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# Thermal Expansion Of Pb3O4

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# Thermal Expansion of Pb₃O₄

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Thermal expansion of Pb₃O₄ was investigated by high-temperature X-ray diffraction. The coefficient in the $a_0$ direction is $14.6\times10^{-6}/°C$. Expansion in the $c_0$ direction is 32% greater, with a coefficient of $19.3\times10^{-6}/°C$. Coefficients of expansion are linear from 25° to 490°C and are comparable with those of tetragonal and orthorhombic PbO.

## I. Introduction

THE thermal expansion characteristics of massicot (orthorhombic PbO)[1] and litharge (tetragonal PbO)[2] have been reported and related to crystal structure and bonding characteristics. In both cases, thermal expansion differed somewhat from that expected on purely structural grounds. The structure of the sesquioxide, Pb₃O₄, is quite different from that of either monoxide because of the bonding requirements of plumbic lead, $Pb^{4+}$. Bond distances and angles between plumbous lead, $Pb^{2+}$, and O are similar, however, to those in orthorhombic PbO. Because the structure in the $a_0$ directions is maintained by those bonds, comparison of the thermal expansion characteristics of Pb₃O₄ with those of the modifications of PbO is of interest.

The structure of Pb₃O₄ was determined independently by Bystroem and Westgren[3] and by Gross,[4] using X-ray diffraction data from single crystals. Unlike the modifications of PbO, however, Pb₃O₄ has not been investigated by neutron diffraction, so that the O coordinates are not known accurately. There is, moreover, considerable variation in reported lattice parameters, as indicated in Table I.[3–7] These uncertainties are relatively minor, however; variation of O coordinates and lattice parameters within reasonable limits causes variations

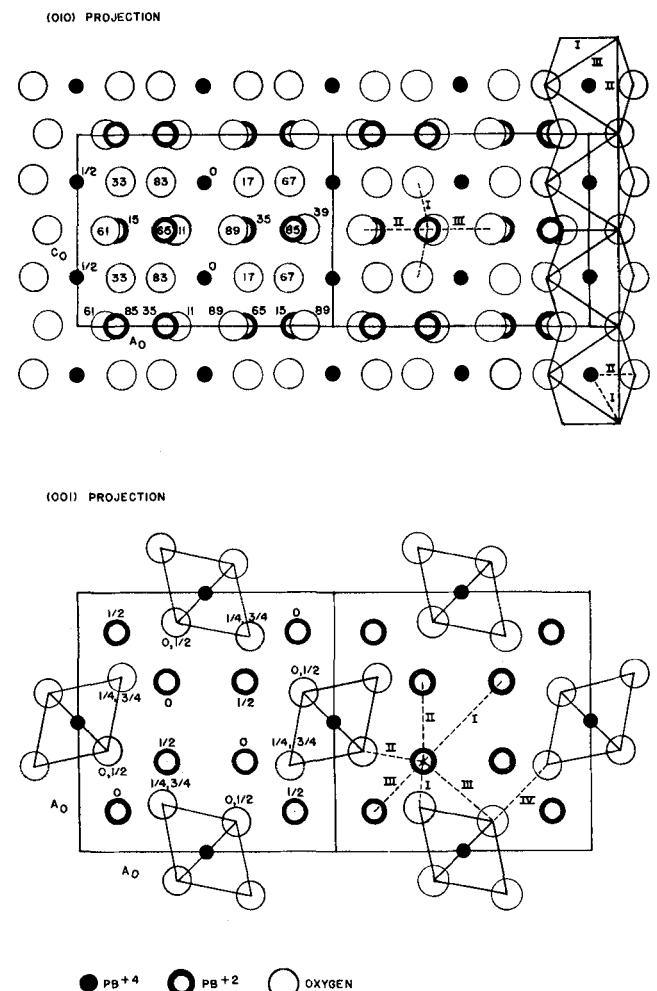**Table I. Unit Cell Parameters of Pb₃O₄**

| Ref. | $a_0$ (A) | $c_0$ (A) |
|---|---|---|
| 5 | 8.875 | 6.51 |
| 3 | 8.80 | 6.56 |
| 4 | 8.86 | 6.66 |
| 6 | 8.815 | 6.565 |
| 7 | 8.788 | 6.551 |
| Present study | 8.815 | 6.565 |

(010) PROJECTION



(001) PROJECTION



● Pb⁺⁴    ○ Pb⁺²    ◯ OXYGEN

**Fig. 1. The Pb₃O₄ structure. Roman numerals indicate bond distances listed in Table II.**

in bond distances and angles of no more than 2 to 3%. The tetragonal structure, drawn from the coordinates of Wyckoff,[7] is shown in Fig. 1. Plumbic lead is coordinated with 6 O

atoms at the corners of an irregular octahedron having a rectangular equatorial section in the (110) planes. The octahedra share 2 edges with adjacent octahedra, forming chains along the $c_0$ axis. The chains are held together by bonds between plumbous Pb and octahedral O atoms. The configuration is such that channels enclosed by 4 octahedral chains extend along the $c_0$ axis. The plumbous Pb atoms are situated in the channels, coordinated with 4 O atoms in a configuration very similar to that in orthorhombic PbO. As in both modifications of PbO, there are no $O^{2-}$ ions between the Pb ions in the channels.*

Important bond distances in the Pb₃O₄ structure, calculated from the lattice parameters of Swanson et al.[6] and the atomic coordinates of Wyckoff,[7] are given in Table II. The bond distances are designated by Roman numerals corresponding to those shown in Fig. 1. The shortest $Pb^{2+}-O^{2-}$ bond distance, II, is with 1 equatorial O; two bonds, I, are with apical O atoms of adjacent octahedra in an adjacent chain; the fourth bond is with an equatorial O atom of the latter chain. The shorter bonds, those 2.08 and 2.26 Å long, are comparable with those in orthorhombic PbO and serve to maintain the structure in the $a_0$ directions. The $Pb^{4+}-O^{2-}$ bond distances are nearly equal, with 4 at 2.17 Å in the equatorial section and 2 at 2.14 Å at the apices of the octahedron. The equatorial section is rectangular, 2.84 by 3.28 Å, as shown by bonds I and II.

Dickens,[8] in an analysis of the bonding scheme in Pb₃O₄, considered the $Pb^{4+}$ and the equatorial $O^{2-}$ entities to be fully ionized; the apical O and $Pb^{2+}$ species, however, were referred to a hybrid covalent bonding scheme similar to that in orthorhombic PbO, with $Pb^{2+}$ using $6p$ orbitals to bond with apical O and accepting an electron pair from 1 equatorial O. The bond with the remaining equatorial O was considered to be of the van der Waals type. The $6s$ orbital was assumed to contain the "inert pair." Geometric considerations suggest $sp^2$ hybrid O orbitals, but energy considerations favor an $sp^3$ configuration; the question was not resolved. In summary, Dickens considered the $Pb^{4+}-O^{2-}$ bonds to be ionic, having little influence on the structure as a whole but requiring an octahedral coordination on the basis of radius ratio. The $Pb^{2+}-O^{2-}$ bonding was considered to be similar to that in orthorhombic PbO in that $6p$ orbitals are used for bonding to O. Mutual repulsion by $Pb^{2+}$ across the central channel was considered negligible by virtue of the covalent bonding. Metallic and van der Waals bonding between Pb atoms is discounted.

## II. Experimental Procedure

Reagent-grade lead monoxide[†] was heated in air for 24 h at 470°C in Al crucibles. Thermogravimetric and X-ray analyses indicated complete oxidation to Pb₃O₄. There was no evidence of reaction between the PbO and the Al crucibles; spectrographic analyses of the oxide and crucible indicated no diffusion in either direction. Thermal expansion of material prepared in Au crucibles agreed closely with that of material prepared in Al crucibles. X-ray measurements at high temperatures were made with a recording diffractometer,[‡] using CuKα radiation with a scanning rate of 0.2° 2θ/min and a chart speed of 24 in./h. A high-temperature diffraction unit,[§] open to the atmosphere, was used to heat the sample. Experimental procedures and estimated accuracy were, in all cases, identical with those reported for the studies of massicot[1] and litharge.[2] Aluminum was used as the internal standard for alignment and as a liner for the stainless-steel sample holder.

Diffraction angles of the (310) and (002) lines (32.11° and 27.17° 2θ, respectively, at 25°C) were measured at each temperature, following alignment on the (111) line of Al, and $a_0$ and $c_0$ parameters were calculated directly from corresponding d values. Measurements were made at fixed temperatures between 25° and 555°C. Data were obtained during two heat-

### Table II. Bond Distances in Pb₃O₄

| Bond | No. of bonds | Distances* (Å) | Designation |
|---|---|---|---|
| Pb²⁺-O | 2 | 2.26 | I |
| Pb²⁺-O | 1 | 2.08 | II |
| Pb²⁺-O | 1 | 3.12 | III |
| Pb⁴⁺-O | 4 | 2.17 | I |
| Pb⁴⁺-O | 2 | 2.14 | II |
| Pb²⁺-Pb²⁺ | 1 | 3.81 | I |
| Pb²⁺-Pb²⁺ | 4 | 4.25 | II |
| Pb²⁺-Pb²⁺ | 2 | 4.08 | III |
| O-O | 1 | 2.84 | I |
| O-O | 2 | 3.28 | II |
| O-O | 2 | 3.05 | III |
| O-O | 2 | 3.13 | IV |

NOTE: $a_0 = 8.815$ Å, $c_0 = 6.565$ Å (Ref. 6); $4Pb^{4+}$ at $\pm(0\frac{1}{2}\frac{1}{4}; \frac{1}{2}0\frac{1}{4})$; $8Pb^{2+}$ and $8O^{2-}$ at $\pm(uvO; vu\frac{1}{2}; u+\frac{1}{2}, \frac{1}{2}-v, 0; v+\frac{1}{2}, u+\frac{1}{2}, \frac{1}{2})$. For $Pb^{2+}$ $u=v=0.153$; for $O^{2-}$ $u=0.114$, $v=0.614$. $8O^{2-}$ at $\pm(u, u+\frac{1}{2}, \frac{1}{4}; \bar{u}, \frac{1}{2}-u, \frac{1}{4}; u+\frac{1}{2}, u, \frac{1}{4}; \frac{1}{2}-u, u, \frac{1}{4})$; $u=0.672$. Space group No. 135, $P4_2/mbc$ $(D_{2h}^{13})$.
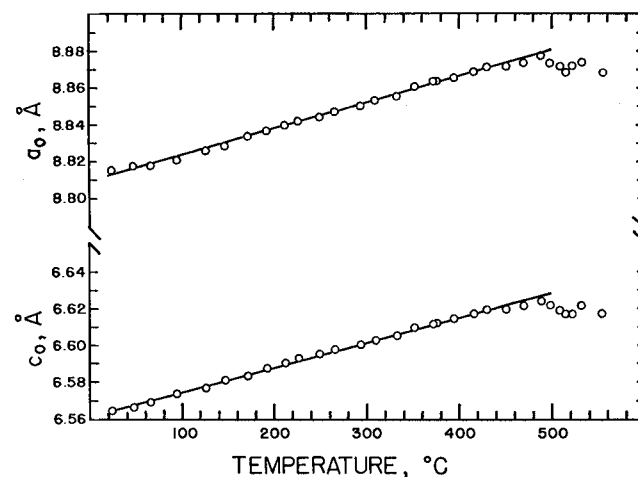
*Calculated from coordinates of Ref. 7.



Fig. 2. Lattice parameters of Pb₃O₄ as functions of temperature.

ing and cooling cycles between 25° and 475°C, using separate samples. A third sample was heated to 555°C; reduction to PbO above ≈490°C caused sample distortion, producing erratic expansion data. No differences were detected between the expansions observed on heating and cooling.

## III. Results

The lattice parameters of Pb₃O₄ are plotted vs temperature in Fig. 2; the data are plotted as $L_T/L_{25}$ vs temperature in Fig. 3. Thermal expansion was essentially linear, with coefficients of $14.6 \times 10^{-6}$ deg⁻¹ for the $a_0$ axis and $19.3 \times 10^{-6}$ deg⁻¹ for the $c_0$ axis. Unit cell volume expansion is shown for comparison in Fig. 4; the scatter observed between 490° and 555°C is the result of sample misalignment during reduction to PbO.

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*Although the bonding in Pb₃O₄ is considered essentially covalent, ionic notation is used so that the distinction between plumbous and plumbic lead will be clear.
†Matheson, Coleman, & Bell, East Rutherford, N. J.
‡XRD-5, General Electric Co., Schenectady, N. Y.
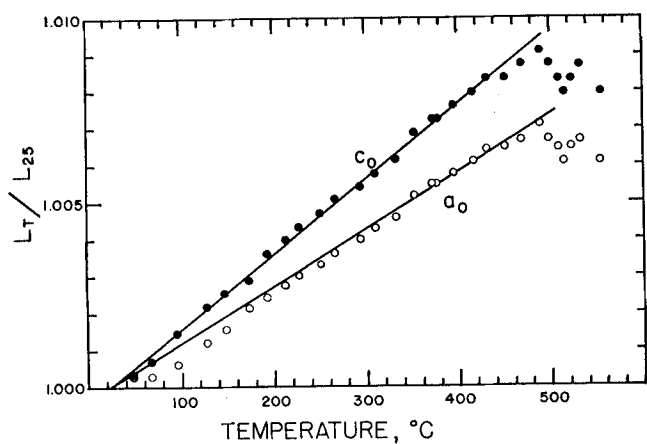§E & A Refractex I, Electronics & Alloys, Inc., Englewood, N. J.
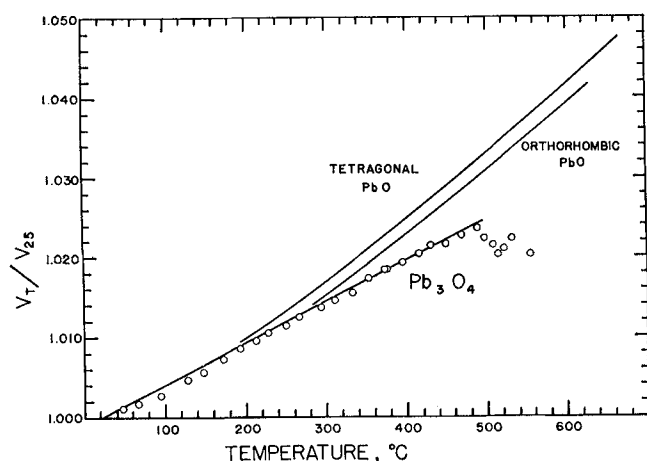
Fig. 3. Lattice parameters relative to values at 25°C.



Fig. 4. Unit cell volumes relative to values at 25°C. Data for orthorhombic PbO (Ref. 1) and tetragonal PbO (Ref. 2) shown for comparison.
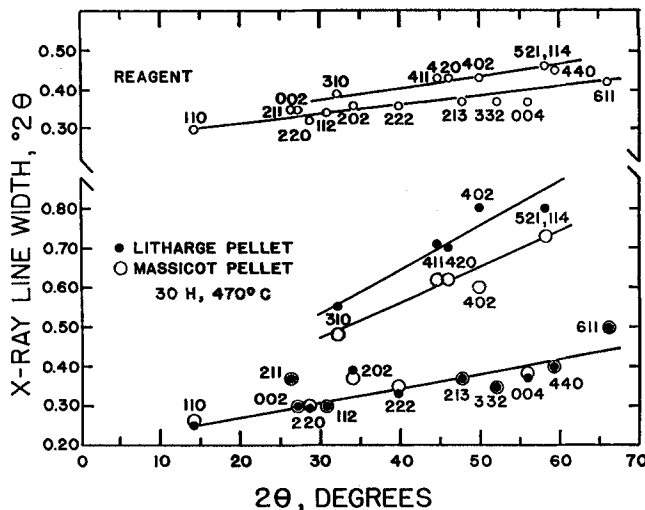


Fig. 5. X-ray line widths measured at half intensity from diffractometer tracings.

$Pb^{4+}-O^{2-}$ bonds, Dickens' characterization of the former as covalent and the latter as ionic seems reasonable. The bonding in $Pb_3O_4$ is undoubtedly more complex, however, and such gross generalization may not be worthwhile.

The assumption that $Pb^{4+}$ and 4 of the 6 octahedral $O^{2-}$ species are completely ionized, for example, does not seem entirely reasonable in a structure in which $Pb^{2+}-O^{2-}$ bonding is dominantly covalent; energy considerations make the reverse more likely. Enough energy levels are available to provide bonding electrons sufficient for Pb to coordinate with 6 O atoms in a covalent octahedral scheme. Although little is known of hybrid orbitals and their spatial arrangements in Pb, one possibility, obtained by promoting a 5d electron to the 5f level and a 6s electron to the 6p level, is a $d^3fsp^3$ hybrid orbital. An alternative $d^5sp^3d$ hybrid would require approximately the same excitation energy. In either case the equatorial O species would be saturated, and the 2.08 Å bond distance between $Pb^{2+}$ and one of the equatorial O species must be explained on other grounds. Thermal expansion data indicate only that the elongate octahedral equatorial section would become more elongate with increasing temperature. The $Pb^{2+}-Pb^{2+}$ bond distances within the channels are comparable with those between layers in orthorhombic PbO; there is no more reason to rule out the possibility of Pb–Pb bonding in $Pb_3O_4$ than in PbO. Expansion of Pb–Pb bonds in $Pb_3O_4$, unlike that in orthorhombic PbO, is anisotropic, although less so than that of the crystal as a whole.

The lattice parameters measured at room temperature agree very closely with those of Swanson et al.,[6] who also prepared $Pb_3O_4$ by oxidation at 470°C. Some diffraction lines in the powder samples were visibly broader than others, as was noted by Bystroem and Westgren,[3] who reported that prism reflections were relatively diffuse although basal reflections were sharp, even at high diffraction angles. Correlation with crystallographic zones was not noted in the patterns of material used in the present study, however. It was further noted that pellets pressed at 20,000 psi, fired for 24 h in air at 470°C, and analyzed without grinding exhibited the same diffraction characteristics in an exaggerated manner. The line widths, measured at half-intensity from diffractometer patterns of powder and pellet samples, are plotted vs $2\theta$ in Fig. 5. There is no apparent relation between line width and crystallographic direction; thus, the statement of Bystroem and Westgren that the line widths are probably related to a peculiar structural irregularity cannot be amplified.

## IV. Discussion

The most striking thermal expansion characteristic of $Pb_3O_4$ is the anisotropy; expansion in the $c_0$ direction is ≈32% greater than that in the $a_0$ direction. If it is assumed that the expansion in the $a_0$ direction is primarily a function of the $Pb^{2+}-O^{2-}$ bonds and that in the $c_0$ direction a function of the

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