SiO_5 and (partly oxidized) $Yb_4Si_2O_7N_2$.

The third, very small and broad exothermic effect due to oxidation is observed only in the DTA curve at 1150 ± 15 °C (see Fig. 1). XRD of the corresponding reaction product showed this DTA effect to conform to a transformation reaction of the low-temperature modification A-Yb_2SiO_5 to the stable high-temperature modification B-Yb_2SiO_5. The chemical composition of the oxidation product at this stage is characterized by a further lowered nitrogen content (0.86 mass% N). Again, this nitrogen content is tentatively attributed to some nitrogen retention in parts of the oxidized sample.

A fourth, very small and somewhat irregular exothermic effect seen in the DTA curve is related to a further loss of nitrogen, as several chemical analyses of small parts of the oxidation sample showed (the analyses detected traces of N up to about 0.3 mass% N). XRD showed that no further change in the oxidation product (B-Yb_2SiO_5) occurred after this fourth peak or after the holding period at 1500 °C.

3.2. Occurrence of A-Yb_2SiO_5

The detection of A-Yb_2SiO_5 as an intermediate oxidation product of $Yb_4Si_2O_7N_2$ requires a more thorough discussion of the two different modifications of RE_2SiO_5 compounds, namely, A and B.

In the systems RE_2O_3–SiO_2 (RE = La to Lu, including Y and Sc), the rare-earth silicate compound RE_2SiO_5 (with mole ratio RE_2O_3:SiO_2 = 1:1) is a stable phase in all systems. Its melting point ranges between 1930 and 1980 °C. RE_2SiO_5 forms two modifications designated A and B [3, 9–14]. A-RE_2SiO_5 exists for large RE^{3+} ions (RE = La to Tb) and is monoclinic (space group, $P2_1/c$). B-RE_2SiO_5 exists for small RE^{3+} ions (RE = Tb to Lu, including Y and Sc) and is monoclinic as well (space group, $I2/a$; note that earlier space group designations $B2/b$, $B2/a$, $B2/c$, $C2/c$ or $I2/c$ are overruled by current nomenclature). Sc_2SiO_5, in contrary to what is stated by Leskelä and Jurkäs [15], also doubtlessly forms the B-type structure [12, 16, 17]. La_2SiO_5 does not have an unknown structure, as suggested by Leskelä and co-workers [11, 18] but definitely forms the A-type modification [13]. A "third" RE_2SiO_5 modification reported by Wanklyn *et al.* [19] for RE = Gd, Tb or Dy has unambiguously been demonstrated to be in fact the well-known A modification [14]. The misinterpretation of the respective X-ray diffractograms was shown to be caused by a strong preferred orientation effect of the X-ray samples due to the perfect cleavage of A-RE_2SiO_5 parallel to {100} [9].

As seen from the above data, the "boundary" between the A and B modifications seems to be situated at RE = Tb. Felsche [3] states that A-Tb_2SiO_5 is the stable modification. On the other hand, flux-grown B-Tb_2SiO_5 is also known [20]. Gentner [13], on firing a stoichiometric mixture of terbium oxide and silica at 1200 °C in air, first obtained A-Tb_2SiO_5 after a firing period of 30 days (including intermediate grinding); then, after firing for 40 days, a mixture of A- and B-Tb_2SiO_5, which subsequently transformed into single-phase B-Tb_2SiO_5 after firing for 80 days. A report on the A modification for the small Dy^{3+} ion by Anan'eva *et al.* [9] must be regarded with suspicion, since the sample of Anan'eva *et al.* was doped with 1–2 mass% Nd, thus presumably promoting a ionic size-related stabilization of the otherwise unstable A-Dy_2SiO_5.

Table I gives the measured X-ray powder data for A-Yb_2SiO_5. The X-ray pattern is similar to that of (stable) A-Y_2SiO_5 (also known as X_1-Y_2SiO_5 [12, 21]). The refined unit-cell parameters of A-Yb_2SiO_5 are as follows: $a = 8.951(3)$ Å, $b = 6.772(2)$ Å, $c = 6.588(2)$ Å, $\beta = 105.36(4)^\circ$ and $V = 385.1(1)$ Å^3. Fig. 2 illustrates

TABLE I X-ray powder data for A-Yb_2SiO_5[a]

A-Yb_2SiO_5 (this work)

d_{obs}[b] (Å)	I_{obs}	*hkl*	d_{calc} (Å)
8.64	6	100	8.63
5.332	56	110	5.328
4.633	32	011	4.633
4.313	27	200	4.316
3.788	20	111	3.789
3.639	14	210	3.639
3.511	7	$21\bar{1}$	3.515
3.274	31	$10\bar{2}$	3.275
2.987	79	021	2.988
2.962	69	$20\bar{2}$	2.960
2.877	65	300	2.877
2.748 (s)	54	102	2.754
2.720	100	121	2.721
2.646 (s)	22	310	2.648
2.613	68	$22\bar{1}$	2.614
2.331 (b)	4	$31\bar{2}$	2.333
		221	2.325
2.216	4	$32\bar{1}$	2.215
2.181	6	130	2.184
2.167	6	212	2.165
2.128	12	031	2.127
2.054 (b)	21	410	2.056
		$40\bar{2}$	2.056
2.041	21	$21\bar{3}$	2.039
2.026 (b)	11	131	2.024
		013	2.021
1.955	29	321	1.954
1.899 (b)	3	302	1.897
		$31\bar{3}$	1.894
1.866 (s)	7	113	1.866
		$42\bar{1}$	1.863
1.842 (b)	54	231	1.844
		$12\bar{3}$	1.842
		032	1.840
1.789 (b)	14	$23\bar{2}$	1.795
		$33\bar{1}$	1.788
		023	1.776
1.729 (b)	10	$51\bar{1}$	1.731
		500	1.726
1.702 (s)	11	$32\bar{3}$	1.705
1.692 (b)	16	040	1.694
		123	1.684
1.667 (b)	15	$33\bar{2}$	1.671
		$51\bar{2}$	1.667
		140	1.661
1.641	6	331	1.642
		$10\bar{4}$	1.641
1.596 (b)	15	402	1.599
		$11\bar{4}$	1.595
1.583 (b)	19	141	1.588
		$43\bar{1}$	1.587
		$52\bar{1}$	1.583
1.572 (b)	17	240	1.576
		$13\bar{3}$	1.574
1.563 (b)	16	$24\bar{1}$	1.566
		$42\bar{3}$	1.564
		430	1.560
1.540 (b)	10	033	1.544
		223	1.540
		520	1.538
1.505 (bb)	4	$51\bar{3}$	1.515
		$14\bar{2}$	1.504
		241	1.496
1.468 (b)	13	133	1.472
		$24\bar{2}$	1.470
		$34\bar{1}$	1.466
1.455 (b)	14	114	1.458
		$61\bar{1}$	1.456
		332	1.452
1.445 (b)	15	422	1.446
		$41\bar{4}$	1.446
		142	1.442

[a] Measured by XRD (Siemens D5000 with position-sensitive detector; Cu Kα radiation; Si as internal standard). Indexing for space group $P2_1/c$: $a = 8.951(3)$ Å, $b = 6.772(2)$ Å, $c = 6.588(2)$ Å, $\beta = 105.36(4)^\circ$ and $V = 385.1(1)$ Å^3.

[b] s, shoulder of adjacent stronger reflection; b, broad; bb, very broad.

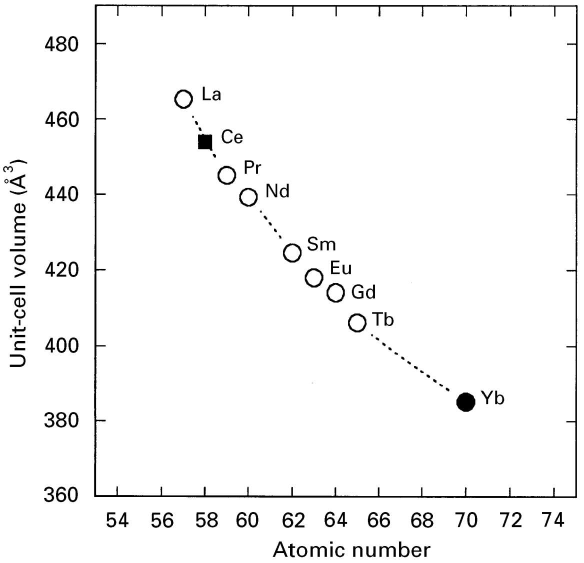

Figure 2 Unit-cell volume of A-type RE_2SiO_5. (○), from [3]; (■), from [22]; (●), from this work. The value for A-Yb_2SiO_5 measured in this work fits well into this series.

the relation between the A-type RE_2SiO_5 unit-cell volume and the RE atomic number using the available literature data [3, 22] and the present results for A-Yb_2SiO_5. One sees that the volume of A-Yb_2SiO_5 fits well into the series.

The thermodynamic stability of A-Yb_2SiO_5 is not clarified at the moment. The observation of this modification A-Yb_2SiO_5 in the temperature range between about 1025 and about 1150 °C may firstly indicate that it is a thermodynamically stable phase from room temperature up to its transformation temperature (about 1150 °C) where it transforms into the high-temperature modification B-Yb_2SiO_5. On the other hand, A-Yb_2SiO_5 may represent a metastable phase whose genesis is related to its state as an oxidation product.

At the present stage of investigations, nothing specific is known about the long-term stability of A-Yb_2SiO_5 at temperatures below about 1150 °C. The observed transformation temperature may represent the thermodynamic transformation temperature. Kinetically induced shifts of the transformation temperature towards higher temperatures are considered improbable since the oxidation products are extremely fine grained and therefore highly reactive, and since the heating rate used was small (2 K min^{-1}). Although the A–B transformation reaction might be reversible it would prove useless to verify this reversibility since all phase transformations in rare-earth silicates are of the reconstructive type and therefore extremely sluggish [3, 13, 14, 23, 24]. Long-term anneals in the temperature range between 900 and 1200 °C are planned to evaluate the thermodynamic stability of A-Yb_2SiO_5.

Y_2SiO_5 is the only RE_2SiO_5 compound that is definitely known to occur in both stable modifications A and B. The low-temperature phase A-Y_2SiO_5 on heating slowly transforms into the high-temperature phase B-Y_2SiO_5; the transformation temperature is roughly given as about 1190 °C [12, 21]. Since the Yb^{3+} ionic radius (0.868 Å [25]) is smaller than the Y^{3+} ionic radius (0.900 Å), any thermodynamically fixed transformation temperature of Yb_2SiO_5 must be lower than that of Y_2SiO_5. The observed transformation temperature for Yb_2SiO_5 (about 1150 °C) would support this assumption.

The present results illustrate that it may prove possible that A-type RE_2SiO_5 modifications of Dy, Ho, Er, Tm and Lu, which probably all have temperature stability ranges below approximately 1250–1100 °C, may be prepared in a similar manner by oxidation of the respective $RE_4Si_2O_7N_2$ compounds.

4. Conclusions

On oxidation of $Yb_4Si_2O_7N_2$, a previously unknown modification of Yb_2SiO_5 (A-Yb_2SiO_5) is formed as an intermediate oxidation product. Its crystallography, stability and relation to other RE_2SiO_5 compounds are evaluated.

The results of our investigation lead to the general assumption that oxidation of oxynitride phases might prove to be a fruitful method to obtain phases and/or modifications that either are metastable or cannot be prepared as stable phases by standard methods since their low-temperature stability range would require unrealistically long firing periods. Structural similarities between oxynitrides and desired oxidation products may be used to prepare specific modifications.

For example, oxidation of nitrogen-containing members along the solid solution series $RE_4Si_2O_7N_2$–$RE_4Al_2O_9$ (with general formula $RE_4Si_{2-x}Al_xO_{7+x}N_{2-x}$) [1] might be used to synthesize the nitrogen-free limited solid solution $RE_4Al_{2(1-x)}Si_{2x}O_{9+x}$ which has been observed in the systems RE_2O_3–Al_2O_3–SiO_2 for RE = Gd, Y or Yb [24, 26, 27].

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References

1. V. A. IJEVSKII, U. KOLITSCH, H. J. SEIFERT, I. WIEDMANN and F. ALDINGER, to be published.
2. V. A. IJEVSKII, U. KOLITSCH, I. WIEDMANN, H. J. SEIFERT and F. ALDINGER, to be published.
3. J. FELSCHE, *Struct. Bonding* **13** (1973) 99.
4. J.-B. VEYRET, M. VAN DE VOORDE and M. BILLY, *J. Amer. Ceram. Soc.* **75** (1992) 3289.
5. J. P. GUHA, *J. Mater. Sci.* **15** (1980) 262.
6. K. J. D. MACKENZIE, G. J. GAINSFORD and M. J. RYAN, *J. Eur. Ceram. Soc.* **16** (1996) 553.
7. YU. I. SMOLIN and S. P. TKACHEV, *Sov. Phys.—Crystallogr.* **14** (1969) 14.
8. YU. I. SMOLIN, *ibid.* **14** (1970) 854.
9. G. V. ANAN'EVA, A. M. KOROVKIN, T. I. MERKULYAEVA, A. M. MOROZOVA, M. V. PETROV, I. R. SAVINOVA, V. R. STARTSEV and P. P. FEOFILOV, *Inorg. Mater.* **17** (1981) 754.
10. I. A. BONDAR, *Ceram. Int.* **8** (1982) 83.

11. M. LESKELÄ and L. NIINISTO, in "Handbook on the physics and chemistry of rare earths", Vol. 8, edited by K. A. Gschneidner Jr and L. Eyring (Elsevier, Amsterdam, 1986) p. 203.
12. K. LIDDELL and D. P. THOMPSON, *Brit. Ceram. Trans. J.* **85** (1986) 16.
13. T. GENTNER, Diploma Thesis, University of Heidelberg, Heidelberg (1988).
14. U. KOLITSCH, Diploma Thesis, University of Stuttgart, Stuttgart (1992).
15. M. LESKELÄ and K. JYRKÄS, *J. Amer. Ceram. Soc.* **70** (1987) C-160.
16. N. A. TOROPOV and V. A. VASIL'EVA, *Russ. J. Inorg. Chem.* **7** (1962) 1001.
17. J. DODSWORTH and D. P. THOMPSON, *Proc. Brit. Ceram. Soc.* **31** (*Spec. Ceram.* 7) (1981) 51.
18. M. LESKELÄ and J. SUIKKANEN, *J. Less-Common Metals* **112** (1985) 71.
19. B. M. WANKLYN, F. R. WONDRE, G. B. ANSELL and W. DAVISON, *J. Mater. Sci.* **10** (1975) 1494.
20. G. BUISSON and C. MICHEL, *Mater. Res. Bull.* **3** (1968) 193.
21. J. ITO and H. JOHNSON, *Amer. Miner.* **53** (1968) 1940.
22. H. A. M. VAN HAL and H. T. HINTZEN, *J. Alloys Compounds* **179** (1992) 77.
23. J. FELSCHE, *Naturwissenschafter* **57** (1970) 127.
24. U. KOLITSCH, PhD Thesis, University of Stuttgart, Stuttgart (1995).
25. R. D. SHANNON, *Acta Crystallogr. A* **32** (1976) 751.
26. U. KOLITSCH, H. J. SEIFERT and F. ALDINGER, *J. Alloys Compounds* (1997) (in press).
27. *Idem.*, *Z. Metallkde* (1997) (submitted).

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