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The crystal structure and lattice parameters of some rare earth mono-seleno oxides.

By HARRY A. EICK, *Kedzie Chemical Laboratory, Michigan State University, East Lansing, Michigan, U.S.A.*

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The following study was undertaken when no information could be found either on the preparation or crystal structure of samarium mono-seleno oxide.

Rare earth sesquioxides of 99·9 % or greater purity were reacted with H_2Se gas diluted with hydrogen and helium at temperatures varying between 900 and 1130 °C. Attempts to grow single crystals by extended heating (2–4 weeks) failed when only a slight increase in particle size was noted and partial decomposition of the sample resulted. Monophasic samples of Pr_2O_2Se were analyzed for selenium by direct analysis (obs.: 19·0 %, calc.: 19·7 %) and by oxidation of the selenide to the hexagonal sesquioxide in a 10^{-3} mm. oxygen pressure (obs.: 20 % Se). X-ray intensity data were obtained on a sample of La_2O_2Se with a Norelco diffractometer equipped with a proportional counter. Copper radiation ($\lambda\alpha_u = 1{\cdot}5418$; $\lambda\alpha_1 = 1{\cdot}54050$) was used exclusively. Structure-factor calculations were carried out on digital computers using $I \propto jLPF^2$.

Table 1. *Interplanar spacings and intensity values of* La_2O_2Se

	d Value		Intensity	
hkl	Observed (Å)	Calculated (Å)	Observed (Å)	Calculated (Å)
001	—	7·13	—	6
002	3·58	3·56	166	138
100	3·56	3·52	115	89
101	3·13	3·16	1550	1616
102	2·50	2·50	646	633
003	2·37	2·38	139	158
110	2·03	2·04	560	588
103	1·97	1·97	308	260
111	—	1·96	—	1
004	—	1·78	—	32
112	1·77	1·77	140	129
200	—	1·76	—	14
201	1·71	1·71	250	254
104	1·59	1·59	120	137
202	1·58	1·58	154	150
113	1·55	1·54	231	239
005	—	1·42	—	10
203	1·417	1·415	85	81
114	1·342	1·340	76	71
210	—	1·332	—	10
105	1·323	1·321	93	79
211	1·310	1·309	200	197
204	1·255	1·253	32	59
212	1·251	1·248	137	130
006	—	1·187	—	0
300	1·177	1·175	83	78
115	1·170	1·167	46	31
213	1·164	1·162	100	77
301	—	1·159	—	0
106	1·128	1·125	82	73
302	1·118	1·116	21	27
205	1·110	1·108	46	45
214	1·069	1·067	76	76
303	1·055	1·053	74	70
116	—	1·026	—	2
220	1·020	1·017	91	60
007	—	1·018	—	16

The rare earth mono-seleno oxides are isostructural with the corresponding mono-thio oxides (Zachariasen, 1949). The space group is D_{3d}^3–$P\bar{3}m$, and the unit cell which contains one molecule has a selenium atom at (0, 0, 0), two metal atoms at $\pm(\frac{1}{3}, \frac{2}{3}, z_1)$, where $z_1 = 0{\cdot}29$, and two oxygen atoms at $\pm(\frac{1}{3}, \frac{2}{3}, z_2)$, where $z_2 \approx 0{\cdot}62$. The value of z_1 is probably accurate to within $\pm 0{\cdot}01$. In Table 1 the observed and calculated *d* values and relative intensities of La_2O_2Se are tabulated. Some interatomic distances are La–O, 2·42 Å; O–O, 2·90 Å; and La–Se, 3·08 Å.

Table 2. *Lattice parameters and calculated densities of some rare earth mono-seleno oxides*

	a (Å)	*c* (Å)	ϱ (g.cm.$^{-3}$)
La_2O_2Se	$4{\cdot}07_0$	$7{\cdot}12_4$	6·32
Pr_2O_2Se	$4{\cdot}00_9$	$7{\cdot}03_1$	6·72
Nd_2O_2Se	$3{\cdot}97_5$	$6{\cdot}98_5$	6·95
Sm_2O_2Se	$3{\cdot}91_6$	$6{\cdot}91_2$	7·46
Gd_2O_2Se	$3{\cdot}87_3$	$6{\cdot}85_4$	7·94
Ho_2O_2Se	$3{\cdot}80_7$	$6{\cdot}76_6$	8·65
Er_2O_2Se	$3{\cdot}79_2$	$6{\cdot}74_3$	8·81
Yb_2O_2Se	$3{\cdot}76_1$	$6{\cdot}69_7$	9·25

Estimated error: (*a*: ±0·02), (*c*: ±0·02).

Table 2 lists the lattice parameters of eight members of the rare earth series. A plot of the *a* and *c* parameters versus the ionic radii of the plus 3 ion as determined from the sesquioxides and trichlorides (Templeton & Dauben, 1954) yields a fairly smooth curve, indicative of an 'ionic' type of bonding. Good high angle X-ray photographs were obtained for the lanthanum, praseodymium, and neodymium compounds. The others produced diffuse lines in the region of $\theta > 30°$. Lattice parameters were obtained from the lines considered most accurate. Checks on various films indicated the overall agreement was within ±0·02 Å and this value is listed as the error.

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