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Thermal Expansion Of Tetragonal PbO

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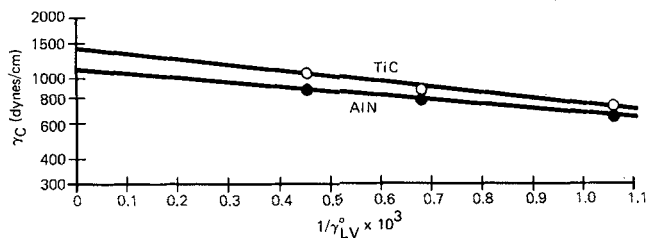


Fig. 4. Critical surface tension as a function of $1/\gamma^{\circ}_{LV}$.

dynes/cm corresponds to a liquid metal with a surface tension of infinity. Thus, a critical surface tension value which lies somewhere between 1083 and 1400 dynes/cm will be equal to the surface energy of TiC with no adsorbed vapor layer. Because the exact value of that critical surface tension cannot be estimated, the averages of 1083 and 1400 dynes/cm may be taken as an estimate of the surface tension of TiC: 1242 ± 158 dynes/cm.* This value is very near the 1190 ± 350 ergs/cm² estimated for TiC at 1100°C by Livey and Murray.¹¹ Similarly, the surface tension of AlN is estimated to be 990 ± 110 dynes/cm. For TiC, the decrease in surface tension resulting from vapor adsorption is about 142 dynes/cm in the case of Cu and about 500 dynes/cm in the case of Al. These values are comparable to the decrease in surface energy of W resulting from adsorption of Cu vapor from 2830 ± 470 to 2230 ± 180 ergs/cm² at 1500°C and of Mo from 2050 ± 370 to 1650 ± 90 ergs/cm² at 1500°C.¹²

V. Conclusions

(1) The surface tension of liquid Ag can be expressed by the equation γ_{LV} (Ag) (dynes/cm) = $1092 - 0.14T$ (°C).

*This value should be adjusted to 1100°C for comparison with the value estimated in Ref. 11. However, since the temperature coefficient of solid surface energy is not well known and is generally assumed to be about 0.1 dyne/cm °C, such a correction will not greatly improve the accuracy of this estimate.

(2) The surface tension of liquid Cu can be expressed by the equation γ_{LV} (Cu) (dynes/cm) = $1462 - 0.27T$ (°C).

(3) The cosine of the contact angle increases linearly with increasing temperature in the systems investigated.

(4) The cosine of the contact angle increases linearly with decreasing surface tension of the liquid sessile drop in the systems investigated.

(5) The critical surface tension for spreading (γ_c) is the surface tension of a solid with adsorbed vapor.

(6) For a given liquid metal, TiC exhibits better wettability than AlN, and γ_c is always greater for TiC than for AlN.

(7) The surface tension of TiC is estimated to be 1242 ± 158 dynes/cm and that of AlN 990 ± 110 dynes/cm.

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Thermal Expansion of Tetragonal PbO

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Thermal expansion of tetragonal PbO, investigated by high-temperature X-ray diffraction in vacuum, is nearly isotropic, with the coefficient in the c_0 direction only slightly greater than that in the a_0 direction. Volume thermal expansion is only slightly greater than in massicot. Retardation of the litharge-massicot transformation is tentatively interpreted as the result of very low oxygen partial pressures caused by catastrophic

oxidation of the stainless-steel sample holder and resulting oxygen scavenging by lead vapor.

I. Introduction

THE thermal expansion characteristics of massicot, the orthorhombic modification of lead monoxide, have been reported¹ and related to the structure. The chain-like arrangement of Pb-O polymeric units within the basal layers was shown to be related to the thermal expansion character-

istics, and reference was made to Pb_nO_n species in the vapor, to the structure of $PbSiO_3$, and to recent structural analyses of lead silicate glasses to indicate the significance of the chain-like units as structural entities.

Litharge, the tetragonal modification, which is structurally similar to massicot, although less complex, is also of interest because of the layer structure and unusual bonding scheme. The structure was first investigated by Dickinson and Friauf,² who used single crystals grown from a potassium hydroxide melt. The structure was established by X-ray diffraction methods as a layer type, with a $Pb-O-Pb-Pb-O \dots$ sequence in the [001] direction. Levi and Natta³ subsequently reported different oxygen coordinates, however, indicating a distorted sodium chloride structure. The structure was again investigated by Moore and Pauling⁴ and by Byström,⁵ who substantiated the results of Dickinson and Friauf. The validity of the Dickinson and Friauf structure has been proven unequivocally by the neutron diffraction study of Leciejewicz.⁶

The structure is shown in Fig. 1, and structural data are given in Table I, with all bond distances less than 5 Å calculated using the unit cell parameters of Swanson and Fuyat.⁷ The structure may be visualized as the cesium chloride type expanded in the [001] direction or, more appropriately, as the fluorite type with alternate oxygen layers absent in the [001] direction. Lead is coordinated with four oxygen atoms at 2.32 Å within the layer rather than with two oxygen atoms at 2.22 and 2.21 Å in the a_0 direction and two at 2.48 Å in the b_0 direction as in massicot. The shortest Pb-O distance between layers is 4.31 Å, compared with 3.81 Å in massicot. Lead-lead distances within the layer are slightly greater than in massicot but those between layers are less. Oxygen-oxygen distances within the layer are appreciably less than in massicot.

Dickens⁸ analyzed the bonding in litharge in terms of hybridized covalent orbitals, as he had done for massicot.⁹ Oxygens are assigned to the sp^3 hybrid state; lead bonds to four oxygens within the layer using two $6p$ orbitals, the $6d_{x^2-y^2}$ orbital, part of the $6s$ orbital, and part of the other $6p$ orbital. Interlayer bonding is attributed to the remainder of the $6s$ orbital and the $6p$ orbital; the lone pair of electrons thus bonds adjacent layers by van der Waals forces.

Thermal expansion was measured, using high-temperature X-ray diffraction methods, to relate expansion to structure and to compare expansion with data for massicot.

II. Experimental Procedure

Litharge was prepared by dissociation of basic lead carbonate* in vacuum at 325°C. X-ray analyses of the dissociation product indicated litharge was the only crystalline phase; line-width measurements indicated well-crystallized material, and weight loss measurements of material heated to 750°C indicated complete dissociation to lead monoxide. X-ray measurements at high temperatures were made with a recording diffractometer,[†] using $CuK\alpha$ radiation with a scanning rate of $0.2^\circ 2\theta/\text{min}$ and a chart speed of 24 in./h. A high-temperature diffraction unit,[‡] evacuated to less than 0.1 torr total air pressure, was used to heat the sample. Experimental procedures were, in all cases, identical with those reported for the study of massicot.¹ Gold and aluminum were used as internal standards for alignment and as liners for the stainless-steel sample holder.

Diffraction angles of the (110) and (002) lines (31.86° and $35.77^\circ 2\theta$, respectively, at 27°C) were measured at each temperature, following alignment on the (111) line of Al or Au,

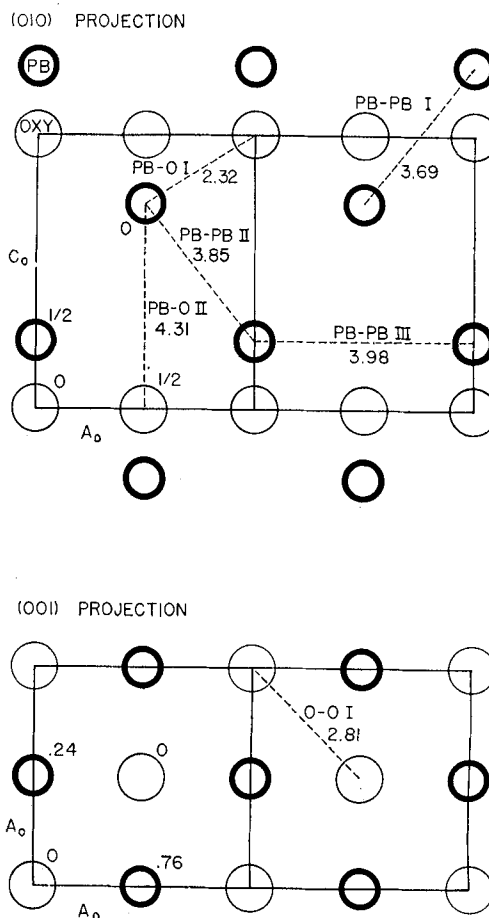


Fig. 1. Litharge structure. Roman numerals indicate bond distances listed in Table I.

Table I. Bond Distances in Litharge*

Bond	No. of bonds	Distance (Å)	Designation
Pb-O			
Within layer	4	2.32	I
Between layers	4	4.31	II
Pb-Pb			
Within layer	4	3.69	I
Between layers	4	3.98	III
O-O			
Within layer	4	2.81	I

NOTE: $a_0=3.975$ Å, $c_0=5.023$ Å. Lead atoms at $0, \frac{1}{2}, u; \frac{1}{2}, \frac{1}{2}, 0$. Oxygen atoms at $0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0$. For all atoms $u=0.2385$. Space group No. 129, $P 4/nmm (D_{4h}^1)$.

*Calculated from coordinates of Ref. 4.

and a_0 and c_0 parameters were calculated directly from corresponding d values. Measurements were made at fixed temperatures between 25° and 657°C, in all cases at a total air pressure of less than 0.1 torr. The specimen was held at each fixed temperature for at least 10 min before the parameters were measured.

III. Results

The lattice parameters, shown as functions of temperature in Fig. 2, were measured during three runs, one with Au as an internal standard and two with Al. The curves are composites of measurements at fixed temperatures during heating and cooling cycles. Lattice parameters relative to values

*Matheson, Coleman, and Bell, East Rutherford, N. J.

†XRD-5, General Electric Co., Schenectady, N. Y.

‡E & A Refractex I, Electronics & Alloys, Inc., Englewood, N. J.

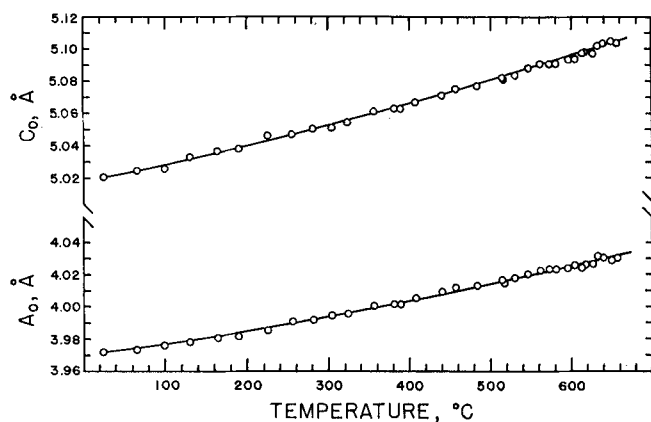


Fig. 2. Lattice parameters of litharge as functions of temperature.

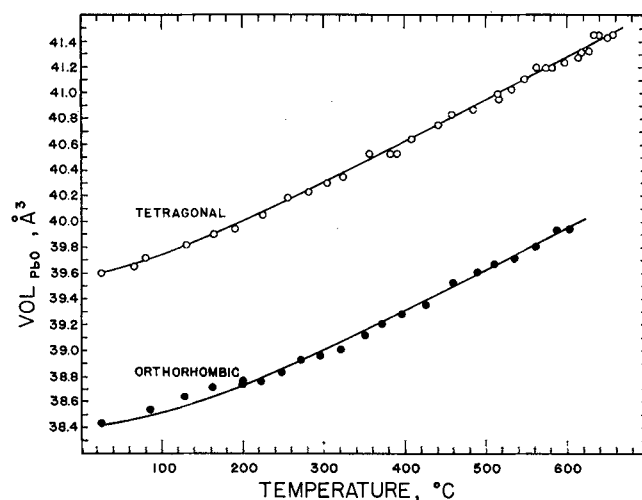


Fig. 4. Volumes of litharge and massicot/PbO unit as functions of temperature.

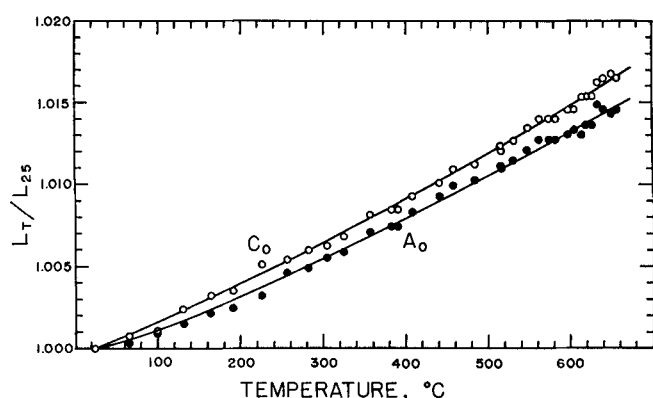


Fig. 3. Lattice parameters relative to values at 25°C.

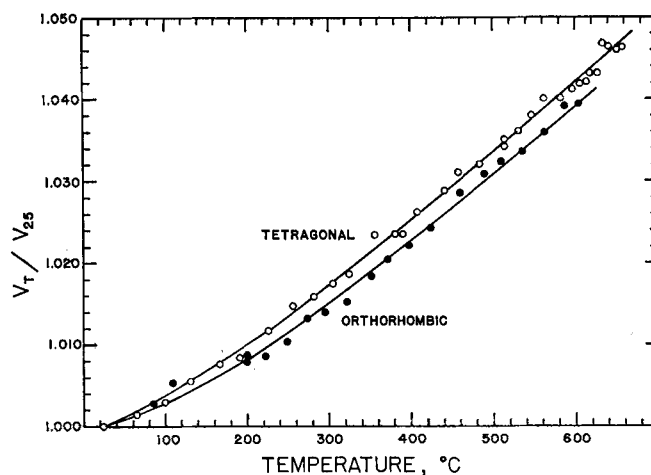


Fig. 5. Unit cell volumes of litharge and massicot relative to values at 25°C.

Table II. Coefficients of Thermal Expansion of Litharge*

Temp. range (°C)	$\alpha \times 10^6$		Unit cell vol.
	a_0	c_0	
25-100	13.3	21.3	49.3
25-200	17.1	22.3	56.0
25-300	19.3	23.3	61.1
25-400	20.8	24.3	65.9
25-500	22.1	24.8	70.1
25-600	23.0	25.6	73.0
25-650	23.4	25.9	74.6

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

at 25°C are shown in Fig. 3, and measured coefficients of thermal expansion are listed in Table II. Thermal expansion is nearly isotropic, with expansion of the c_0 axis only slightly greater than that of the a_0 axes. Volumes per PbO unit at each temperature for both litharge and massicot¹ were calculated from measured unit cell parameters (Fig. 4); volumes relative to values at 25°C are shown in Fig. 5. The volume expansion of litharge is only slightly greater than that of massicot.

Although the litharge-massicot transformation temperature has not been well established, White *et al.*¹⁰ indicated that values in the literature range from 475° to 585°C and that the transformation is sluggish and pressure-sensitive. It was ob-

served in the present study that litharge is stable well above the reported range. At a total pressure of 0.12 torr, measured approximately with a thermocouple gage, massicot lines were first observed in the diffraction pattern at 657°C. After 16 h at that temperature, the sample contained approximately 70% massicot. At a pressure of 0.09 torr, massicot formed in detectable amounts at 700°C, but the transformation rate was very low. At this point, the goniometer was oscillated over the (110) line of litharge and the (200) line of massicot at 2°2 θ /min with the chart running. After 20 min, the vacuum pump was switched off and scanning was continued. The peak heights were measured and plotted versus time, with approximate pressures, read from the thermocouple gage, noted (Fig. 6). The admission of air produced a very rapid increase in the transformation rate, so that only massicot remained after approximately 10 min.

IV. Discussion

The nearly isotropic thermal expansion of litharge is not expected on the basis of the layer structure and observed

physical properties. The coefficients of thermal expansion of the Pb–Pb distances are nearly the same as were observed for massicot. The Pb–O coefficients in litharge are intermediate between those observed in the b_c direction in massicot and those in the a_c and c_c directions. The volume coefficients of thermal expansion in these modifications are, consequently, nearly equal.

In both massicot and litharge, the thermal expansion of Pb–Pb bonds is very nearly isotropic; it appears, therefore, that Pb–Pb bonding is the controlling structural variable. The litharge structure is such that expansion of the Pb–O bonds is necessarily isotropic. The massicot structure is unusual in that isotropic expansion of Pb–Pb bonds, concurrent with highly anisotropic expansion of Pb–O bonds, is possible. The litharge–massicot transformation is unusual in that the high-temperature modification, massicot, has the lower symmetry and is the denser phase at room temperature. Density has not been measured at high temperatures, but lead vacancies in massicot (near 3%) could produce convergence of the density curves for the two phases at the transformation temperature. Apparent densities, calculated from unit cell parameters, would not reflect such a situation, however, so the question must remain open. The PbO structures are highly covalent, however, and the transformation involves drastic changes in orbital configurations. The transformation probably represents a structural compromise whereby, on expansion of the Pb–O bonds within the layer to a maximum, the Pb–O bonding is shifted to a more molecular arrangement. The Pb–Pb bonds, although changed slightly in length, remain essentially the same; consequently, the volume coefficients of expansion of the phases are nearly the same.

The persistence of litharge to temperatures well above the range of reported transformation temperatures seems to be peculiar to the experimental conditions of the present study. In separate experiments, litharge transformed readily at 500°C at pressures as low as 10^{-5} torr. Coussaert *et al.*¹¹ reported transformation at 490°C in a nitrogen atmosphere in which the oxygen partial pressure was undoubtedly lower than that in the present study. No reaction appeared to have occurred with the sample holder liners or internal standards used in this work. The transformation is unaffected, moreover, by the composition of the liner, Al or Au. It was observed, however, that the stainless-steel sample holder and supporting shaft were corroded. Sawyer¹² reported that lead oxide vapor causes catastrophic oxidation of stainless steel in the temperature range of the present study. The mechanism is not clearly defined, but weight gain measurements indicated no direct reaction between steel and lead oxide, but rather acceleration of oxidation. The lead monoxide vapor thus appears to act as a highly reactive oxygen donor and the steel as an oxygen getter. Lead vapor, formed by removal of oxygen, could then serve as an oxygen scavenger. Oxygen partial pressure in the system could have been very low even though the total pressure was near 0.1 torr.

Although stabilization of litharge by pump oil impurities cannot be dismissed, the results suggest that the transformation depends on oxygen partial pressure. This dependence, in turn, suggests that the O:Pb ratios are different in the two phases. In such a system the low-temperature phase is normally the most highly oxidized; a lower oxygen partial pressure thus favors the high-temperature phase. The results of this study indicate that the opposite behavior occurred: substoichiometric litharge was formed at a very low oxygen partial pressure, and the transformation was eliminated or shifted to a higher temperature. Similar behavior was observed in WO_3 by Ackermann and Sorrell.¹³ Stoichiometric

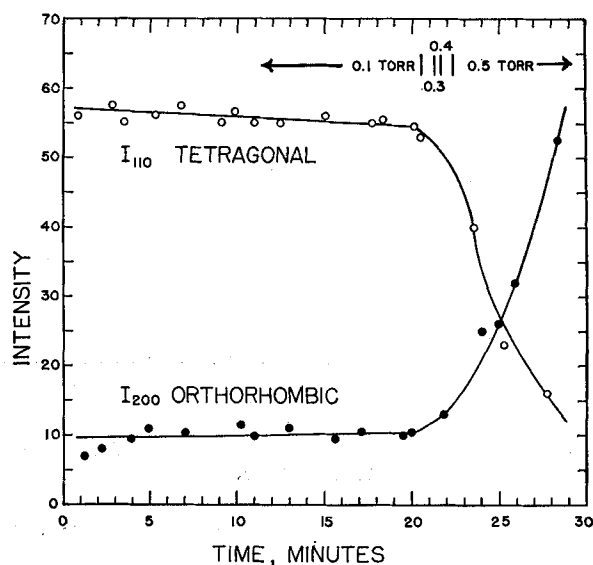


Fig. 6. Intensities, in arbitrary units, of diagnostic X-ray lines of litharge and massicot as functions of time and approximate total pressure at 700°C.

WO_3 transforms from orthorhombic to tetragonal symmetry, with an appreciable range of two-phase coexistence and hysteresis, between 710° and 770°C. The substoichiometric species $WO_{2.96}$, however, retains orthorhombic symmetry to at least 900°C.

Detailed investigation of the transformation is beyond the scope and purpose of the present study; this and other puzzling aspects of litharge–massicot relations require further investigation.

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