

for assessing the degree of perfection of crystals. For instance, if $r_C(\varphi)$ is the experimental value for a crystal, one may define the degree of perfection as

$$\{r_C(\varphi) - r_M(\varphi)\} / \{r_P(\varphi) - r_M(\varphi)\}.$$

This ratio is found to be approximately constant for different values of φ for NaNO_3 crystals grown from solution and has a mean value of about 0.5. An important advantage of this method of finding the degree of perfection of crystals is that the difficulty of determining absolute integrated reflexions is not present, as it requires only relative measurements for different azimuths.

It must be mentioned that the theoretical curve for $r_P(\varphi)$ relates to a perfect *non-absorbing* crystal. Preliminary theoretical studies show that, when there is a

finite absorption, the curve for $r_P(\varphi)$ departs from this, approaching that for $r_M(\varphi)$ for increasing absorptions and coinciding with the latter for large absorption coefficients. This is in agreement with the theoretical result obtained by Hirsch & Ramachandran (1950) that perfect and mosaic crystals give the same integrated reflexions when absorption is large. When the effect of finite absorption is taken into account, it is seen that the degree of perfection of the grown crystal of NaNO_3 should be higher than the value 0.5 given above. Further investigations are in progress.

Reference

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Concerning the so-called $\text{Y}(\text{OH})_3$ -type structure, and the structure of $\text{La}(\text{OH})_3$. By RUSTUM ROY and H. A. MCKINSTRY,* *School of Mineral Industries, The Pennsylvania State College, State College, Pennsylvania, U.S.A.*

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Schubert & Seitz (1946) and later Schubert & Seitz (1947) and Fricke & Seitz (1947) described the structures of the trihydrates of the rare earths, including lanthanum, neodymium, samarium, erbium and yttrium. In comprehensive papers Zachariasen (1948*a, b*) also described the structures of some of the same rare-earth hydrates, classifying them into the UCl_3 type, which structure he determined in detail. In *Structure Reports for 1947-1948* (1951) one type of structure has been classified under the name $\text{Y}(\text{OH})_3$ structure, and some 20 isotypic structures are listed, including the hydroxides and chlorides of the 4*f* and 5*f* elements. Although *Structure Reports* lists the values of Zachariasen and those of Fricke, Seitz *et al.* as though they were compatible, a glance will suffice to show that there are irreconcilable differences between the two. Thus for $\text{La}(\text{OH})_3$ Zachariasen gives $c = 3.850$, $a = 6.523 \text{ \AA}$, giving $D_X = 4.44$; whereas Fricke & Seitz give $c = 3.55$ and $a = 6.29 \text{ \AA}$, with $D_X = 5.19$. A further striking anomaly in the results of Fricke & Seitz is the fact that the unit-cell size, and hence the unit-cell volume, hardly changes at all when passing from lanthanum (121.6 \AA^3) to yttrium hydroxide (119.1 \AA^3).

Experimental

In connection with an investigation into the phase equilibrium relationships in the rare earth oxide-water systems at elevated temperatures and high water pressures it was found that single crystals (1-2 mm. long) of the various hydrates could be grown quite easily. At least four different structure types, two of them monohydrates, were recognized.

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The oxides of the elements used, La_2O_3 , Nd_2O_3 , Sm_2O_3 , Gd_2O_3 and Y_2O_3 were of 99% purity grade. However, confirmatory runs were made with material of stated 99.9% purity obtained from a different commercial source. Spectrographic examination of the 99.9% Y_2O_3 showed no impurity in excess of 0.01-0.05%. The oxides were dissolved in nitric acid, precipitated by ammonia and thoroughly washed, in order to obtain them in a reactive form. They were wrapped in platinum envelopes and heated to the desired temperature (up to a maximum of 800° C.) under the desired water vapour pressure (up to a maximum of 20,000 lb.in.⁻²) in the usual types of vessels (see Roy, Roy & Osborn, 1950) for periods from a few hours to a few weeks. The vessels were 'quenched', and the products examined by the petrographic microscope and X-ray diffraction. Powder patterns were obtained using filtered copper radiation on a G.E. XRD-3 165° spectrometer unit. The necessary oscillation, rotation and Weissenberg diagrams were obtained with unfiltered Fe, Cu or Mo radiation for the equator, first and second layer lines around the 'c' and 'a' axes.

The single-crystal data for $\text{La}(\text{OH})_3$ yielded a space group ($C6_3/m$) agreeing with that found by Zachariasen and by Fricke & Seitz. The cell dimensions obtained from these data and from the indexing of the powder pattern data, using Bunn-type charts, are given in Table 1, and the agreement with Zachariasen for $\text{La}(\text{OH})_3$ and $\text{Nd}(\text{OH})_3$ is fair. The density measured pycnometrically on a 5 g. sample was found to be $4.453 \pm 0.005 \text{ g.cm.}^{-3}$ compared with Zachariasen's X-ray density of 4.44 g.cm.^{-3} . Optical data obtained on $\text{La}(\text{OH})_3$ gave $n_e = 1.768 \pm 0.005$, $n_o = 1.740 \pm 0.005$; uniaxial positive; pronounced positive elongation. The neodymium, samarium (as also the gadolinium) hydroxides proved to be isomorphous, having the same positive elongation and very slightly higher refractive indices. Moreover, the powder patterns which are listed in Table 1 compare well among themselves and with that given by Fricke & Seitz (1947) for ' $\text{Er}(\text{OH})_3$ '. However, their unit-cell size for ' $\text{Er}(\text{OH})_3$ '

Table 1. Powder diffraction data for rare earth hydrates

<i>hkl</i>	La(OH) ₃ type						Y(OH) ₃	
	La(OH) ₃		Nd(OH) ₃		Sm(OH) ₃		<i>d</i> ' (Å)	<i>I</i> / <i>I</i> ₀
	<i>d</i> ' (Å)	<i>I</i> / <i>I</i> ₀	<i>d</i> ' (Å)	<i>I</i> / <i>I</i> ₀	<i>d</i> ' (Å)	<i>I</i> / <i>I</i> ₀		
100	5.65	65	5.57	80	5.54	100	8.4	10
110	3.26	75	3.20	65	3.16	70	8.12	100
101	3.19	85	3.08	85	3.03	55	5.82	5
200	2.823	25	2.768	10	2.734	15	4.69	20
111	2.50	5	2.45	5	—	—	4.57	15
201	2.276	100	2.217	100	2.183	90	4.41	10
210	2.136	10	2.092	10	2.069	15	4.09	70
002	1.922	10	—	—	—	—	3.677	65
300	1.884	25	1.848*	50	1.821	50	3.07	70
211	1.870	90	1.842	100	1.795	65	3.00	45
220	1.631	20	1.605	30	1.575	15	2.857	5
310	1.565	15	1.540	10	1.519	7	2.730	20
311	1.452	2	1.417	20	1.400	20	2.660	20
400	1.411	5	1.392	10	1.366	10	2.344	15
401	—	—	1.311	15	1.284	10	2.217	3
320	1.296	5	—	—	—	—	2.117	3
410	1.231*	20	1.290*	10	1.194	10	2.040	15
	<i>a</i> ₀ = 6.523 ± 0.003 Å		<i>a</i> ₀ = 6.421 ± 0.010 Å		<i>a</i> ₀ = 6.312 ± 0.01 Å		1.997	20
	<i>c</i> ₀ = 3.855 ± 0.02 Å		<i>c</i> ₀ = 3.74 ± 0.02 Å		<i>c</i> ₀ = 3.59 ± 0.03 Å		1.866	15

* Unresolved doublet.

is only a little smaller than that obtained by us for Sm(OH)₃ and their cell sizes for the other hydroxides range from a maximum of *c* = 3.55 and *a* = 6.25 Å (for La) to *c* = 3.53 and *a* = 6.24 Å (for Y). These anomalous results of Fricke, Seitz and Schubert may therefore be ascribed to the use of mixtures of rare earths rather than pure oxide fractions.

In Table 1 we also list the powder pattern for Y(OH)₃; this is seen to bear no resemblance to the patterns of the other hydroxides. The identification of this phase is based on the following criteria: (i) It is prepared from only Y₂O₃ and H₂O. (ii) It forms under conditions where La(OH)₃ is also stable. (iii) It yields another hydrate, then Y₂O₃ on successive equilibrium dehydration, and no hydrates other than mono- and tri-hydrates are known for the trivalent elements. (iv) Its refractive indices bear a reasonable relationship to those of both La(OH)₃ and Y₂O₃·H₂O. The optical character of Y(OH)₃ was also found to be quite different from the other rare earth hydrates, being needle-like with negative elongation, *n*_p = 1.676 ± 0.003, *n*_g = 1.714 ± 0.003. Single-crystal work

on Y(OH)₃ is in progress. It is clear, therefore, that the structure listed for Y(OH)₃ is incorrect, and it is not analogous to the La(OH)₃ or UCl₃ structure, and therefore cannot give its name to this structure type. Indeed it is apparent that instead of separate rare earths Fricke & Seitz (1947) had nearly the same mixture of oxides giving an approximate ionic radius of 1.12 Å (of Goldschmidt-type radii, with La 1.22 and Sm 1.13 Å).

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