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Synthesis and Structure of New Double Oxides of Mercury and Rare Earth Elements: R_2HgO_4 (R = La, Nd, Sm, Eu, and Gd)

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New double oxides with mercury and five rare earth elements, R_2HgO_4 (R = La, Nd, Sm, Eu, and Gd), were synthesized and characterized by X-ray powder diffraction, EDS analysis, electron microscopy, and thermal analysis. They all have the structure which was determined for one of the compounds, Nd_2HgO_4, from powder diffractometer data. Nd_2HgO_4 has a monoclinic unit cell, space group $C2/m$, $Z = 4$, and the cell parameters $a = 13.8737(8)$ Å, $b = 3.7936(4)$ Å, $c = 10.240(2)$ Å, and $\beta = 121.200(9)°$. The mercury atoms are linearly coordinated to two oxygen atoms, and the two independent neodymium atoms coordinate seven oxygen atoms, which form polyhedra of slightly different shapes and sizes. © 1991 Academic Press, Inc.

Introduction

Double oxides with mercury are relatively rare, although in the literature, alkali metal mercury oxides, for example, Na_2HgO_2, have been reported (*1*). In a previous paper by Putilin *et al.* (*2*), the new compounds $SrHgO_2$ and $CaHgO_2$ were described. These two phases, of the same structure type, were found to possess a rhombohedral unit cell, in which mercury is linearly coordinated to oxygen as in the alkali metal mercury oxides.

In a search of new compounds that may have superconducting properties we have investigated the system La_2CuO_4–HgO and noticed the formation of a new phase when the reaction was performed in a closed tube. We did not see this phase when the oxides were heated in a flowing-oxygen reactor, because the mercury oxide decomposes and evaporates. The double oxides in the systems CuO–HgO and La_2O_3–HgO were also investigated. We did not obtain any copper mercury oxide, but in a sample with the starting composition La_2O_3 : HgO = 1 : 1 the same phase was formed. Therefore we started an investigation of the compounds R_2HgO_4, where R is La or other rare earth elements.

Experimental

The samples were prepared from stoichiometric amounts of HgO (Mallinckrodt, *p.a.*) and Y_2O_3 (99.999%), La_2O_3 (Reacton, 99.9%), CeO_2 (Schering, *puriss*), Pr_6O_{11} (Light & Co., 99.999%), Nd_2O_3 (Reacton, 99.9%), Sm_2O_3 (Light & Co., 99.9%), Eu_2O_3 (Ventron, 99.999%), Gd_2O_3 (Light & Co.,

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99.9%), $TbO_{1.82}$ (Light & Co., 99.9%), and Dy_2O_3 (Light & Co., 99.9%). The powders were ground under acetone in an agate mortar and placed into a silica tube. After evacuating, the tubes were sealed and placed into a steel container. Approximately $\frac{1}{20}$ of the volume of the container was filled with water to create an overpressure during heating, after closing the container. Without water the tubes often exploded because at this temperature HgO decomposes, creating excess pressure in the tubes. The container was then heated at 550°C for at least 24 hr. The container was cooled to room temperature before the silica tubes were taken out.

X-ray powder diffraction photographs of all specimens were taken with $CuK\alpha_1$ radiation (λ = 1.5405981 Å) using a Guinier–Hägg focusing camera with subtraction geometry. Finely powdered silicon (a = 5.430880 Å at 25°C (*3*)) was used as internal standard. The film blackening was evaluated by means of an automatic film scanner (*4*). The unit cell parameters were determined and refined with the programs TREOR (*5*) and PIRUM (*6*). For all structure calculations the crystal structure determination package CSD was used (*7*).

Three electron microscopes were used for characterizing the samples: a JEOL 820 scanning electron microscope with microanalysis equipment (LINK QX200), a JEOL 200CX high-resolution transmission electron microscope (TEM), and a JEOL 2000FX analytical TEM, having an EDS system (LINK QX200) with the detector in the high angle (70°) position. The samples investigated in the TEMs were ground in butanol, and the crystal fragments were placed on a metal grid covered with an amorphous holey carbon film.

The thermal decomposition of the compounds was investigated with a Perkin–Elmer thermogravimetric analyzer (TGS-2). The samples were heated in oxygen with a heating rate of 10°C min^{-1} in the temperature range 50–1000°C.

X-ray powder data for structure determination of one of the phases, Nd_2HgO_4, were collected on a STOE STADI/P powder diffractometer, using a rotating flat sample in symmetric transmission mode. A germanium crystal monochromator with a 220-mm radius of curvature was used to obtain strictly monochromatized $CuK\alpha_1$ radiation. The data were collected with a small linear-position sensitive detector covering 4.6° in 2θ. In order to reduce the influence of errors in intensity calibration of the detector, it was moved in steps of 0.2°, thus giving an average intensity from 23 (=4.6/0.2) measurements at each θ position. Step intensities in the 2θ range 5°–120° were collected for structure determination.

Results

X-Ray Diffraction

X-ray powder films from all synthesized products with the starting compositions $R:Hg = 2:1$ were examined. The new phase was formed only when the rare earth elements were La, Nd, Sm, Eu, and Gd. When the starting oxides were those of Y, Ce, Pr, Tb, and Dy, however, no lines of this phase could be detected.

The neodymium mercury oxide turned out to be the most purely monophasic one. The X-ray powder patterns of the other four compounds showed weak extra lines from HgO and the starting rare earth oxide. Occasionally weak lines from rare earth silicon oxides could be detected (*8*). This minor phase is probably formed when the rare earth oxides on the sample surface react with the silica ampoule.

The X-ray powder pattern of the neodymium mercury oxide could be indexed to give a C-centered monoclinic unit cell with parameters that refined to a = 13.8737(8) Å, b = 3.7936(4) Å, c = 10.240(2) Å, and β = 121.200(9)° ($M(20)$ = 51 (*9*)). The indexed powder pattern of this phase is shown in Table I. The observed Laue diffraction

TABLE I

Powder X-Ray Data for Nd_2HgO_4 Obtained from Powder Diffractometer

h	*k*	*l*	*d*(o)	*d*(c)	*I*(o)	*I*(c)	*h*	*k*	*l*	*d*(o)	*d*(c)	*I*(o)	*I*(c)
2	0	−1	6.8250	6.8194	8	7	2	0	−5	1.9826	1.9819	2	1
2	0	0	5.9463	5.9335	3	3	5	1	−4		1.9756		1
2	0	−2	4.9713	4.9585	7	7	0	2	0	1.8966	1.8968	32	33
0	0	2	4.3841	4.3795	13	12	6	0	−5	1.8812	1.8815	4	3
2	0	1	4.0359	4.0366	10	11	3	1	−5	1.7966	1.7968	61	47
1	1	0	3.6161	3.6135	26	25	5	1	1		1.7964		14
1	1	−1	3.5454	3.5432	54	54	2	0	4	1.7740	1.7770	4	2
2	0	−3	3.4121	3.4118	56	28	2	2	−2		1.7716		1
4	0	−2		3.4097		12	5	1	−5	1.7540	1.7577	11	2
4	0	−1		3.3946		16	1	1	4		1.7541		7
1	1	1	3.1683	3.1688	67	66	0	0	5		1.7518		3
1	1	−2	3.0323	3.0318	17	14	6	0	1	1.7399	1.7448	48	3
4	0	−3	2.9970	2.9972	47	47	7	1	−2		1.7407		40
4	0	0	2.9657	2.9668	73	74	0	2	2		1.7406		1
3	1	−1	2.9198	2.9295	70	7	8	0	−3		1.7341		4
0	0	3		2.9196		63	2	2	1	1.7136	1.7167	9	1
3	1	−2	2.8205	2.8202	100	100	3	1	3		1.7139		8
3	1	0	2.7363	2.7380	20	20	4	0	−6	1.7054	1.7059	5	3
1	1	2	2.5930	2.5936	76	76	8	0	−4		1.7049		3
2	0	−4	2.5222	2.5220	8	6	4	0	3	1.6878	1.6890	14	16
3	1	−3	2.4922	2.4922	6	7	2	2	−3	1.6576	1.6578	11	6
4	0	−4	2.4785	2.4793	8	8	4	2	−2		1.6576		2
1	1	−3	2.4691	2.4694	8	8	4	2	−1		1.6558		3
4	0	1	2.4508	2.4506	5	5	6	0	−6	1.6527	1.6528	3	2
3	1	1	2.3805	2.3814	49	50	2	0	−6	1.6267	1.6264	7	6
6	0	−2	2.3038	2.3053	8	6	8	0	−1	1.6027	1.6059	15	4
6	0	−3	2.2713	2.2731	8	7	4	2	−3		1.6028		11
5	1	−2	2.2381	2.2390	5	6	4	2	0	1.5981	1.5981	21	18
2	0	3	2.2052	2.2058	6	6	7	1	−5	1.5920	1.5923	39	24
6	0	−1	2.1820	2.1881	5	1	0	2	3		1.5906		16
5	1	−1		2.1811		4	5	1	2	1.5830	1.5835	10	3
3	1	−4	2.1087	2.1208	32	2	5	1	−6	1.5481	1.5482	3	1
1	1	3		2.1138		9	7	1	0		1.5478		1
6	0	−4		2.1083		20	2	2	−4	1.5162	1.5159	3	2
4	0	−5	2.0406	2.0407	4	4	4	2	−4	1.5054	1.5065	2	3
3	1	2	2.0183	2.0189	3	2	4	2	1	1.4992	1.5000	2	2
4	0	2		2.0183		1	1	1	5	1.4869	1.4869	13	10
							8	0	0		1.4834		4

Note: d(o) and *d*(c) are observed and calculated data, respectively, obtained with a Guinier–Hägg camera using an internal Si standard. *I*(o) and *I*(c) are integrated intensities of reflections from diffractometer data and theoretical calculations, respectively. The values of $\sigma(I(o))$ are within the range 0.3 (for the strongest reflections) to 10% (for the weakest). All reflections with $I(c) < 1$ are omitted in this table, but they were used for structure determination. Two weak lines from neodymium silicate are also omitted. For overlapping peaks only one experimental value is shown, that with the highest *d*-value.

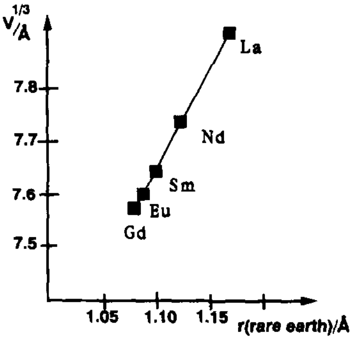

FIG. 1. Variation of cube root of the unit cell volume *vs* the radius of the rare earth ion (R^{3+}, 6-coordination) for R_2HgO_4.

group was $2/m$, and the subsequent structure determination and refinement verified space group $C2/m$ (No. 12). The X-ray powder patterns of the other four compounds were also indexed and refined (Table II). The relation between $V^{1/3}$ and the 6-coordinated ionic radii (*10*) of the rare earth elements is shown in Fig. 1.

Electron Microscopy and EDS Analysis

Thin crystal fragments of the La_2HgO_4 and Nd_2HgO_4 samples were examined in the transmission electron microscopes. Selected area electron diffractions along different zone axes were compatible with a monoclinic C-centered cell. An electron diffraction photograph from the Nd_2HgO_4 phase is shown in Fig. 2. The diffraction pattern disappeared during irradiation for several minutes in an intense electron beam. The EDS analyses of nine thin La_2HgO_4 fragments indicated that the weighed-in stoichiometry was preserved. The average metal ratio La : Hg was 66(2) : 33(2). Minor quantities of the rare earth silicon oxides and the starting oxides mentioned above could also be detected by EDS analyses.

Structure Determination

Powder diffractometer data for Nd_2HgO_4 were used for structure determination. In the $2\theta > 62°$ region almost all reflections were affected by overlap; therefore only reflections with $2\theta \leq 62°$ were used. The integral intensities of the reflections in this region were calculated with the program PROFI (CSD (*7*)). When a separation of the overlapping reflections was impossible, the total integral intensity corrected for background was used in the calculation as the sum of the intensities. Absorption correction was made because of the high value of the linear absorption coefficient (μ = 2188 cm^{-1}; μR = 2.5).

The locations of the heavy atoms were determined from the Patterson function. A least-squares refinement of the structure with only the metal atoms included gave an R-value of 0.20. A sequence of difference Fourier syntheses made it possible to localize the oxygen positions. A common isotropic temperature factor was used for all oxygen atoms, and a least-squares refinement of an isotropic thermal vibration model produced an R-value of 0.042. Since the

TABLE II

THE COLORS AND REFINED LATTICE PARAMETERS OF THE PREPARED COMPOUNDS

Compound	Color	a (Å)	b (Å)	c (Å)	β	V (Å^3)
La_2HgO_4	White	14.1020(5)	3.9110(2)	10.3791(6)	120.393(4)	493.8(1)
Nd_2HgO_4	Green	13.8737(8)	3.7936(4)	10.240(2)	121.200(9)	461.0(2)
Sm_2HgO_4	White	13.755(2)	3.7342(5)	10.159(2)	121.53(1)	444.8(3)
Eu_2HgO_4	White	13.720(6)	3.7079(5)	10.144(2)	121.75(3)	438.8(8)
Gd_2HgO_4	White	13.673(4)	3.6901(8)	10.116(6)	121.87(3)	433.5(6)

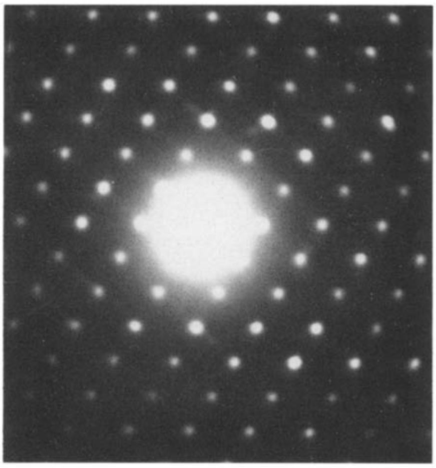

FIG. 2. Electron diffraction pattern in the ⟨010⟩ zone direction of Nd_2HgO_4.

mercury turned out to have a linear oxygen coordination, we also tested an anisotropic temperature factor for this atom. With this model, the same atomic coordinates resulted, within the standard deviations, but the anisotropic temperature factor component B_{22} became significantly larger than B_{11} and B_{33}; moreover the distances obtained from this refinement were more convincing. In particular, the two Hg–O distances became more equal. Final refinement with the anisotropic model yielded $R = 0.040$. Crystallographic data for Nd_2HgO_4 are shown in Table III. The atomic coordinates, thermal parameters, and selected interatomic distances are listed in Tables IV and V.

A full-profile Rietveld refinement of data in the range $9° < 2\theta < 110°$ has been performed as well. The final result led to an R-value of 8% and approximately the same atomic coordinates for the heavy atoms. The coordinates of the oxygen atoms did change slightly and resulted in, for example, two rather different Hg–O distances. The result from this refinement is considered less reliable, however, as the powder pattern contained impurity lines, which could be excluded in the low-angle part used in the intensity refinement but not for larger angles, included in the Rietveld refinement.

Thermal Decomposition

The decomposition of the prepared oxides La_2HgO_4, Nd_2HgO_4, Sm_2HgO_4, Eu_2HgO_4, and Gd_2HgO_4 was studied by heating in oxygen in a TG apparatus. A large weight loss of approximately 36% was noted for all compounds, between 800 and 900°C. It corresponds to the decomposition,

$$R_2HgO_4 \rightarrow R_2O_3 + Hg + \tfrac{1}{2}O_2,$$

which should give a 39% loss for R = Nd.

The starting temperature of the decomposition is approximately 820°C for all compounds. All samples with small quantities of unreacted starting oxides, revealed by their powder diffraction films, showed a small (<5%) weight loss at approximately 500°C. This is probably due to the decomposition of unreacted HgO.

Description of the Structure and Discussion

The crystal structure of Nd_2HgO_4 arrived at is, as far as we know, of a new type. A projection onto the *ac*-plane is shown in Fig. 3. There are two independent Nd atoms with similar environments. The neodymium–oxygen polyhedra can be described as octahedra in which one oxygen atom is replaced by a pair of atoms, to form seven-cornered polyhedra. The shapes of these polyhedra are rather similar to those of the R–O_7 polyhedra in the A-type rare earth sesquioxides (*11*), but they have a different site symmetry and Nd–O distances. The Nd–O_7 polyhedra share vertices and edges to form a three-dimensional network. The Nd–O_7 polyhedra are connected by shared edges to six other polyhedra at different levels. The Nd(1)–O_7 polyhedron also shares one corner with a Nd(2)–O_7 polyhedron at the same level, while the Nd(2)–O_7 polyhedron in addition shares an edge with another Nd(2)–O_7 polyhedron related by a diad.

TABLE III

CRYSTALLOGRAPHIC DATA FOR Nd_2HgO_4

Space group $C2/m$	
a (Å)	13.8737(8)
b	3.7936(4)
c	10.240(2)
β (degree)	121.200(9)
Cell volume (Å^3)	461.0(2)
Volume occupancy (%)	63.67
Unit cell mass (amu)	2212.28
F(000) (electrons)	928.
Calculated density (g/cm^3)	7.968(4)
Absorption coefficient (1/cm)	2189.24
Radiation and wavelength	Cu, 1.5405981
Diffractometer	Powder STADI/P
Weighting scheme	Unit
Number of atoms in cell	28.0, $Z = 4$
Number of atom sites	7
2θ and sin T/l (max)	62.66, 0.337
Number of measured reflections	85
R, R_w	0.0404, 0.0404
Goodness of fit	81.890
Scale factor	0.5(1)

TABLE IVA

ATOMIC PARAMETERS AND ISOTROPIC TEMPERATURE FACTORS FOR Nd_2HgO_4

Atom	x/a	y/b	z/c	$B(i/e)$	N
Hg(1)	0.1154(7)	0	0.1624(9)	2.3(4)[a]	4
Nd(1)	0.3418(7)	1/2	0.1989(9)	1.7(3)	4
Nd(2)	0.1189(8)	1/2	0.4585(11)	2.1(4)	4
O(1)	0.251(8)	1/2	0.363(9)	0.6(8)	4
O(2)	0.415(5)	0	0.353(7)	0.6(8)	4
O(3)	0.026(6)	0	0.271(8)	0.6(8)	4
O(4)	0.216(7)	0	0.070(8)	0.6(8)	4

[a] $B(\text{eq}) = \frac{4}{3}[B_{11}\, a^{*2}\, a^2 + \cdots 2B_{23}\, b^*\, c^*\, b\, c \cos(\alpha)]$.

TABLE IVB

ANISOTROPIC THERMAL PARAMETERS FOR Hg

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg(1)	1.8(6)	2.9(4)	1.8(5)	0	0.6(5)[a]	0

[a] $T = \exp[-\frac{1}{4}(B_{11}\, a^{*2}\, h^2 + \cdots 2B_{23}\, b^*\, c^*\, k\, l)]$.

TABLE V

SELECTED DISTANCES (Å) FOR Nd_2HgO_4

Hg(1)–O(3)	2.05(9)	Hg(1)–O(4)	2.06(11)	Hg(1)–Hg(1)	3.204(12)
Nd(1)–O(3)	2.26(9)	Nd(1)–O(4)	2.44(7)	Nd(1)–O(1)	2.56(11)
Nd(1)–O(2)	2.34(4) × 2	Nd(1)–O(4)	2.45(6) × 2		
Nd(2)–O(2)	2.21(8)	Nd(2)–O(2)	2.44(8)	Nd(2)–O(1)	2.50(12)
Nd(2)–O(3)	2.53(5) × 2	Nd(2)–O(1)	2.60(6) × 2		
O(1)–O(2)	3.00(12)	O(2)–O(2)	2.69(10)	O(2)–O(4)	2.78(11)
O(2)–O(3)	2.83(9)	O(4)–O(4)	2.81(10)		

The mercury atoms are situated in tunnels running along *b* and are nearly linearly coordinated to two oxygen atoms (see Fig. 3). The Hg–O distances are similar to those found in other compounds with mercury (*1*, *2*, *12*). There is good agreement between the sum of the ionic radii of mercury and oxygen (1.2 + 0.83 Å (*10*)) and the Hg–O distance (2.05 Å). The small deviation from linear coordination observed (O–Hg–O angle is 176(3)°) is not really significant.

Concerning the anion position it can be seen that the oxygen atoms at $y = 0$ are arranged in rows parallel to the [203] direction, with one-ninth of them omitted in every row (see Fig. 4). The sheet of oxygens at $y = \frac{1}{2}$ is identical but translated due to the *C*-centering. The cations are situated in holes in this oxygen network. The anions form approximately square nets on the $(60\bar{4})$ planes, and in between the positions of the absent oxygens a pair of Hg atoms is situated (see Fig. 5).

This new structure type forms with the rare earth elements La, Nd, Sm, Eu, and Gd. The cell parameters and $V^{1/3}$ (Fig. 1) for these compounds increase linearly with the ionic radii. The relative increase of the *b*-axis is approximately twice that of other cell parameters, which may be due to the fact that the mercury–oxygen bonds are parallel to the *ac*-plane.

With R = Y, Tb, and Dy the new compound was not formed, probably due to the small ionic radii for these rare earth elements. Ce and Pr, however, might be suitable for this structure type under other syn-

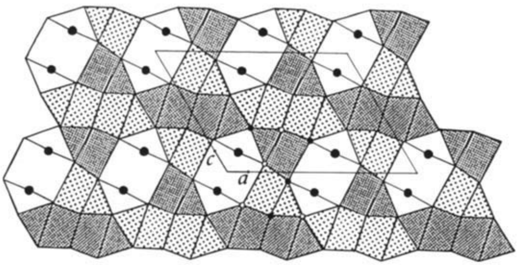

FIG. 3. Projection on the *ac*-plane of the Nd_2HgO_4-type structure. The mercury atoms are shown as large filled circles. The neodymium atoms are situated inside the $Nd–O_7$ polyhedra. Polyhedra at the same elevation have the same shading. The different oxygen elevations are marked in two polyhedra as small filled ($z = \frac{1}{2}$) and unfilled ($z = 0$) circles.

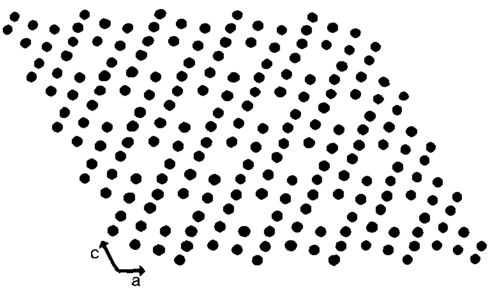

FIG. 4. One sheet of oxygen atoms in the *ac*-plane.

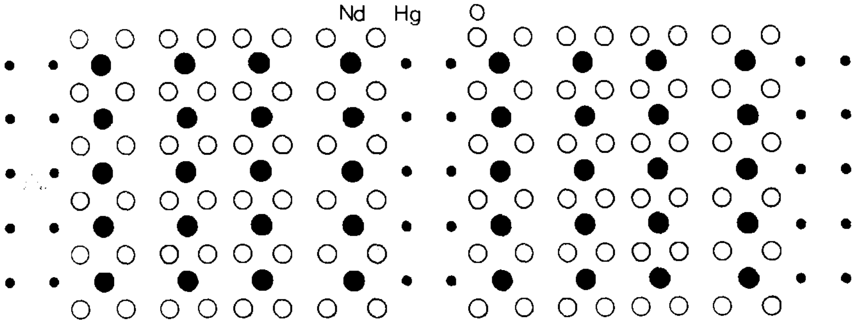

FIG. 5. Projection of atoms in the (60$\bar{4}$) plane. The oxygen atoms are shown as circles. The mercury and neodymium atoms are shown as small and large filled circles, respectively.

thetic conditions or using other starting oxides (in this investigation we only used CeO_2 and Pr_6O_{11}, respectively).

The samples were found to be very poor electric conductors at room temperature.

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