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Thermal expansion of orthorhombic PbO was investigated by high-temperature X-ray diffraction. The coefficients in the a_0 and c_0 directions are equal and $<\frac{1}{2}$ the coefficient in the b_0 direction. The structure is described in terms of Pb–O chains extended in the a_0 direction and bonded into layers in the b_0 direction; appreciable Pb–Pb bonding is indicated. Coordination and bond distances observed in $PbSiO_3$ and lead silicate glasses, which are similar to those of massicot, and Pb_nO_n polymeric units reported in PbO vapor are interpreted as additional evidence of the importance of PbO chains as structural entities.

I. Introduction

THE structure of massicot, the orthorhombic modification of lead monoxide, was first studied by Byström,[1] who determined the lead coordinates by X-ray diffraction. The structure was resolved completely and independently by Kay[2] and by Leciejewicz,[3] who determined the oxygen coordinates by neutron diffraction. The lead and oxygen coordinates are in reasonable agreement. Leciejewicz adopted the lattice parameters of Byström, which correspond to space group *Pbcm*, and Kay adopted those of Swanson and Fuyat,[4] which correspond to the alternative setting *Pbma*.

The structure, with the coordinates and axial designations of Kay, is shown in Fig. 1; all interatomic distances <5 Å are listed in Table I, with the bonds designated by Roman numerals corresponding to those in Fig. 1. The structure is distinctively layered, with a Pb–O–O–Pb–Pb–O... sequence in the [001] direction. The shortest Pb–O and Pb–Pb bonds between layers are 3.81 and 3.97 Å, respectively. Within the layers, the Pb–O bonds are considerably shorter, 2.21 and 2.22 Å in the [100] direction and 2.48 Å in the [010] direction. Pb–Pb distances within the layer are between 3.46 and 3.86 Å, only slightly less than those between layers. The layers may thus be pictured as consisting of Pb–O–Pb–O... zigzag chains extended along the a_0 axis and held together into layers by longer, and presumably weaker, bonds along the b_0 axis.

Dickens[5] analyzed the structure in terms of purely covalent bonding. Alternative hybridized states of oxygen can account for the observed bond directions; oxygen may be hybridized (1) completely as sp^3 or (2) as sp^2 along the chains with $sp^2 \pm p$ between the chains. Along the chains, lead uses two $6p$ atomic orbitals to bond to two of the oxygen hybrid orbitals; between the chains, lead uses $6d_z^2 \pm 6p_z$ hybridized orbitals to bond to the other two oxygen hybrid orbitals. Interlayer bonding is attributed to van der Waals forces, but it is suggested that sp^3d^2 lead orbitals may permit significant Pb–Pb bonding between layers.

The wide variation observed in bond distances and the chain-layer structure lead to questions about the bonding requirements of lead in other compounds and in glasses containing plumbous lead. If the layerlike characteristics of the structure are dominant, as suggested by the platy habit and lubricating properties, thermal expansion should be highly anisotropic,
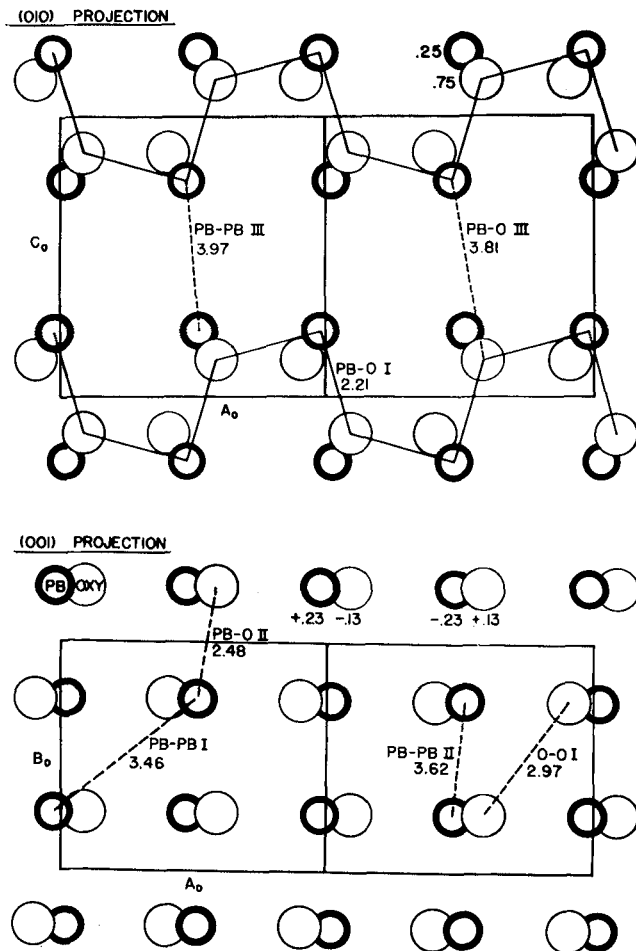
with a much larger coefficient in the c_0 direction than the a_0 and b_0 directions, as in graphite and bismuth.[6] On the other hand, if the characterization of the layers as assemblages of parallel chains is valid, a larger coefficient of thermal expansion would be expected in the b_0 direction than in the a_0 direction. To obtain further understanding of the bonding characteristics, thermal expansion coefficients were measured by high-temperature X-ray diffraction; an attempt was made to correlate them with vaporization characteristics and other structures.

II. Experimental Procedure

Reagent-grade lead monoxide* which contained $85 \pm 3\%$ massicot (the remainder was tetragonal PbO, litharge) was used as-received. X-ray diffraction analyses were made with a recording diffractometer,† using CuKα radiation, a scanning rate of 0.2°2θ/min, and a chart speed of 24 in./h, providing reproducible readings to the nearest 0.005°2θ. A high-temperature diffraction unit‡ powered by a saturable core reactor

Fig. 1. Massicot structure. Atomic coordinates are those of Ref. 2.

Table I. Bond Distances in Massicot*

Bond	No. of bonds	Distance (A)	Designation
Pb–O			
Within layer	1	2.21	I
	1	2.22	
	2	2.48	II
Between layers	1	3.81	III
Pb–Pb			
Within layer	2	3.46	I
	2	3.81	
	2	3.62	II
	2	3.86	
Between layers	2	4.19	
	2	3.97	III
O–O			
Within layer	2	2.97	I
	2	4.41	
	2	3.00	
	2	3.15	

NOTE: $a_0 = 5.489$ Å, $b_0 = 4.775$ Å, $c_0 = 5.891$ Å. Atoms at x, $\frac{1}{4}$, z; $\bar{x}$, $\frac{3}{4}$, $\bar{z}$; $\frac{1}{2}+x$, $\frac{1}{4}$, $\bar{z}$; $\frac{1}{2}-x$, $\frac{3}{4}$, z. For Pb, $x = 0.0208$, $y = 0.25$, and $z = 0.2309$; for O, $x = 0.0886$, $y = 0.25$, and $z = -0.1309$. Space group No. 57, $Pbma$ ($=Pbcm$) (D_{2h}^{11}).
*Calculated from coordinates of Ref. 2.

and a digital set-point controller was used. Radiation from Pt resistance windings symmetrically arranged about the recessed stainless-steel sample holder heated the powder which was packed into it; the sample holder was lined with Al foil so that a circular diffracting area 0.5 in. in diameter was exposed and was mounted on a stainless-steel shaft, which also shielded the controller thermocouple, attached to the rear of the furnace housing. The junction of a sheathed Chromel-Alumel thermocouple was located at the sample surface near the top center of the beam impingement area. The entire water-cooled housing, with Be X-ray windows, was evacuated with a mechanical pump to <0.1 torr to prevent oxidation of the sample to Pb₃O₄.

Aluminum and gold powders, whose thermal expansion coefficients are known,[6] were used as internal standards to adjust the alignment at high temperatures; the powders were sprinkled evenly over the packed sample surface and pressed into place with a glass slide. Diffraction angles of the (200), (020), and (002) lines of massicot (32.63°, 37.85°, and 30.34°2θ, respectively, at 27°C) were measured at each temperature, and the lattice parameters were calculated directly from the corresponding d values. The (111) lines of Al (38.49°2θ at 27°C) and of Au (38.20°2θ at 27°C), corrected for thermal expan-
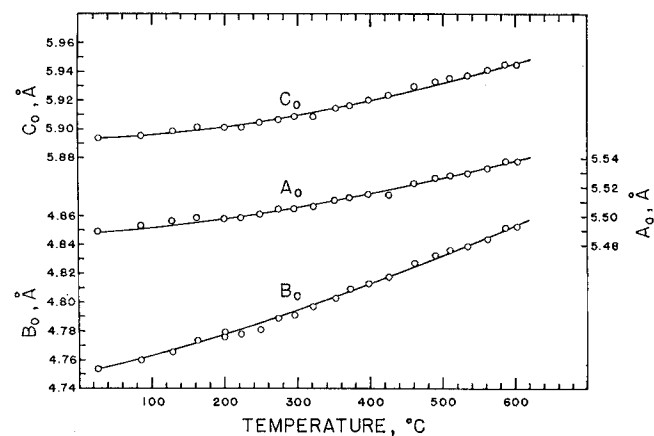
sion, were used for alignment at each temperature. The apparatus was aligned at room temperature over the entire 2θ range of interest; at high temperatures only the transverse adjustment, to compensate for expansion of the mounting shaft and sample holder, was necessary.
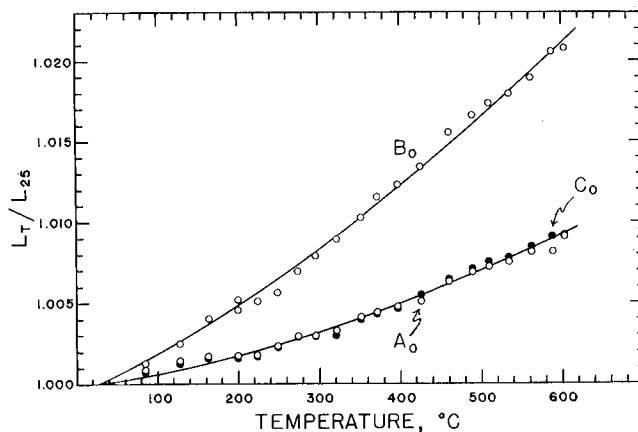
Measurements were made at fixed temperatures between 25° and 603°C, in all cases at a total air pressure <0.1 torr. Diffraction angles could not be measured at higher temperatures because of severe sample shrinkage and deposition of PbO on the Be windows. At each temperature, the transverse position of the sample was adjusted so that the reference line of the internal standard was within 0.005°2θ of the accepted value at that temperature. The three pinacoidal lines of massicot were then scanned and read to the nearest 0.005°2θ. The estimated total accumulated error in measured 2θ values for the lines of massicot is ±0.02°, corresponding to an approximate error of ±0.003 Å in the calculated lattice parameters. Although the geometry of the heating unit corresponds very closely to a blackbody situation and although no line broadening caused by thermal gradients was observed, the error in measured temperature, controlled within a ±1°C range, may be as much as ±5°C because of heat conduction from the resistance windings through the thermocouple sheathing to the junction.

III. Results

The lattice parameters of orthorhombic PbO, plotted as a function of temperature in Fig. 2, were obtained during separate heating and cooling cycles, two with an Al standard and one with Au. The data plotted as L_T/L_{25} vs temperature in Fig. 3, from which the thermal expansion coefficients in Table II were obtained, show that expansion of the b_0 axis is more

Fig. 3. Lattice parameters relative to values at 25°C.

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

Table II. Coefficients of Thermal Expansion of Massicot*

Temp. range (°C)	$\alpha (\times 10^6)$		
	a_0 and c_0	b_0	Unit cell vol
25–100	8.0	25.2	40.8
25–200	9.8	27.8	48.6
25–300	11.7	30.7	54.5
25–400	13.3	33.2	60.0
25–500	14.7	34.9	64.7
25–600	15.9	36.3	68.6

*$L_T = L_{25} (1 + \alpha T)$ or $V_T = V_{25} (1 + \alpha T)$.

than twice that of the a_0 and c_0 axes over the entire temperature range. The expansions of the a_0 and c_0 axes are identical within the limits of experimental error.

The bond distances (designated by Roman numerals in Fig. 1 and Table I) were calculated from unit cell parameters as a function of temperature, assuming no change in atomic coordinates (Fig. 4). This assumption appears to be valid in view of the nearly isotropic expansion observed in the (010) plane. No appreciable changes in relative intensities were observed during heating or cooling over the entire temperature range, indicating no significant shift in atomic coordinates.

Pb–O bond distances I and III reflect the observed expansion in the a_0 and c_0 directions, and distance Pb–O II reflects that in the b_0 direction. The Pb–Pb distances, however, increase with very nearly identical coefficients of expansion, regardless of crystallographic direction. Although Pb–Pb I and II are between chains within a layer, there are components in the a_0 and c_0 directions; Pb–Pb III, between layers, also has components in the a_0 and b_0 directions. The anisotropic expansion observed in the unit cell parameters and the Pb–O distances is thus not exhibited by expansion of the Pb–Pb distances.

IV. Discussion

The thermal expansion characteristics of massicot are not closely correlated with the physical characteristics. Whereas the platy habit, cleavage, and related lubricating properties focus attention on the layerlike aspects of the structure, the thermal expansion data show that the chain-layer concept, as noted by Kay[2] and by Leciejewicz,[3] is important. Isotropic expansion of the Pb–Pb bonds also indicates that Pb–Pb bonding, as suggested by Dickens,[5] is significant and might be important in connection with the electronic properties of lead oxides.

The low thermal expansion coefficient in the a_0 direction compared with that in the b_0 direction also suggests that the zigzag chains are maintained by relatively strong covalent Pb–O bonds and that they might well exist as molecular entities, independent of the massicot structure, in the vapor and liquid phases and in glasses and compounds containing PbO. Several studies support this reasoning. Drowart et al.[7] found by mass-spectrometric techniques that the vapor of massicot consists of neutral Pb_nO_n units, with $n=1$ to 6. They interpreted the thermodynamic data in terms of linear polymer units. It is highly probable that vaporization occurs by removal and fragmentation of chains from the (010) planes of massicot.

Boucher and Peacor,[8] by X-ray analysis, found that alamosite, $PbSiO_3$, is a chain silicate with Pb atoms coordinated with 3 or 4 oxygen atoms located on one side, with two distances in the range 2.2 to 2.3 Å and one or two in the range 2.45 to 2.60 Å; all other Pb–O distances are greater than 2.86 Å. They also called attention to the fact that, although there are no nontetrahedral oxygen atoms in the structure, a continuous spiral of Pb–O–Pb–O... bonds connects the silicate chains in the [010] direction. The striking similarity in bond distances in $PbSiO_3$ and massicot and the similar coordination schemes indicate that the bonding requirements of the lead atom are the same in both structures. The structures of Pb_2SiO_4 and Pb_4SiO_6,
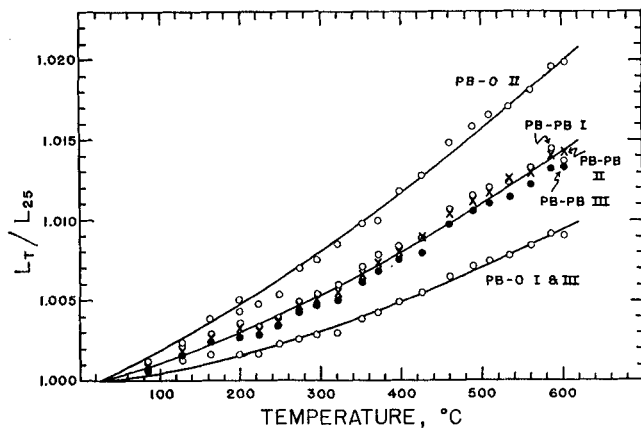

Fig. 4. Interatomic distances relative to values at 25°C.

found in the same system by Geller et al.,[9] have not been analyzed in detail; Pb_4SiO_6 should be particularly interesting in view of the probable existence of nontetrahedral oxygen atoms.

Further evidence for existence of chainlike PbO units is found in available information on the structure of lead silicate glasses, particularly in the work of Mydlar et al.,[10] who observed a radial distribution maximum at 3.8 Å, corresponding to a strong Pb–Pb interaction; the position did not change with increasing Pb content, indicating nonrandom distribution. The data for $PbO \cdot 2SiO_2$ glass were interpreted in terms of a simple, nearly straight chain, those for $PbO \cdot SiO_2$ glass in terms of a twisted or spiral chain, and those for $2PbO \cdot SiO_2$ glass in terms of an even sharper spiral chain. The apparent polymeric characteristics of PbO chains may explain the relatively wide glass-forming range in the system PbO-SiO_2.

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