

High-Pressure HgTiO₃ and HgPbO₃: Preparation, Characterization, and Structure

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Received July 13, 1972

Two new ternary oxides of mercury, HgTiO₃ and HgPbO₃, have been prepared at high pressure. Both compounds possess rhombohedral structures which probably are similar to the high-temperature LiNbO₃ structure. The hexagonal cell dimensions for HgTiO₃ are $a = 5.3781 \text{ \AA}$ and $c = 13.604 \text{ \AA}$; for HgPbO₃, $a = 5.7515 \text{ \AA}$ and $c = 14.534 \text{ \AA}$. The structure of HgTiO₃ has been studied from "single" crystal X-ray data.

Introduction

The crystal chemistry of mercuric oxides is interesting because of the unusual bonding characteristics of mercury. Despite its large size, mercury generally forms only two strong bonds to oxygen. For example, in both modifications of HgO (1), mercury has two nearly linear bonds to oxygen at 2.03 Å; other Hg-O distances are at least 2.80 Å.

As part of a program on new ternary oxides of mercury at this laboratory, Hg₂Nb₂O₇, Hg₂Ta₂O₇, Hg₂Sb₂O₇, Hg₂V₂O₇-II, HgWO₄, and HgMoO₄(2-5) have been prepared previously. In all of these compounds, mercury exhibits its usual tendency to form only two strong bonds. This paper reports two new ternary oxides of mercury where mercury has three, instead of two, strong bonds to oxygen.

Experimental

Synthesis. The reactants were reagent grade PbO₂ and spectroscopic grade HgO and TiO₂. Appropriate amounts of reactants were intimately mixed and placed in gold containers. The reactions were carried out at high pressure in equipment previously described (6).

X-Ray Data. Powder patterns were recorded at 25°C using a Hägg-Guinier camera with CuK α_1 radiation and an internal standard of high purity KCl ($a = 6.2931 \text{ \AA}$ at 25°C). Cell dimensions were refined by least squares using the Guinier data. Precession photographs were obtained on both HgTiO₃ and HgPbO₃ crystals using Mo radiation.

A crystal of HgTiO₃ measuring 0.03 × 0.03 × 0.05 mm was selected for precession photography and subsequent diffraction intensity collection. Precession photographs of this and other crystals showed that the hkl reciprocal lattice spots with l odd are very weak with respect to those with l even. All crystals also appear to be twinned with all upper reciprocal lattice levels showing sixfold rather than threefold rotational symmetry as would be expected for a rhombohedral crystal. Two sets of three-dimensional diffraction data were obtained with an automatic Picker diffractometer using both MoK α and AgK α radiation. Each reflection was scanned at 0.5°/min for 1.5° plus the α_1 - α_2 dispersion and 40-sec backgrounds were measured at the extremes of each scan. The linear absorption coefficients are 722 cm⁻¹ for MoK α and 398 cm⁻¹ for AgK α X-radiations, and transmission factors

calculated using the method of Wuensch and Prewitt (7) ranged from 0.07 to 0.16 for $\text{MoK}\alpha$ and from 0.23 to 0.30 for $\text{AgK}\alpha$. Because of the large absorption and small crystal volume, neither type of radiation resulted in adequate intensity data. However, due to the smaller transmission factors for $\text{AgK}\alpha$ radiation, the 70 observed reflections obtained with this radiation were selected for the refinements discussed below.

Results

Mercuric titanate, HgTiO_3 , can be prepared at 800 to 1100°C under 65 kbars pressure, but attempts to prepare it at 30 kbars or lower pressure were unsuccessful. As prepared, HgTiO_3 is light yellow, but it darkens on exposure to light. Four-probe electrical resistivity measurements on a crystal indicate that HgTiO_3 is electrically insulating ($\rho \sim 10^9$ ohm-cm at 25°C). The X-ray powder pattern of HgTiO_3 was readily indexed as rhombohedral. The refined cell dimensions based on the hexagonal cell are: $a = 5.3781 \pm 0.0005$ Å and $c = 13.604 \pm 0.001$ Å. For the rhombohedral cell, $a = 5.4959$ Å and $\alpha = 58.59^\circ$.

Mercuric plumbate, HgPbO_3 , can be prepared at 600 to 1000°C under 30 to 65 kbars pressure, but attempts to prepare it at 3 kbars pressure were unsuccessful. HgPbO_3 is black, and crystals were found to be electrically conducting at room temperature ($\rho \sim 10^{-3}$ ohm-cm). The X-ray powder pattern of HgPbO_3 was also indexed as rhombohedral, and the refined hexagonal cell is: $a = 5.7515 \pm 0.0005$ Å and $c = 14.534 \pm 0.001$ Å. For the rhombohedral cell, $a = 5.8735$ Å and $\alpha = 58.63^\circ$.

From the powder patterns and the twinned single-crystal patterns, it seems likely that the Laue group for HgTiO_3 is $\bar{3}m$ which includes the noncentrosymmetric space groups $R\bar{3}2$, $R\bar{3}m$, and $R\bar{3}c$ plus the centrosymmetric groups $R\bar{3}m$ and $R\bar{3}c$. The second-order harmonic test indicates that the structure is noncentrosymmetric which narrows the space group possibilities to three. No reflections of type $h0l$ or $0kl$ with l odd were observed in consistency with the presence of a c glide plane. However, reflections with l odd are so weak, this may not be definitive. Nevertheless, if these criteria are adopted, the space group must be $R\bar{3}c-C_{3v}^2$, the space group of LiNbO_3 (8, 9). The LiNbO_3 structure is similar to that of ilmenite except the pairs of face-sharing Li and Nb octahedra are aligned in the same

direction parallel to the c axis. In ilmenite, the Fe-Ti pairs are aligned in anti-parallel fashion to give a centrosymmetric structure. When an attempt was made to refine HgTiO_3 in the LiNbO_3 model, the refinement converged at a rather large R ($R = \Sigma ||F_o - F_c|| / \Sigma |F_o|$) of 0.15. In all of these attempts, with Ti fixed at 0,0,0 Hg always moved to 0,0,0.25, indicating these atoms should be placed $\frac{1}{4}c$ apart. Because of the overpowering effect of Hg, it made little difference where oxygen was placed. This arrangement of Ti and Hg seemed to be correct for the x and y coordinates because the R for all $hk0$ reflections was 0.045.

Notwithstanding ideas about the noncentrosymmetric nature of HgTiO_3 , the curious separation between Hg and Ti seemed to suggest that because of the twinning, the apparent space group is $R\bar{3}c$ and the structure is more like that of calcite, with Ti at the origin in an octahedral environment and Hg at $0,0,\frac{1}{4}$ in a triangle of three oxygen atoms. Refinement in this arrangement resulted in a slightly lower R of 0.12 and reasonable temperature factors. To test the possibility that this structure represented the average of LiNbO_3 -type with domain structure, subsequent refinement cycles were run with Hg split into two half-atoms along z . The R immediately dropped to 0.060 and again the temperature factors were reasonable, but when Ti was also split into two half-atoms the R increased and the temperature factor of Ti became very large. At this point, Hg was again fixed at $z = 0.25$ and the temperature factor for Hg refined anisotropically. The R dropped only slightly to 0.059 and the oxygen x coordinate remained almost the same as before. Refinement was terminated at this stage and the final observed and calculated structure factors for the observed reflections are given in Table I. The refined coordinates are in Table II.

Discussion

Table III lists the interatomic distances for HgTiO_3 . The observed Ti-O octahedral distance of 1.96 Å is close to the value calculated using the Shannon and Prewitt (10) effective ionic radii. Hg is coordinated by three oxygen atoms at 2.20 ± 0.04 Å and by six more at 2.77 Å. The expected distance for three-coordinated Hg obtained by averaging the radii for $^{11}\text{Hg}^{2+}$ and $^{10}\text{Hg}^{2+}$ is 2.19 Å. Therefore, because of the relatively small R factor, the well-behaved

TABLE I
OBSERVED AND CALCULATED STRUCTURE
FACTORS FOR HgTiO₃

<i>h k l</i>	<i>F</i> _{obsd}	<i>F</i> _{calcd}	<i>h k l</i>	<i>F</i> _{obsd}	<i>F</i> _{calcd}
4 1 0	889	900	0 3 6	804	733
1 1 0	1369	1386	1 4 6	510	530
2 2 0	1141	1143	1 3 7	116	97
3 3 0	778	797	2 1 7	126	72
0 3 0	1279	1287	2 0 8	1065	1179
1 4 0	890	900	5 0 8	785	794
0 6 0	669	695	3 1 8	875	818
1 3 1	140	121	0 1 8	1044	1115
2 1 1	131	100	1 2 8	1024	974
2 0 2	1072	1057	4 2 8	711	652
5 0 2	634	666	2 3 8	921	829
3 1 2	436	638	0 4 8	906	821
0 1 2	1001	896	1 0 10	562	581
1 2 2	871	785	4 0 10	454	474
4 2 2	492	512	2 1 10	503	539
2 3 2	683	689	0 2 10	643	765
0 4 2	666	664	3 2 10	519	498
3 4 2	461	486	1 3 10	507	452
1 5 2	490	493	0 5 10	561	493
1 1 3	209	178	3 1 11	99	76
4 0 4	994	959	0 0 12	895	1004
5 1 4	727	715	3 0 12	732	767
2 1 4	1233	1181	4 1 12	633	596
0 2 4	1528	1485	1 1 12	743	766
3 2 4	845	961	2 2 12	733	709
1 3 4	700	963	0 3 12	767	767
2 4 4	745	745	1 4 12	653	596
0 5 4	915	907	2 0 14	465	479
4 2 5	98	53	3 1 14	336	324
1 2 5	140	84	0 1 14	424	409
0 0 6	1007	1124	1 2 14	386	385
4 1 6	558	530	1 0 16	567	582
1 1 6	718	684	2 1 16	548	544
2 2 6	719	657	0 2 16	635	634
3 3 6	473	471	0 0 18	365	365

TABLE II
REFINED PARAMETERS FOR HgTiO₃

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Hg	0	0	1/4	0.75 ^a
Ti	0	0	0	0.39(19)
O	0.415(7)	0	1/4	0.41(52)

^a Equivalent isotropic *B*. The anisotropic parameters are $\beta_{11} = \beta_{22} = 2\beta_{12} = 0.0052$ (11); $\beta_{33} = 0.0018(2)$; $\beta_{13} = \beta_{23} = 0$.

TABLE III
INTERATOMIC DISTANCES FOR HgTiO₃

Hg-O	2.20(4) Å	(× 3)
-O'	2.77(4)	(× 6)
Hg-O(av)	2.58	
Ti-O	1.96(4)	(× 6)
O-O	2.77	

temperature factors, and the good correspondence in interatomic distances with published radii values, we believed this structure is close to the correct one. Abrahams et al. (9), discussed the possible changes that take place in the structure of LiNbO₃ at the Curie temperature (~ 1200°C). One alternative, suggested by H. D. Megaw, is that the Li moves away from the octahedral face it shares with Nb until it moves into the opposite face and becomes three-coordinated, and the space group becomes *R3c*. Assuming that this is correct, we believe that the HgTiO₃ structure is similar to that of LiNbO₃ close to its Curie temperature and that the anisotropic behavior of Hg represents either a true thermal motion or a statistical average due to the domain structure of the crystal.

The calculated rms amplitude of vibration for Hg is 0.074 Å and 0.131 Å normal and parallel to the *c* axis, respectively. Although the X-ray data cannot distinguish between true thermal motion and the statistical average situation, the presence of a second harmonic signal is strong evidence that the anisotropic behavior of mercury is not entirely true thermal motion.

The structure of HgPbO₃ is presumably closely related to that of HgTiO₃. Although crystals of HgPbO₃ were prepared and examined, structure analysis was not attempted because problems with oxygen placement would be even more severe than for HgTiO₃.

Mercury forms two short bonds to oxygen in all its previously known oxides. Thus, HgTiO₃ and HgPbO₃ are exceptional in having mercury that forms three short bonds to oxygen. Such a coordination for mercury has, however, been found in two halides. In (CH₃)₄NH₂HgBr₃ (11) there are HgBr₃⁻ ions, and in (CH₃)₃SHgI₃ (12) there are HgI₃⁻ ions. Neither HgBr₃ nor HgI₃ is a planar ion; the mercury is displaced out of the halide plane by 0.3 and 0.08 Å, respectively. Thus, the coordination we find for mercury in HgTiO₃ is not entirely new, but it is new for an oxide.

Furthermore, it appears that this coordination for mercury is stable in oxides only at high pressures.

Acknowledgments

We thank C. L. Hoover for supervising the high pressure experiments, J. D. Bierlein for performing the second harmonic generation test, E. P. Moore for assistance in obtaining the X-ray data, and J. L. Gillson for performing electrical resistivity measurements.

References

1. K. AURIVILLIUS, *Ark. Kemi* **24**, 151 (1965).
2. A. W. SLEIGHT, *Inorg. Chem.* **7**, 1704 (1968).
3. A. W. SLEIGHT, *Mater. Res. Bull.* **7**, 827 (1972).
4. A. W. SLEIGHT AND M. S. LICIS, *Mater. Res. Bull.* **6**, 365 (1971).
5. W. JEITSCHKO AND A. W. SLEIGHT, *Z. Naturforsch.* **27b**, 203 (1972).
6. A. W. SLEIGHT AND T. A. BITHER, *Inorg. Chem.* **8**, 566 (1969).
7. B. J. WUENSCH AND C. T. PREWITT, *Z. Kristallogr. Kristallgeometrie Kristallphys. Kristallchem.* **122**, 24 (1965).
8. S. C. ABRAHAMS, J. M. REDDY, AND J. L. BERNSTEIN, *J. Phys. Chem. Solids* **27**, 997 (1966).
9. S. C. ABRAHAMS, H. J. LEVINSTEIN, AND J. M. REDDY, *J. Phys. Chem. Solids* **27**, 1019 (1966).
10. R. D. SHANNON AND C. T. PREWITT, *Acta Crystallogr.* **B25**, 925 (1969).
11. J. G. WHITE, *Acta Crystallogr.* **16**, 397 (1963).
12. R. H. FENN, J. W. H. OLDHAM, AND D. C. PHILLIPS, *Nature* **198**, 381 (1963).