

# The Identity of Monoclinic $\text{La}_2\text{O}_3$ and Monoclinic $\text{Pr}_2\text{O}_3$ with $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ and $\text{Pr}_{9.33}(\text{SiO}_4)_6\text{O}_2$ , Respectively

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A critical comparison of X-ray powder diffraction data, combined with experimental work, shows that “monoclinic B-type”  $\text{La}_2\text{O}_3$  and  $\text{Pr}_2\text{O}_3$  described in the literature are in fact rare earth silicates of the hexagonal apatite-type structure. A comparison of X-ray powder data reveals that both compounds are identical with  $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$  and  $\text{Pr}_{9.33}(\text{SiO}_4)_6\text{O}_2$ , respectively. This confirms the currently acknowledged stability diagram of the rare earth sesquioxides. © 1995 Academic Press, Inc.

## INTRODUCTION

Compounds involving rare earth elements have widespread and ever-increasing applications in science and industry. In our laboratory we are especially interested in compounds and phase equilibria in the systems  $\text{RE}_2\text{O}_3$ – $\text{Al}_2\text{O}_3$ – $\text{SiO}_2$  (RE = rare earth element). These quasiternary systems are important for the liquid phase sintering of several high-performance nonoxide ceramics ( $\text{Si}_3\text{N}_4$ , SiAlON, SiC, and AlN). In this paper we present some results of our investigations of stability ranges of rare earth oxides.

Rare earth sesquioxides  $\text{RE}_2\text{O}_3$  (RE = La to Lu, and Y) exhibit pronounced temperature-dependent polymorphism due to the well-known lanthanide contraction (1–3). The polymorphs A (hexagonal, space group  $P\bar{3}m1^2$ ), B (monoclinic,  $C2/m$ ), and C (cubic,  $Ia\bar{3}$ ) are known. In addition, there are two well-established high-temperature polymorphs, H (hexagonal,  $P6_3/mmc$ ) and X (cubic,  $Im\bar{3}m^3$ ) (3, 4). At ambient temperature, the A-type is stable for the large ions from  $\text{La}^{3+}$  to  $\text{Nd}^{3+}$ , with  $\text{Nd}_2\text{O}_3$  possibly also crystallizing in the B- and/or C-type. The B-type is stable for medium sized  $\text{Sm}^{3+}$  to  $\text{Gd}^{3+}$ , with  $\text{Gd}_2\text{O}_3$  possibly also crystallizing in the C-type. Finally,  $\text{Tb}_2\text{O}_3$  to  $\text{Lu}_2\text{O}_3$ , and  $\text{Y}_2\text{O}_3$  only form the C-type.

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<sup>2</sup> Ref. (3) erroneously gives  $C\bar{3}$  in the text, and  $C\bar{3}m$  in the figure legend.

<sup>3</sup> Ref. (3) erroneously gives  $Im\bar{3}m$ .

Three reports on “monoclinic B-type  $\text{La}_2\text{O}_3$ ” (hereafter “MLO”) and “monoclinic B-type  $\text{Pr}_2\text{O}_3$ ” (hereafter “MPO”) have been published by Daire and Willer (5–7). MLO was found during a study of the phase diagram  $\text{La}_2\text{O}_3$ –NiO (5, 7). As starting oxides  $\text{La}_2\text{O}_3$  of 99.99% purity and NiO of RP (7) quality were used. The samples were prepared by three different procedures: (I) firing of an oxide mixture; (II) dissolution of the starting oxides in acids and subsequent decomposition of the resulting salts; and (III) dissolution of the starting oxides in hydrochloric or nitric acid, coprecipitation by neutralization with a sodium carbonate solution, rinsing, filtering, drying, grinding in an agate mortar, and placing in a platinum container. All mixtures obtained by procedures I–III were then fired at 1200°C for 24 hr. Equimolar mixtures of  $\text{La}_2\text{O}_3$  and NiO used in procedures I and II yielded  $\text{La}_2\text{NiO}_4$  and, occasionally, additional small quantities of  $\text{LaNiO}_3$ . Procedure III, however, yielded very different X-ray diagrams: First, formation of  $\text{La}_2\text{NiO}_4$  occurred in a nonsystematic fashion, and second, new X-ray reflections which could not be attributed to known compounds of the  $\text{La}_2\text{O}_3$ –NiO system appeared. The amount of the new compound was highly variable, ranging between 0 and about 70 vol%. Since excess NiO was always observed in these reacted mixtures, the authors presumed the existence of a new allotropic modification of  $\text{La}_2\text{O}_3$  with monoclinic symmetry (MLO) in analogy to the other known monoclinic B-type rare earth oxides. An attempt to prepare pure MLO through procedure III resulted in X-ray reflections of hexagonal  $\text{La}_2\text{O}_3$  and additional weak reflections of MLO. Method III was also applied to the preparation of pure praseodymium oxide, resulting in similar unidentified X-ray reflections and leading the authors to the assumption of the existence of an analogous monoclinic modification of  $\text{Pr}_2\text{O}_3$  (MPO). The authors assumed that the presence of NiO may stabilize MLO and MPO but did not analyze the chemistry of their new compounds.

X-ray powder data and lattice parameters for MLO and MPO were published in another report (6). Lattice param-

eters were determined using a variant of Ito's method of computer-calculated trial-and-error indexing. The authors proposed two possible unit cells with two possible indexings for each oxide (see Tables 1 and 2). Space groups were not proposed. During a comprehensive literature survey and some experimental investigations on rare earth oxides and silicates (8, 9), we found that X-ray powder data for MLO (6) (see also PDF card 22-641 (10)) and MPO (6) (PDF card 22-880) are obviously identical with those for the hexagonal rare earth silicate apatites La<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> and Pr<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> (11, 12), respectively. The aim of this paper is to evidence this identity.

### EXPERIMENTAL

La<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> was synthesized from La<sub>2</sub>O<sub>3</sub> powder (Johnson Matthey, Karlsruhe, Germany; purity 99.9%) and amorphous SiO<sub>2</sub> powder (Aerosil 200, Degussa, Hanau, Germany, purity >99.8%) by solid state reaction. A stoichiometric powder mixture was thoroughly homogenized in isopropanol in an ultrasonic mixer, dried, and reground under isopropanol in an agate mortar. The mixture was then cold-pressed and sintered in air at 1600°C for 15 hr. A detailed description of the synthesis procedure is given elsewhere (8, 9). X-ray powder data of La<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> have been measured with an X-ray powder diffractometer (Siemens D5000, position sensitive detector) using Ni-filtered CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at 40 kV acceleration voltage and 30 mA tube current. A step width of 0.02°  $2\theta$  and a counting time of 20 sec were used. Quartz (purity 99.995%) was employed as internal standard. Lattice parameters were refined using a least-squares procedure. Indexed X-ray powder data are presented in Table 1 and compared with the data for MLO (6). Table 2 shows a comparison of X-ray powder data of MPO (6) with those of Pr<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> (13).<sup>4</sup>

We also refined the lattice parameters of MLO and MPO in the space group of RE<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>. The results are presented in Table 3 and compared with lattice parameters of some rare earth silicate apatites (6, 8, 9, 11-13, 17, 21, 22).

### RESULTS AND DISCUSSION

#### (1) X-Ray Crystallography

The comparison in Tables 1 and 2 shows that MLO and MPO are most probably identical with La<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> and Pr<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>, respectively. Deviations between respec-

TABLE 1  
Comparison of X-Ray Powder Data for Monoclinic La<sub>2</sub>O<sub>3</sub> (MLO) and La<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>

MLO Ref. (6), PDF card 22-641				La <sub>9.33</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub> Refs. (8, 9, this work)		
$d_{\text{obs}}$ (Å)	$I_{\text{obs}}$	$hkl^a$	$hkl^b$	$d_{\text{obs}}$ (Å)	$I_{\text{obs}}$	$hkl^c$
—	—	—	—	4.851	7	110
4.20	17	20-2	102	4.204	25	200
4.02	20	301	301	4.022	21	111
3.593	23	202, 400	400	3.592	16	002
3.303	45	210, 111	210	3.304	37	102
3.174	43	401	302	3.179	34	210
2.905	100	50-1	40-2	2.907	100	211
2.887	50	31-1	012	2.889	56	112
2.799	44	012	112	2.804	26	300
—	—	—	—	2.731	3	202
—	—	—	—	2.427	2	220
—	—	—	—	2.380	2	212
2.331	13	30-3	11-3	2.333	7	310
2.298	4	21-3	113	2.301	4	221
—	—	—	—	2.220	3	311
2.208	6	20-4	104	2.210	7	302
2.144	18	104	50-3	2.148	10	113
—	—	—	—	2.103	6	400
—	—	—	—	2.081	2	203
2.008	43	511	503	2.012	25	222
1.950	20	70-2	611	1.9570	13	312
1.937	10	61-2	60-3	—	—	—
1.922	50	—	413	1.9299	4	320
1.910	27	611	70-2	1.9131	31	213
1.857	33	020	404	1.8638	12	321
1.829	37	005	31-4	1.8354	20	410
1.807	19	61-3	10-5	1.8152	23	402
1.795	2	404	800	1.7968	10	004
—	—	—	—	1.7777	2	411
—	—	—	—	1.7052	2	223
—	—	—	—	1.6528	3	204
—	—	—	—	1.5893	4	420
—	—	—	—	1.5790	6	331
—	—	—	—	1.5639	9	214
—	—	—	—	1.5516	2	421
—	—	—	—	1.5235	9	502
—	—	—	—	1.5126	5	304
—	—	—	—	1.5026	4	323
—	—	—	—	1.4787	4	511
—	—	—	—	1.4762	6	332
—	—	—	—	1.4535	2	422
—	—	—	—	1.4240	2	314
—	—	—	—	1.3930	2	512
—	—	—	—	1.3774	1	115
—	—	—	—	1.3656	2	404
—	—	—	—	1.3578	2	431
—	—	—	—	1.3241	3	423, 521
—	—	—	—	1.3149	2	324
—	—	—	—	1.3095	5	215
—	—	—	—	1.3059	3	602
—	—	—	—	1.2838	9	414
—	—	—	—	1.2782	3	513
—	—	—	—	1.2615	7	522

<sup>4</sup> Note. The originally given formula, Pr<sub>8</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> (mole ratio Pr<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub> = 6:9) (13), is better written as Pr<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> (mole ratio = 7:9), since the latter formula has been determined using single crystal structure analysis of several rare earth silicate apatites. This has been discussed in review papers (8, 9, 11, 12).

<sup>a</sup> Space group not given; indexing for  $a = 14.60(1) \text{ \AA}$ ,  $b = 3.717(3) \text{ \AA}$ ,  $c = 9.278(8) \text{ \AA}$ ,  $\beta = 99.85(5)^\circ$ ,  $V = 496 \text{ \AA}^3$ .

<sup>b</sup> Space group not given; indexing for  $a = 14.39(1) \text{ \AA}$ ,  $b = 3.750(3) \text{ \AA}$ ,  $c = 9.036(8) \text{ \AA}$ ,  $\beta = 94.29(5)^\circ$ ,  $V = 486.5 \text{ \AA}^3$ .

<sup>c</sup> Indexing for space group  $P6_3/m$ ,  $a = 9.7128(5) \text{ \AA}$ ,  $c = 7.1858(5) \text{ \AA}$ ,  $V = 587.07(6) \text{ \AA}^3$ .

TABLE 2  
Comparison of X-Ray Powder Data for Monoclinic Pr<sub>2</sub>O<sub>3</sub>  
(MPO) and Pr<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub><sup>a</sup>

MPO Ref. (6), PDF card 22-880				Pr <sub>9.33</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub> <sup>a</sup> Ref. (13), PDF card 23-1389		
<i>d</i> <sub>obs</sub> (Å)	<i>I</i> <sub>obs</sub>	<i>hkl</i> <sup>a</sup>	<i>hkl</i> <sup>c</sup>	<i>d</i> <sub>obs</sub> (Å)	<i>I</i> <sub>obs</sub>	<i>hkl</i> <sup>d</sup>
—	—	—	—	4.80	4	110
4.17	20	20-2	102	4.16	35	200
3.981	16	102	—	3.97	25	111
3.900	2	301	20-2	—	—	—
3.553	16	400	400	3.53	16	002
3.260	45	111	210	3.26	40	102
3.146	35	401	302	3.15	40	210
2.875	100	50-1, 31-1, 11-2	40-2	2.873	100	211
2.851	70	012	012	2.847	45	112
2.772	95	21-2	112	2.774	35	300
2.739	35	112	311	—	—	—
—	—	—	—	2.692	4	202
2.354	5	11-3	600	—	—	—
2.303	9	21-3	11-3	2.309	8	310
—	—	—	—	2.277	6	103, 221
—	—	—	—	2.116	12	113
2.074	7	40-4	30-4	2.079	6	400
1.985	30	313	503	1.986	25	222
—	—	—	—	1.932	14	312
—	—	—	—	1.909	6	320
1.887	45	31-4	413, 70-2	1.885	30	213
1.838	25	120	404	1.842	16	321
1.811	25	41-4	31-4	1.815	20	410
1.790	40	005	10-5	1.792	25	402
1.771	20	800	800	1.767	12	004

<sup>a</sup> The originally given formula, Pr<sub>8</sub>(SiO<sub>4</sub>)<sub>6</sub> (13), should be written as Pr<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> according to single crystal structure analysis (see Experimental).

<sup>b</sup> Space group not given; indexing for  $a = 14.45(1)$  Å,  $b = 3.720(3)$  Å,  $c = 9.080(8)$  Å,  $\beta = 100.60(5)^\circ$ ,  $V = 479.7$  Å<sup>3</sup>.

<sup>c</sup> Space group not given, indexing for  $a = 14.20(1)$  Å,  $b = 3.698(3)$  Å,  $c = 8.967(8)$  Å,  $\beta = 94.05(5)^\circ$ ,  $V = 470.0$  Å<sup>3</sup>.

<sup>d</sup> Indexing for space group  $P6_3/m$ ,  $a = 9.613$  Å,  $c = 7.068$  Å,  $V = 565.6$  Å<sup>3</sup>.

tive *d*-spacings are very small. In general, there is also a very good match of the reflection intensities (exceptions are discussed below). Seven low-intensity reflections (*I*<sub>obs</sub> ranging from 2 to 7) of La<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> are not present in the powder data of MLO. Similarly, some low-intensity reflections of Pr<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> are not present in the powder data of MPO.

Two reflections of MLO (*d*-spacings 1.937 and 1.922 Å in Table 1) and four reflections of MPO (*d*-spacings 3.900, 2.772, 2.739, and 2.354 Å in Table 2) cannot be attributed to the silicate compounds because they are not indexable according to the space group  $P6_3/m$  established for

La<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> and Pr<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>, and/or because they have rather different intensities. These reflections are probably due to impurity phases. In case of MLO, they may be attributed to reflections of the other reaction products that Willer and Daire (5, 7) found, i.e., La<sub>2</sub>NiO<sub>4</sub> and/or LaNiO<sub>3</sub>. The four impurity reflections in MPO could not be attributed to other possible reaction products.

None of the detected impurity reflections can be attributed to the other known lanthanum and praseodymium silicates, viz., La<sub>2</sub>SiO<sub>5</sub>, Pr<sub>2</sub>SiO<sub>5</sub>, and the high- and low-temperature polymorphs of La<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> and Pr<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (G- and A-type, respectively) (8, 9, 12, 14–16), nor can they be attributed to any known nickel oxides or nickel silicates (10). There are no X-ray powder data for possibly existing lanthanum and praseodymium nickel silicates.

Waller and Daire (6) admit that for some reflections of MLO and MPO (*d*-spacings 4.02, 2.208, 1.922, and 1.910 Å in Table 1, and *d*-spacings 3.981 and 1.887 Å in Table 2), there is a large discrepancy between observed and calculated *d*-spacings for either one or both of the two proposed indexing models.

If MLO and MPO were indeed monoclinic B-type rare earth oxides, their X-ray powder data should correspond rather closely to the data for the other B-type rare earth oxides. However, there is only a very minor resemblance regarding both *d*-spacings and intensities. Additionally, numerous *hkl* given (19 *hkl* in Table 1 and 15 *hkl* in Table 2) are not consistent with space group  $C2/m$  established for the monoclinic B-type rare earth oxides. X-ray powder data for another monoclinic Pr<sub>2</sub>O<sub>3</sub> were measured in 1970 by Kern and Perakis (17) (see also PDF card 24-912, current status: deleted). This monoclinic Pr<sub>2</sub>O<sub>3</sub> was prepared by firing black PrO<sub>1.83</sub> (equals Pr<sub>6</sub>O<sub>11</sub>) at 1400 K in vacuum-sealed quartz tubes, and subsequent quenching. The obtained light green compound was stable in air and at room temperature. Firing at 1700 K for 140 hr did not change its properties. The expected B ↔ A transformation of Pr<sub>2</sub>O<sub>3</sub> could not be observed. No chemical analysis was performed on this monoclinic Pr<sub>2</sub>O<sub>3</sub>.

The powder data of Kern and Perakis' monoclinic Pr<sub>2</sub>O<sub>3</sub> are very similar to those for MPO, although more reflections (including impurity reflections) are present. This leads again to the assumption that one is dealing with a praseodymium silicate apatite compound. The indexing of this monoclinic Pr<sub>2</sub>O<sub>3</sub> is based on exactly the same unit cell as the one used for MPO (Table 2, third column). Again, there are seven *hkl* (including three corresponding to very strong reflection intensities 100, 70, and 40) which are not consistent with the extinction conditions required by space group  $C2/m$ . Six impurity reflections detected were found to correspond closely to the strongest reflections given for the low-temperature (A-type) polymorph of Pr<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> (14). We found that the lattice parameters of this monoclinic Pr<sub>2</sub>O<sub>3</sub> can be easily refined in the space

TABLE 3  
Comparison of Lattice Parameters

	Ref.	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )
Lanthanum silicate apatites La <sub>9.33</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub> and related compounds				
MLO <sup>a</sup>	(6)	9.682(4)	7.179(4)	582.8(5)
La <sub>9.33</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub>	(8, 9, this work)	9.7128(5)	7.1858(5)	587.07(6)
La <sub>9.33</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub>	(11, 12)	9.713(2)	7.194(1)	587.8
La <sub>9.33</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub>	(21)	9.704	7.178	585.4
La <sub>9.33</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub>	(22)	9.71	7.18	586.3
LiLa <sub>9</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub>	PDF card 32-567	9.692(2)	7.182(2)	584.3
NaLa <sub>9</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub>	(11)	9.687(2)	7.180(1)	583.5
NaLa <sub>9</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub>	PDF card 32-1109	9.692(2)	7.182(2)	584.3
Ca <sub>2</sub> La <sub>8</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub>	PDF card 29-337	9.651(3)	7.151(2)	576.8
Ca <sub>3</sub> La <sub>6</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub>	PDF card 27-78	9.659	7.149	577.6
Praseodymium silicate apatites Pr <sub>9.33</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub> and related compounds				
MPO <sup>a</sup>	(6)	9.583(2)	7.086(3)	563.6(3)
Monoclinic Pr <sub>2</sub> O <sub>3</sub> <sup>a</sup>	(17) (deleted PDF card 24-912)	9.582(3)	7.042(3)	559.9(4)
Pr <sub>9.33</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub>	(11, 12)	9.607(2)	7.073(1)	565.3
Pr <sub>9.33</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub> <sup>b</sup>	(13) (PDF card 23-1389)	9.613	7.068	565.6
NaPr <sub>9</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub>	(11)	9.580(2)	7.080(1)	562.6
Ca <sub>2</sub> Pr <sub>8</sub> (SiO <sub>4</sub> ) <sub>6</sub> O <sub>2</sub>	PDF card 29-362	9.565(2)	7.060(2)	559.4

<sup>a</sup> Lattice parameters refined in this work.

<sup>b</sup> The originally given formula, Pr<sub>8</sub>(SiO<sub>4</sub>)<sub>6</sub> (13), should be written as Pr<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> according to single crystal structure analysis (see Experimental).

group *P6<sub>3</sub>/m* of the rare earth silicate apatites. We present the lattice parameters which were calculated from the data of Kern and Perakis (17) in Table 3. Obviously, the lattice parameters agree quite well with those of the other praseodymium silicate apatites.

The use of silica containers, as described by Kern and Perakis (17), leads to the formation of silicate apatites, as was shown by McCarthy *et al.* (18): Firing of Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, or Eu<sub>2</sub>O<sub>3</sub> in fused silica boats to 1500°C for several hours always resulted in the formation of rare earth silicate apatites. The color of Pr<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> is light green (13) which is identical with the color of the Kern and Perakis' monoclinic Pr<sub>2</sub>O<sub>3</sub>.

According to recent reviews dealing with the polymorphism of rare earth oxides, La<sub>2</sub>O<sub>3</sub> and Pr<sub>2</sub>O<sub>3</sub> do not form the monoclinic B-type structure (1-3). These reviews neither cite the work of Willer and Daire or Kern and Perakis, nor discuss MLO or MPO. Monoclinic La<sub>2</sub>O<sub>3</sub> or Pr<sub>2</sub>O<sub>3</sub> has never been observed when using preparation methods that favor the formation of metastable rare earth oxide polymorphs, e.g., (19, 20).

## (2) Chemistry

If MLO and MPO are identical with La<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> and Pr<sub>9.33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>, respectively, as Tables 1, 2, and 3 strongly suggest, then the following question arises: What is the source for SiO<sub>2</sub> (or any other Si-containing substance) in the compounds prepared by Daire and Willer? There may

be two possible sources: (i) SiO<sub>2</sub> may have been present as an impurity in the chemicals used for procedure III of Daire and Willer (5, 7); or (ii) SiO<sub>2</sub> may have entered the mixtures by some treatment before or during firing.

As noted above, Willer and Daire did not analyze the chemistry of their samples. They state that the new compounds, when prepared via procedure III (with mixtures containing NiO), were accompanied by an unspecified amount of NiO. Willer and Daire assume that some NiO may have been incorporated in the MLO samples obtained from their NiO-containing mixtures, resulting in a solid solution with MLO (6). However, they found no difference in unit cell parameters between MLO prepared from La<sub>2</sub>O<sub>3</sub>-NiO mixtures or from pure La<sub>2</sub>O<sub>3</sub>. During the present work, a close to very close match of X-ray powder data for MLO and MPO was also noted for the following alkaline and earth alkaline rare earth silicate apatites: LiLa<sub>9</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>, LiLaSiO<sub>4</sub> (note doubtful formula), NaLa<sub>9</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>, NaLa<sub>4</sub>Si<sub>3</sub>O<sub>12</sub>(OH), Ca<sub>2</sub>La<sub>8</sub>(SiO<sub>4</sub>)<sub>6</sub>, and Ca<sub>3</sub>La<sub>6</sub>(SiO<sub>4</sub>)<sub>6</sub>, all for MLO, and NaPr<sub>9</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> and Ca<sub>2</sub>Pr<sub>8</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> for MPO, respectively.<sup>5</sup> The lattice parameters of these compounds are given in Table 3 for comparison purposes.

If the identity of MLO and MPO with one of these apatites is assumed, an additional metal cation (besides

<sup>5</sup> No match was observed for strontium or barium rare earth silicate apatites, or for any rare earth phosphate apatites.

SiO<sub>2</sub>) would have been present in the samples of Willer and Daire. However, it is known that alkaline rare earth silicate apatites lose all their alkali ions by vaporization at temperatures >1150°C (11). Since Willer and Daire fired their samples at 1200°C for 24 hr, any alkali ions would have been partly or completely vaporized.

Table 3 shows that the unit cell values for *a*, *c*, and *V* calculated for MLO and MPO are somewhat lower than those of La<sub>9,33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> and Pr<sub>9,33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>, respectively. As for MLO, a slightly better agreement is found with the values of LiLa<sub>9</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> and NaLa<sub>9</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>.

It was also noted that X-ray powder data for La<sub>9,33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> and the nitrogen-containing lanthanum silicate apatite La<sub>10</sub>(SiO<sub>4</sub>)<sub>6</sub>N<sub>2</sub> (PDF card 36-571) are quite similar. Thus, there would also be the (theoretical) possibility that MLO is identical with La<sub>10</sub>(SiO<sub>4</sub>)<sub>6</sub>N<sub>2</sub>. However, the sintering atmospheres used by Willer and Daire (air, oxygen, or argon) precludes this possibility.

### CONCLUSION

Monoclinic La<sub>2</sub>O<sub>3</sub> and monoclinic Pr<sub>2</sub>O<sub>3</sub> (5–7, 17) do not exist. By comparison of X-ray powder data, they are identified as La<sub>9,33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub> and Pr<sub>9,33</sub>(SiO<sub>4</sub>)<sub>6</sub>O<sub>2</sub>, respectively, or as chemically closely related alkaline or earth alkaline lanthanum and praseodymium silicate apatite compounds. Thus, the currently acknowledged stability diagram of the rare earth sesquioxides is confirmed.

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