ELSEVIER Journal of Alloys and Compounds 216 (1994) 255–258

Journal of ALLOYS AND COMPOUNDS

The crystal structure of the low-temperature A-type modification of Pr_2O_3 from X-ray powder and electron single crystal diffraction

O. Greis[a], R. Ziel[a], B. Breidenstein[b], A. Haase[b], T. Petzel[c]

[a]*Technical University Hamburg-Harburg, Central Division of Electron Microscopy, Eissendorfer Strasse 42, D-21071 Hamburg, Germany*
[b]*Rich. Seifert & Co., Research and Application Division, Bogenstrasse 41, D-22926 Ahrensburg, Germany*
[c]*University of the Federal Armed Forces, Division of Inorganic Chemistry, Holstenhofweg 85, D-22043 Hamburg, Germany*

Received 28 April 1994

Abstract

The crystal structure of A-Pr_2O_3 has been studied by X-ray powder diffraction and high-energy electron diffraction (HEED) from single crystals. The space group has been unambiguously established as $P\bar{3}m1$ (No. 164) by HEED, though the intensities of *hhl* reflections with $l=2n+1$ are very weak. These reflections are difficult to observe in X-ray diffractometry and could mislead one to consider the existence of a *c*-glide plane and, therefore, to a wrong space group. The structure is in agreement with the usually accepted so-called Pauling model for the A-type of rare-earth sesquioxides. The final value of $R_{\text{conv}}=2.1\%$ indicates an excellent refinement. Slightly distorted OPr_4 tetrahedra are the most important polyhedra in this structure. They share edges and form $(PrO)_2{}^{2+}$ layers, which are embedded in O^{2-} layers. The OPr_4 tetrahedron has four O–Pr distances of 2.344 Å on average. Three of them are very short with distances of 2.305 Å. These partially covalent bonds should be emphasized with respect to similar short distances in ordered PrOF structures.

Keywords: X-ray powder diffraction; Electron single crystal diffraction

---

1. Introduction

In the course of extensive studies on the thermal and structural properties of individual phases in the system Pr_2O_3–PrOF–PrF_3 [1,2], we recognized a very interesting structural problem. Surprisingly, we found in the crystal structures of the fully ordered β-PrOF and α-PrOF phases evidence that the Pr–O distances are about 0.1–0.2 Å shorter than the Pr–F distances, in spite of the reference radii of 1.40 Å for O^{2-} and 1.33 Å for F^- of the generally accepted set of effective ionic radii [3]. Similar results have been described for YOF [4] and ScOF [5,6], though the *R* values of 7.6% of these structure determinations are not very convincing with respect to these very subtle details. Additional support, however, comes from a ^{19}F-NMR study in the case of ScOF [6] with $R=3.0\%$. The difficulties in structure determinations with isoelectronic ions, like O^{2-} and F^-, arise from almost identical atomic scattering factors for X-rays. Exchange of these particles on their crystallographic sites does not alter the *R* values in an unambiguous way and one has to rely on judgements from 'usual' atomic distances, lattice energy calculations etc.

To get more insight into the structural details of β-PrOF and α-PrOF, we also studied the crystal structures of both constituent compounds by X-ray powder diffraction and high-energy electron diffraction from single crystals with main emphasis on the determination of the shortest Pr–F and Pr–O distances in tysonite-type PrF_3 [7] and A-type Pr_2O_3. The results of the latter structure analysis are presented in this paper.

2. Experimental details

Pure Pr_2O_3 was prepared by reduction of $Pr(III,IV)_6O_{11}$ with highly purified hydrogen at 930 °C. Subsequently, the light green sesquioxide was stored and handled under dry argon to prevent re-oxidation and re-contamination with hydroxides and carbonates. X-ray powder diffraction showed no other reflections than those of the hexagonal-trigonal A-type of Pr_2O_3 with the lattice parameters of $a=3.8591(4)$ Å and

SSDI 0925-8388(94)01265-J

$c = 6.0173(8)$ Å (Guinier technique, Cu-Kα_1, silicon NBS-SRM-640a as internal standard).

The X-ray powder diffraction data for the structure determination were collected on an automated Seifert-XRD-3000 system using a primary quartz monochromator and Cu-Kα_1 radiation with $\lambda = 1.5406$ Å, Bragg–Brentano geometry in the $\Theta/2\Theta$-mode, geometric calibration against external silicon NBS-SRM-640a, secondary soller block and 0.2 mm slit, step scan with 60 s for each 2Θ-step $= 0.03°$, measurement range of $10° \leqslant 2\Theta \leqslant 162°$, and a scintillation counter. A quartz zero-background holder was used as support for the very finely pulverized A-Pr_2O_3, which was mounted by means of a double-sided tesafilm in a very thin layer of <0.1 mm thickness, to keep absorption corrections to a minimum. In many cases, absorption can be neglected when applying this method.

The Seifert-XDAL-3000 program package has been used for the measurements (PMEAS), peak integration and peak de-convolution (SPECTRA-2). A total of 44 reflections with intensities of peak hights I/I_{999} were used for the preparation of the ICDD file (in press). A total of 39 symmetry-independent reflections were integrated, from which 36 reflections with $J \geqslant 0.01 J_{max}$ were actually used for the structure determination. The calculations and least squares refinements were carried out by means of the program POWLS-80 [8]. The drawings of structural units were made with the program ATOMS-2.3 [9].

To check on the appearance or absence of systematic extinctions for an appropriate selection of space groups, high-energy electron diffraction (HEED) from single crystals <800 Å was carried out in a transmission electron microscope JEOL-STEM-2000FX-II with $\lambda = 0.025$ Å. The chemical composition of Pr_2O_3 was controlled by energy-dispersive X-ray spectroscopy (EDXS) in a scanning electron microscope JEOL-SEM-840A and in the above STEM using a windowless or an ultra-thin window Si(Li) detector, respectively. No contaminations could be detected, e.g. carbon from newly formed carbonates by absorption of CO_2.

3. Structure determination

With respect to the size of the unit cell and to the experimental density of $\rho = 6.94$ g cm^{-3} [10], there is only one formula unit of Pr_2O_3 in the hexagonal-trigonal cell. HEED experiments from several small single crystals proved that no systematic extinctions exist. Rotation analyses were carried out around [001] and several patterns of [100]-, [110]- and [410]-type zones were taken. It has been unambiguously established that $00l$ and hhl reflections with $l = 2n+1$ and hkl reflections with $h-k=3n$ and $l=2n+1$ were very weak indeed, but definitely not absent or caused by multiple diffraction. Analogous results have been obtained in an earlier paper on A-La_2O_3 and A-Nd_2O_3 [11]. Therefore, trigonal space groups without systematic extinctions are the only ones to be considered. In particular, the space group $P6_3/mmc$, which has been reported in earlier X-ray diffraction studies on A-type rare-earth sesquioxides [12,13], has to be rejected. This space group, however, is true for the hexagonal high-temperature H-form of R_2O_3 [14]. From an empirical judgement on our HEED intensities and from the inspection of the calculated intensities of the reflections in question based on our A-Pr_2O_3 structure (see below), it is obvious that these reflections are difficult to observe by X-ray diffraction, misleading one to the assumption of a c-glide plane.

The A-type Pr_2O_3 structure can be considered as a derivative of the hexagonal close-packed structure of praseodymium cations with $r = 1.06 \pm 0.07$ Å. The cationic sub-lattice has to be expanded significantly to accommodate the larger oxygen anions with $r = 1.40$ Å/1.38 Å on octahedral and tetrahedral interstices in $Pr_2\square t_4\square O_2$. However, only half of them have to be occupied with respect to the stoichiometry of Pr_2O_3. Following the selection of atomic sites by Pauling [15], we started our structure calculations with this idealized model in the space group $P\bar{3}m1$ (No. 164) with Pr in 1/3, 2/3, 1/4, O1 in 1/3, 2/3, 5/8 and O2 in 0, 0, 0. Using scattering factors for O^{2-} and Pr^{3+} and an overall temperature factor ov-B_0 of 0.4 Å^2, we obtained a conventional reliability value of $R = 3.8\%$. Refinement of z for Pr and O1 lead to $z = 0.246$ and 0.65 ($R = 2.8\%$). The reliability of the structure improved finally to $R = 2.1\%$ after introduction of corrections for anomalous dispersion for Pr^{3+} and individual isotropic temperature factors as well as the application of an empirical correction corresponding to $f = b \cdot \exp(a \cdot 2\Theta)$ for integrated intensities $J_{cor} = f \cdot J_{obs}$. This kind of correction simultaneously takes care of absorption, insufficiencies in LPG corrections and changes of the irradiated sample volume. The coefficients a and b are recalculated at each step of the refinement. We would not overestimate the absolute B_0 values, because insufficient absorption and LPG corrections as well as related errors usually also cause shifts for B_0 values. The relative magnitude of B_0 values for different atoms, however, is not affected by these corrections. No improvement could be obtained by calculations in space groups of lower symmetry with further relaxations of atomic coordinates and application of anisotropic temperature factors. Detailed results of our structure determination and refinements are listed in Table 1.

4. Discussion

An analysis of the listed coordination polyhedra shows that the 'monocapped octahedron PrO_7' should not be

Table 1

Results of the structure determination of the low-temperature A-type modification of Pr_2O_3

Crystal symmetry and space group: trigonal, $P\bar{3}m1$ (No. 164)

Lattice parameters: $a = 3.8589(1)$ Å, $c = 6.0131(2)$ Å, $V = 77.543(4)$ Å^3, $Z = 1$

Density: $\rho_{calc} = 7.06$ g cm^{-3}, $\rho_{exp} = 6.94$ g cm^{-3} [10]

Powder diffraction data with peak hights I/I_{999}: ICDD in press

---

Atomic parameters from 36 symmetry-independent reflections with $J \geqslant 0.01 J_{max}$,
atomic scattering factors for Pr^{3+} and O^{2-},
anomalous dispersion correction for Pr^{3+}, isotropic temperature factors B_0, empirical correction for absorption and geometry,
final $R_{con'} = 2.1\%$:

Pr	in (2d)	1/3, 2/3, 0.24630(5)	$B_0 = 0.42$ Å^2
O1	in (2d)	1/3, 2/3, 0.6555(8)	$B_0 = 0.50$ Å^2
O2	in (1a)	0, 0, 0	$B_0 = 0.90$ Å^2

Coordination for Pr^{3+}: monocapped octahedron PrO_7 with CN = 7

Pr–O1 = 2.305(5) Å (3x) and Pr–O1′ = 2.461(5) Å (1x) → aver. = 2.344 Å

Pr–O2 = 2.675(5) Å (3x)

O1–O1′ = 2.909(8) Å (3x) and O1–O2 = 3.042(8) Å (6x)

O1 and O2 within the planes parallel to (001) are not in contact

---

Coordination for $O^{2-}(1)$: tetrahedron OPr_4 (CN = 4) forming $\infty(PrO)_2{}^{2-}$ layers

O1–Pr = 2.305(5) Å (3x) and O1–Pr′ = 2.461(5) Å (1x) → aver. = 2.344 Å

Pr–O1–Pr/Pr′ angles between 104.8° and 113.7°

Coordination for $O^{2-}(2)$: octahedron OPr_6 with CN = 6

O2–Pr = 2.675(5) Å (6x), Pr–O2–Pr angles between 87.7° and 92.3°

---

considered due to three Pr–O2 distances of 2.675 Å. The involved atoms are certainly not in contact at all. The remaining four Pr–O1 distances of 2.344 Å on average are much shorter than expected on the basis of simple addition of standard ionic radii, which gives about 2.46 Å. This, however, is exactly the Pr–O1′ distance. The three other Pr–O1 distances of 2.305 Å are very short, obviously caused by the presence of some covalent bonding with sp^2 rather than sp^3 hybridization for oxygen, as generally proposed by Jørgensen et al. [16]. On the other side, we can consider the OPr_4 tetrahedron (see Fig. 1) with these three O1–Pr and one O1–Pr′ distances as the basic structural unit of the A-type rare-earth sesquioxides [17]. They share three edges with one corner being common to four tetrahedra. In this way, layers with up- and down-oriented tetrahedra are formed with the chemical composition of $\infty(PrO)_2{}^{2+}$. They are embedded with ∞O^{2-} layers and one obtains a layer sequence of $\infty[(PrO)_2{}^{2+} - O^{2-}]$ with the formula $(PrO)_2O = Pr_2O_3$. In Fig. 2, a larger section of the A-Pr_2O_3 structure is shown with two c-vectors in the vertical direction. It should be

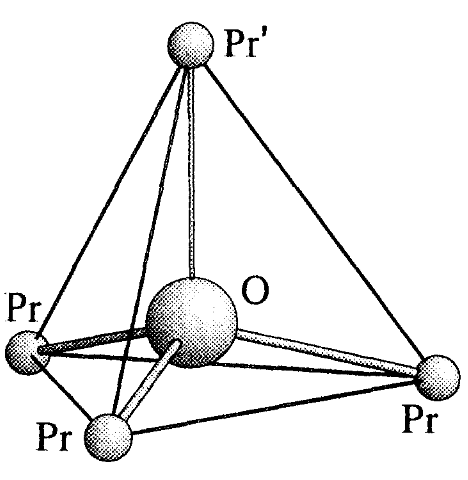

Fig. 1. OPr_4 tetrahedron with three partially covalent O1–Pr bonds of 2.305 Å in the basal 'plane' and one ionic O1–Pr′ distance of 2.461 Å in the vertical [001] direction.

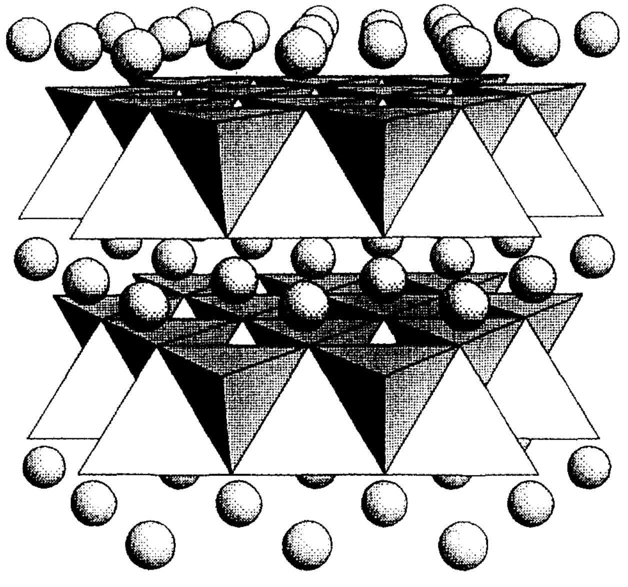

Fig. 2. Extended section of the A–Pr_2O_3 structure displaying edge-sharing OPr_4 tetrahedra embedded in oxygen layers resulting in a layer sequence of $\infty[(PrO)_2{}^{2+}–O^{2-}]$ in the vertical [001] direction.

Table 2

Comparison of some structural data of A-type rare earth sesquioxides R_2O_3: references, *R* values, *z* and B_0 for *R*, *z* and B_0 for O1 and O2, O1–R and O1–R′ distances in OR_4 tetrahedra

R_2O_3	*R* (%)	$z(Pr)+B_0(Pr)$		$z(O1)+B_0(O1)$		$B_0(O2)$	O1–R/O1–R′
Idealized structure		0.250		0.625			
La_2O_3[a]		0.245		0.645			2.37 /2.45
La_2O_3[b]	1.6%	0.2467	0.50	0.6470	0.62	0.82	2.365/2.456
Ce_2O_3[c]	2.9%	0.2454	0.74	0.6471	0.94	1.39	2.339/2.434
Pr_2O_3[d]	6.3%	0.2450		0.6361			2.34 /2.35
Pr_2O_3[e]	2.1%	0.2463	0.42	0.6555	0.50	0.90	2.305/2.461
Nd_2O_3[f]	1.9%	0.2462	0.25	0.6466	0.59	0.85	2.306/2.403
Nd_2O_3[b]	3.0%	0.2465	0.38	0.6470	0.68	1.00	2.303/2.404

[a] Koehler and Wollan [18];
[b] Aldebert and Traverse [14];
[c] Bärnighausen and Schiller [19];
[d] Wolf and Hoppe [20];
[e] Greis et al. (this work);
[f] Boucherle and Schweizer [21].

mentioned that Aldebert and Traverse [14] have slightly modified this model to pay more attention to the covalent basal 'plane' of the above tetrahedra. In this case, the layer sequence would be $\infty[(PrO)^+\text{-}(PrO)^+\text{-}O^{2-}]$, which also gives Pr_2O_3. For comparison, some structural parameters and the short R–O distances of the OR_4 tetrahedra of A-type R_2O_3 are listed in Table 2. The data are selected from the most reliable structural analysis.

References

[1] T. Petzel, V. Marx and B. Hormann, *J. Alloys Comp., 200* (1993) 27.

[2] O. Greis, R. Ziel, V. Marx, T. Petzel, B. Breidenstein and A. Haase, *Mater. Sci. Forum,* (1994) in press.

[3] R.D. Shannon, *Acta Crystallogr., A13* (1976) 751.

[4] A.W. Mann and D.J.M. Bevan, *Acta Crystallogr. Sect. B, 26* (1970) 2129.

[5] B. Holmberg, *Acta Chem. Scand., 20* (1966) 1082.

[6] M. Vlasse, M. Saux, P. Echegut and G. Villeneuve, *Mater. Res. Bull., 14* (1979) 807.

[7] O. Greis, R. Ziel, V. Marx, T. Petzel, B. Breidenstein and A. Haase, to be published.

[8] G. Will, E. Jansen and W. Schäfer, POWLS-80 – program for calculation and refinement of powder diffraction data, Bonn and Jülich, Germany, 1983.

[9] E. Dowty, ATOMS-2.3 – computer program for displaying atomic structures, Kingsport, TN 37663, USA, 1993.

[10] W. Prandtl and K. Huttner, *Z. Anorg. Allg. Chem., 149* (1925) 235.

[11] O. Greis, *J. Solid State Chem., 34* (1980) 39.

[12] H. Müller-Buschbaum and H.-G.v. Schnering, *Z. Anorg. Allg. Chem., 340* (1965) 232.

[13] H. Müller-Buschbaum, *Z. Anorg. Allg. Chem., 343* (1965) 6.

[14] P. Aldebert and J.P. Traverse, *Mater. Res. Bull., 14* (1979) 303.

[15] L. Pauling, *Z. Kristallogr., 69* (1929) 415.

[16] C.K. Jørgensen, R. Pappalardo and E. Ritterhaus, *Z. Naturforsch. Teil A, 19* (1964) 424; *20* (1965) 54.

[17] P.E. Caro, *J. Less-Common Met., 16* (1968) 367.

[18] W.C. Koehler and E.O. Wollan, *Acta Crystallogr., 6* (1953) 741.

[19] H. Bärnighausen and G. Schiller, *J. Less-Common Met., 110* (1985) 385.

[20] R. Wolf and R. Hoppe, *Z. Anorg. Allg. Chem., 529* (1985) 61.

[21] J.X. Boucherle and J. Schweizer, *Acta Crystallogr. Sect. B, 31* (1975) 2745.