JOURNAL OF SOLID STATE CHEMISTRY **34**, 39–44 (1980)

A Contribution to the Structural Chemistry of *A*-Type Rare Earth Sesquioxides

O. GREIS*

School of Physical Sciences, Flinders University, Adelaide, South Australia 5042

Received April 13, 1979; in revised form July 27, 1979

La_2O_3 and Nd_2O_3 have been annealed at temperatures between 1000 and 1600°C for decontamination. Only products annealed at least at these temperatures appeared to be monophasic. Both X-ray powder and electron single-crystal diffraction revealed the *A*-type sesquioxide structure. No difference could be found in samples either quenched or slowly cooled to room temperature. Two space groups, $P\bar{3}m1$ and $P6_3/mmc$, are reported for the *A*-type structure. X-Ray powder studies seemed to support the latter on the evidence of extinctions. Electron diffraction from single crystals, however, indicated the space group $P\bar{3}m1$, confirming the so-called Pauling structure, while $P6_3/mmc$ can now be excluded unequivocally.

1. Introduction

Polymorphism is a very striking feature in the structural chemistry of sesquioxides M_2O_3, and the rare earth sesquioxides RE_2O_3 with RE = Y, La, Ln show the most variations (*1, 2*). At present, at least five structure types are known. They are designated as *A* (hexagonal or trigonal), *B* (monoclinic), *C* (cubic), *H* (hexagonal), and *X* type (cubic). The structural details, such as accurate atom parameters and temperature factors, are unknown for most of the individual rare earths. Surprisingly, however, even the crystal symmetry of some of the structure types is open to question. For example, at least two different structure models exist in the case of *A*-type rare earth oxides (see Part 2).

The aim of this paper is to contribute to the clarification of *A*-type space group problems by means of electron diffraction of single crystals of La_2O_3 and Nd_2O_3. Obviously, this method has not yet been applied to *A*-RE_2O_3 in spite of the fact that electron diffraction is in many cases much more powerful than X-ray diffraction as far as diffraction geometry is concerned (*3–7*). At first, however, the *A*-type structure will be discussed briefly.

2. The *A*-Type Structure Problem

The first structure determinations of La_2O_3, Ce_2O_3, Pr_2O_3, and Nd_2O_3 were carried out by Zachariasen (*8, 9*) by means of X-ray diffraction (powder and Laue methods). These investigations led to the so-called "Anti-Schichten Gitter" model ($P321$, $Z = 1$), which, however, has been modified by Pauling (*10*) on the basis of packing and other physical considerations. The so-called Pauling structure ($P\bar{3}m1$, $Z = 1$) was supported later by neutron diffraction (*11–13*), X-ray powder diffraction (*14*), and infrared and Raman spectroscopy (*15*).

In contrast, two further X-ray single-crystal structure determinations on La_2O_3 (*16*)

---

* Present address: Institute of Minerology and Petrography, University Heidelberg, D-6900 Heidelberg, F.R.G.

0022-4596/80/100039-06$02.00/0

Printed in Great Britain

and Nd_2O_3 (*17*) revealed a different space group on the basis of systematic extinctions (hhl, $l = 2n + 1$ and hkl, $l = 2n + 1$ if $h - k = 3n$). This space group is $P6_3/mmc$, wrongly described as $P6_3/mmm$ in the original paper (*16*). A structure model has been postulated with an overall size occupancy of only 50%, since the minimum number of formula units in $P6_3/mmc$ is two, but the actual unit-cell volume allows only $Z = 1$ (space filling and density). Corresponding to this model the A-type structure is built up from two superposed Pauling-type structures in a 1:1 relationship statistically distributed. All the microdomains are connected over a common c-glide $(1\bar{1}0)$. The free site parameters are in good agreement with the Pauling structure (La, 0.234 and 0.235; O, 0.639 and 0.63). The arrangement of the La^{3+} near neighbors, however, is different in the so-called Müller-Buschbaum/Schnering structure as far as boundaries between the twinned microdomains are concerned.

Therefore, two models exist for the A-type sesquioxides: Pauling ($P\bar{3}m1$) and Müller-Buschbaum/Schnering ($P6_3/mmc$). Discrimination, however, should be easy on the evidence of systematic extinctions. Though much attention has been paid to this problem, the crucial question is still open: What is the space group of the A-type structures? A complication arises also from the fact that the calculated intensities from all reflections in question are weak in the Pauling model and may be unrevealed in X-ray diffraction. This is not the case in neutron diffraction (*11–13*). Electron diffraction from single crystals, however, is the most powerful method of detecting weak reflections, and should lead, therefore, to unambiguous discrimination.

3. Experimental

Commercial rare earth oxides, La_2O_3 (99.999%) and Nd_2O_3 (99.9%), were annealed in platinum boats in air until the weight remained constant. In this way, carbonate contaminations and moisture were removed (weight loss up to ~14%), but only if temperatures of at least 1000–1600°C were applied; otherwise, multiphase mixtures were detected. No difference could be observed in samples either quenched or slowly cooled to room temperature.

All samples were characterized immediately after heat treatment to prevent new contaminations. Otherwise, after 1 day multiple phases could be observed, especially with electron diffraction. Some of these phases showed quite complicated and interesting diffraction patterns (e.g., C-type: La_2O_3 or $La_2O_3 \cdot xH_2O$? (*2*)). Naturally, such a phase characterization does not reveal the chemical compositions of the contaminations. It is not clear from literature studies whether these contamination problems have been considered properly in all the recent structure determinations.

The X-ray powder diffractions have been carried out by means of a Hägg and a Jagodzinski camera ($CuK\alpha_1$ radiation, $\lambda = 1.54056$ Å) and Si powder (NBS-SRM 640, $a = 5.43088 \leqslant$) was used as an internal standard. The Guinier patterns were evaluated using the programs EGUIN (*18*) and LSUCRE (*19*). The electron diffraction from small single crystals were carried out with an electron microscope (AEI-EM 802, pressure $\sim 10^{-5}$ Torr, 100 kV, double tilt/rotation goniometer stage).

4. Results and Discussion

The X-ray powder characterization confirmed the hexagonal lattice parameters of earlier investigations (*2*) very well. It was found for A-La_2O_3: $a = 3.9374(3)$ Å, $c = 6.1324(6)$ Å, $V' = V/Z = 82.334(11)$ Å^3, $z = 1$, and $\rho_{calc} = 6.571$ g cm^{-3}. The results for A-Nd_2O_3 are: $a = 3.8303(1)$ Å, $c = 5.9997(3)$ Å, $V' = V/Z = 76.232(6)$ Å^3, $Z = 1$, and $\rho_{calc} = 7.329$ g cm^{-3}. The standard deviations are given in brackets.

Complete listings of all *d*-values are available on request. The reflections in question, 001, 003, 005, 111, 113, and 301, could not be observed even on very long exposed Guinier patterns. These extinctions can be regarded as systematical though their statistical weight is small. Thus the space group $P6_3/mmc$ would be supported.

In connection with the above calculated densities a comment by Müller-Buschbaum and Schnering (*16*) should be discussed. These authors call attention to a discrepancy between experimental and calculated densities of La_2O_3: $\rho_{exp} = 6.15$ g cm^{-3} and $\rho_{calc} = 5.93$ g cm^{-3}. A higher value of the experimental density is indeed surprising. Müller-Buschbaum and Schnering (*16*) pointed out that this discrepancy could constitute further evidence for their microtwinning model. This argument, however, is weak, especially since their calculated density is obviously wrong. Unfortunately, no lattice parameters are reported in their structural study. Not in any case, however, can a value like 5.93 g cm^{-3} be obtained from reported lattice parameters for *A*-La_2O_3 (*2*), but rather values in the order of 6.6 g cm^{-3} which are higher than the experimental value. This finding corresponds now to the well-known difficulties in measuring high densities, especially in respect to the above described contamination problems.

The electron diffraction from single crystals of La_2O_3 and Nd_2O_3 confirmed the hexagonal/trigonal crystal system and the lattice parameters for both, but not the extinctions observed in X-ray studies. In every case, a primitive lattice without any extinctions has been observed. Some of the reflections in question, however, were significantly weaker. An evaluation of intensities has not been carried out, since multiple diffraction, often falsely mentioned as double diffraction, represents a very serious problem almost without solution in electron diffraction techniques. However, it will be pointed out in the following section that multiple diffraction is clearly not the reason for the observed reflections in question.

At first, the zone [001] of *A*-La_2O_3 is shown in Fig. 1 together with a diagram showing indices, axes, unit cell, and traces of the vertical zones [100] and [1$\bar{1}$0], which are given in Figs. 2 and 3 for *A*-La_2O_3. The analogous zones of *A*-Nd_2O_3 were essentially identical. The reflections *hhl* with $l = 2n + 1$ should be extinct in [100] and [1$\bar{1}$0], if $P6_3/mmc$ is the correct space group. This is not the case. Multiple diffraction from

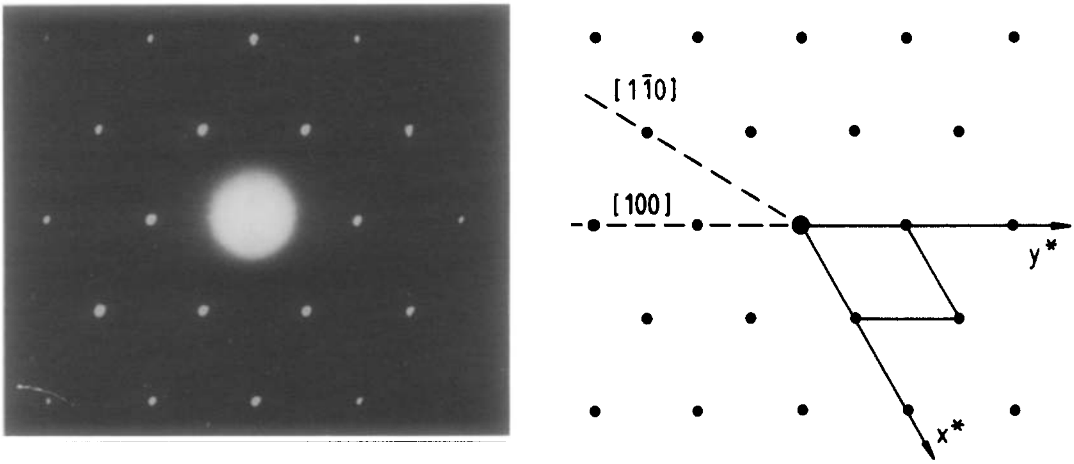

FIG. 1. [001] zone of *A*-La_2O_3.

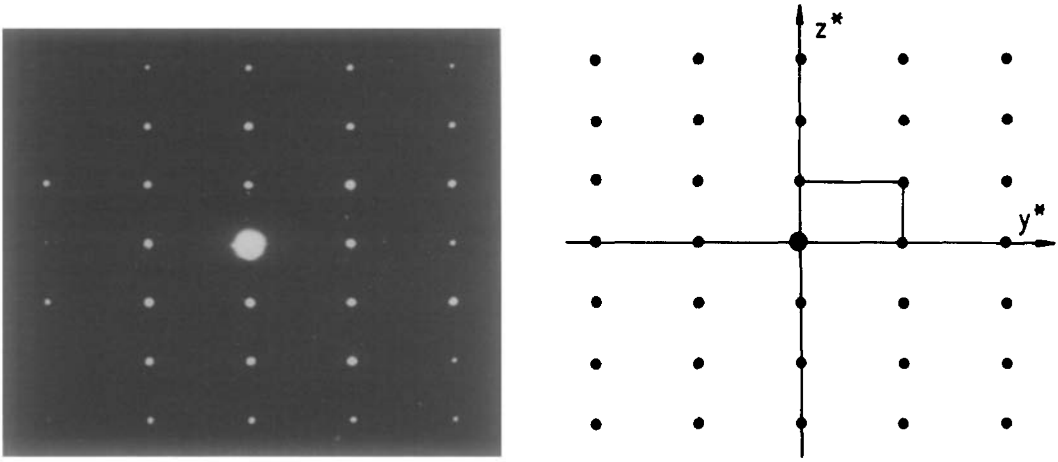

FIG. 2. [100] zone of A-La_2O_3.

reflections in the same zone can create the reflections in question only in [100] but not in [1$\bar{1}$0], since no vector combination is possible from hhl reflections with $l = 2n$. Multiple diffraction from reflections above and below the respective zone is not significant as shown in the example of β-alumina. These phases crystallize with space group $P6_3/mmc$, but have larger lattice parameters, e.g., sodium β-alumina, $a = 5.6000(2)$ Å, $c = 22.622(2)$ Å (7). This leads to a very densely populated reciprocal lattice favoring multiple diffraction strongly. Indeed, forbidden reflections with $l = 2n + 1$ can be observed along the c^*-axis in [100] (Fig. 4), but not in [1$\bar{1}$0] (Fig. 5). Hence the unambiguous conclusion can be drawn that multiple diffraction does not falsify the electron diffraction geometry of A-types and no c-glide, therefore, exists in this structure type.

Furthermore, it should be mentioned that the zone [4$\bar{1}$0] in the case of A-La_2O_3 could be taken, too, but not for A-Nd_2O_3 (Ewald sphere). This zone showed all reflections, but again reflections with $l = 2n + 1$ were significantly weaker. Reflections hkl with

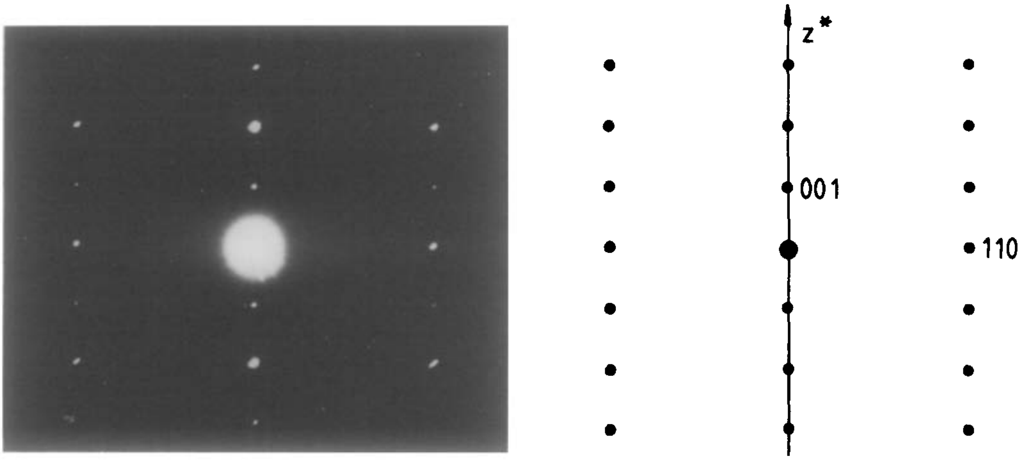

FIG. 3. [1$\bar{1}$0] zone of A-La_2O_3.

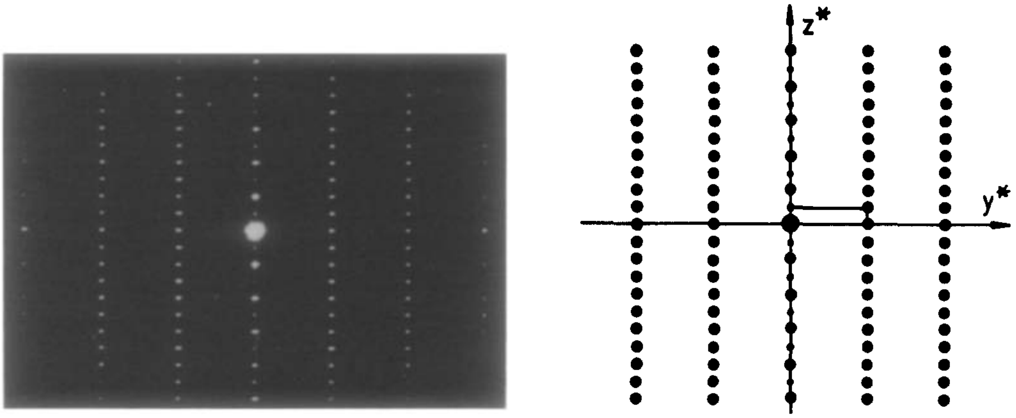

FIG. 4. [100] zone of β-alumina (*7*).

$h-k=3n$ and $l=2n+1$ could also be revealed in [100] zones of La_2O_3 and Nd_2O_3: 031, 033, and so on. In contrast, Müller-Buschbaum and Schnering (*16*) observed systematic extinctions for *hkl* with $h-k=3n$ and $l=2n+1$ and concluded from this and the diffraction symbol $P \cdot\cdot c$ that the space group is $P6_3/mmc$ for the *A*-type.

Many single crystals of *A*-La_2O_3 and *A*-Nd_2O_3 have been scanned step by step with a small selected area diffraction aperture. In no case could disappearance of the reflections in question be observed. Otherwise, such an observation could serve as an indication to the boundaries between microdomains, as postulated by Müller-Buschbaum and Schnering in their microtwinning model (*16*). But such evidence could not be revealed in the present study.

5. Conclusion

Electron diffraction from La_2O_3 and Nd_2O_3 single crystals show that the space group of the *A*-type is not $P6_3/mmc$, but $P\bar{3}m1$. This result is in agreement with a recent neutron diffraction study (*11*), which led to the result that the *A*-type structure with space group $P\bar{3}m1$ is stable for La_2O_3 and Nd_2O_3 between 20°C and at least 1910°C. At 2030 and 2060°C, respectively, however, the so-called *H* type is the stable

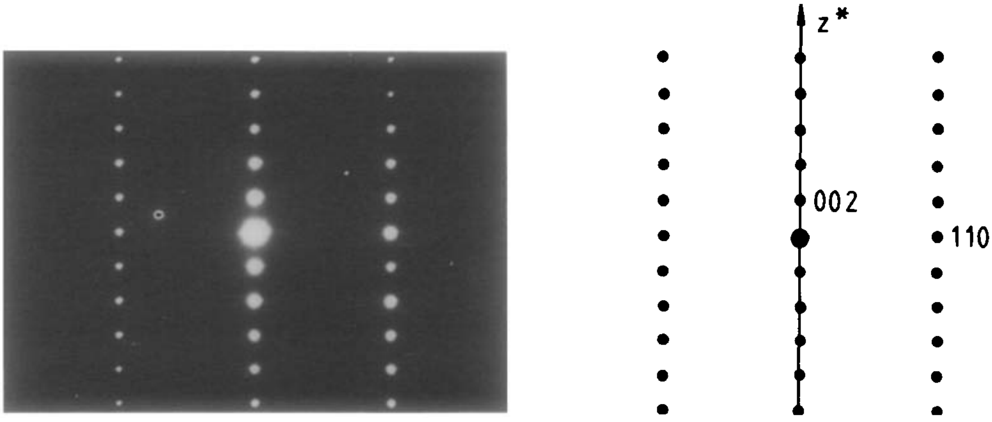

FIG. 5. [$1\bar{1}0$] zone of β-alumina (*7*).

form which is to be described with $P6_3/mmc$. Aldebert and Traverse (*11*) pointed out that the statistical description of this high-temperature phase (as well as the *X* type) can be assumed either by a static or a dynamic model. The latter, however, seems to be more likely, especially with respect to the analogy with β-aluminas (*11*). It is now also clear that the Müller-Buschbaum/Schnering structure does not describe the *A* type. It is possible, however, that these authors described the *H*-type structure. This would imply that their single crystals retained this high-temperature structure on quenching. The preparation obviously took place at temperatures at which the *H* type is the stable form.

Acknowledgments

The author is indebted to Professor D. J. M. Bevan for his support at the Flinders University of South Australia, and to Professor H.-G. v. Schnering, Professor J. P. Traverse, Dr. P. Aldebert, and Professor A. Clearfield for their interesting and helpful discussions. Grants from the Australian Research Grants Committee for the provision and maintenance of the electron microscope facilities are also acknowledged.

References

1. A. F. Wells, "Structural Inorganic Chemistry," pp. 450–453, Oxford Univ. Press (Clarendon), London (1975).
2. Gmelin, "Handbook of Inorganic Chemistry," 8th ed.: "Rare Earth Elements," System-No. 39, Part C, 1, pp. 104–106, 113–123, Springer-Verlag, Berlin/Heidelberg/New York (1974).
3. P. Kunzmann and L. Eyring, *J. Solid State Chem.* **14**, 229 (1975).
4. O. Greis and D. J. M. Bevan, *J. Solid State Chem.* **24**, 113 (1978).
5. O. Greis, *Rev. Chim. Miner.* **15**, 481 (1978).
6. O. Greis, "New Anion-Excess, Fluorite-Related Superstructure Phases in LnF_2–LnF_3, CaF_2YF_3, and Related Systems," 14th Rare Earth Research Conference, Fargo, N. Dak. (1979).
7. O. Greis, D. J. M. Bevan, and Y. Tretyakov, submitted for publication.
8. W. Zachariasen, *Z. Phys. Chem.* **123**, 154 (1926).
9. W. Zachariasen, *Z. Kristallogr.* **70**, 187 (1929).
10. L. Pauling, *Z. Kristallogr.* **69**, 415 (1929).
11. P. Aldebert and J. P. Traverse, *Mater. Res. Bull.* **14**, 303 (1979).
12. W. C. Koehler and E. O. Wollan, *Acta Crystallogr.* **6**, 741 (1953).
13. J. X. Boucherle and J. Schweizer, *Acta Crystallogr. Sect. B* **31**, 2745 (1975).
14. R. M. Douglas, *Anal. Chem.* **28**, 551 (1956).
15. J. H. Denning and S. D. Ross, *J. Phys. C* **5**, 1123 (1972).
16. H. Müller-Buschbaum and H.-G. v. Schnering, *Z. Anorg. Allg. Chem.* **340**, 232 (1965).
17. H. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **343**, 6 (1966).
18. O. Greis and H. Andress, "EGUIN, Program for Length Correction of X-Ray Guinier Patterns," Freiburg i. Br. (1972).
19. "LSUCRE, Program for Least Square Unit Cell Refinements," Freiburg i. Br. (1970).