Trends in the Stability of Ternary Oxides: Systems M-Pb-O (M = Ca, Sr, Ba)

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ABSTRACT

Recent experimental investigations of phase equilibria and thermodynamic properties of the systems M-Pb-O, where M = Ca, Sr or Ba, indicate a regular increase in thermodynamic stability of ternary oxides, $MPbO_3$ and M_2PbO_4, with increasing basicity of the oxide of the alkaline-earth metal. Number of stable interoxide compounds at 1100 K in the systems M-Pb-O (M = Mg, Ca, Sr, Ba) increases in unit increments from Mg to Ba. In this paper, experimentally determined standard Gibbs energies of formation of M_2PbO_4 (M = Ca, Sr, Ba) and $MPbO_3$ (M = Sr, Ba) from their component binary monoxides and oxygen gas are combined with an estimated value for $CaPbO_3$ to delineate systematic trends in thermodynamic stability of the ternary oxides. The trends are interpreted using concepts of tolerance factor and acid-base interactions. All the ternary oxides in these systems contain lead in the tetravalent state. The small Pb^{4+} ions polarize the surrounding oxygen ions and cause the formation of oxyanions which are acidic in character. Hence, the higher oxidation state of lead is stabilized in the presence of basic oxides of alkaline-earth group. A schematic subsolidus temperature-composition phase diagram is presented for the system BaO-PbO-O_2 to illustrate the change in oxidation states in binary and ternary oxides with temperature.

1. INTRODUCTION

The ternary systems M-Pb-O (M = Ca, Sr, Ba) have evoked considerable interest in recent times. The ternaries Ca-Pb-O and Sr-Pb-O are subsystems of the multinary Bi-Pb-Sr-Ca-Cu-O, which contains several superconducting oxides. The compound Ca_2PbO_4 has been identified during the early stages of the reaction leading to the formation of the high-T_c oxide phases /1/. The solid solution $(Ca_{1-y}Sr_y)_2PbO_4$ forms subsequently during synthesis from component oxides or carbonates /2/. Hence, it is useful to know the thermodynamic stability of these ternary oxides for precise control and optimization of high-temperature chemical processing routes for oxide superconductors. Although the system Ba-Pb-O is not related to high-T_c oxide superconductors, the ternary oxides Ba_2PbO_4, $Ba_4Pb_3O_{10}$, and $BaPbO_3$ have fascinating electronic properties /3,4/. Furthermore, it is interesting to explore systematic trends in thermodynamic properties as a function of the properties of the alkaline-earth element.

2. PHASE DIAGRAMS: ISOTHERMAL SECTIONS

The isothermal sections of the ternary phase diagrams at 1100 K of the systems M-Pb-O (M = Ca,

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Sr, Ba) composed from the results of recent studies /5, 6,7/ are presented in Figure 1. The three phase diagrams have a similar topology. The stable binary oxides, MO and PbO, coexist without any significant mutual interaction in all the three systems. There is no liquid phase observed along the join MO-PbO in the three systems. Intermetallic compounds along the binary M-Pb have similar compositions; M_2Pb and M_5Pb_3 for M = Ca, Sr, Ba, and MPb for M = Ca, Ba. For the system Sr-Pb, Sr_5Pb_4 is identified instead of SrPb. In all the three systems, liquid alloys are formed near the terminal ends of the binary M-Pb. The extent of liquid phase at the M-rich side increases gradually from Ca to Ba. At the Pb-rich side of the binaries, composition of alloy is approximately the same for all the three systems. All intermetallic compounds and liquid alloys are in equilibrium with MO. All the ternary oxides are in equilibrium with pure oxygen. There are six phase fields in which three condensed phases coexist in the system Ca-Pb-O, seven in Sr-Pb-O, and eight in Ba-Pb-O. All ternary oxides contain Pb in tetravalent state. Surprisingly, there is no ternary oxide with lead in divalent state. It is clear from the phase diagrams that the ternary oxides can be synthesized from the stable binary monoxides only in atmospheres containing oxygen. Sealed tube techniques cannot be used for the synthesis of ternary oxides from their stable binary monoxides. The isothermal sections of the phase diagrams for the systems M-Pb-O identify suitable three-phase fields which can be used for the determination of thermodynamic properties of the ternary oxides with the aid of solid-state cells. Table 1 summarizes the three-phase fields chosen as measuring electrodes in emf measurements /5,6,7/.

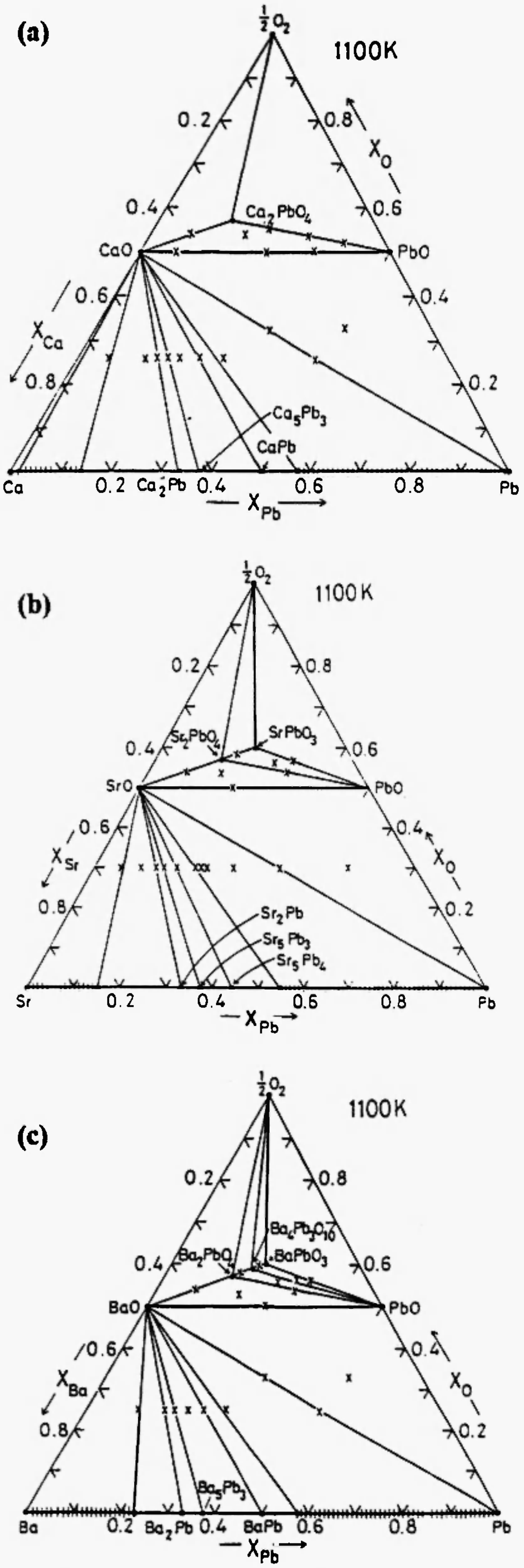

Fig. 1: Isothermal sections of the ternary systems M-Pb-O (M = Ca, Sr, Ba) at 1100 K (a) Ca-Pb-O /5/ (b) Sr-Pb-O /6/ (c) Ba-Pb-O /7/.

3. TERNARY OXIDES

The number of ternary oxides in the systems M-Pb-O (M = Mg, Ca, Sr, Ba) at 1100 K is displayed as a bar diagram in Figure 2. As basicity of alkaline-earth metal increases from Mg to Ba, number of ternary oxides also increases linearly. Table 2 summarizes crystallographic data for the compounds M_2PbO_4 and $MPbO_3$ (M = Ca, Sr, Ba). There is no experimentally

Table 1
Ternary phase mixtures chosen as measuring electrodes for emf measurements /5, 6, 7/

System	Phase fields	Property measured
Ca-Pb-O	$CaO + PbO + Ca_2PbO_4$	Chemical Potential of Oxygen
Sr-Pb-O	$SrO + PbO + Sr_2PbO_4$ $Sr_2PbO_4 + PbO + SrPbO_3$	Chemical Potential of Oxygen
Ba-Pb-O	$BaO + PbO + Ba_2PbO_4$ $Ba_2PbO_4 + PbO + Ba_4Pb_3O_{10}$ $Ba_4Pb_3O_{10} + PbO + BaPbO_3$	Chemical Potential of Oxygen
	$BaPbO_3 + PbO + O_2$	Chemical Potential of BaO

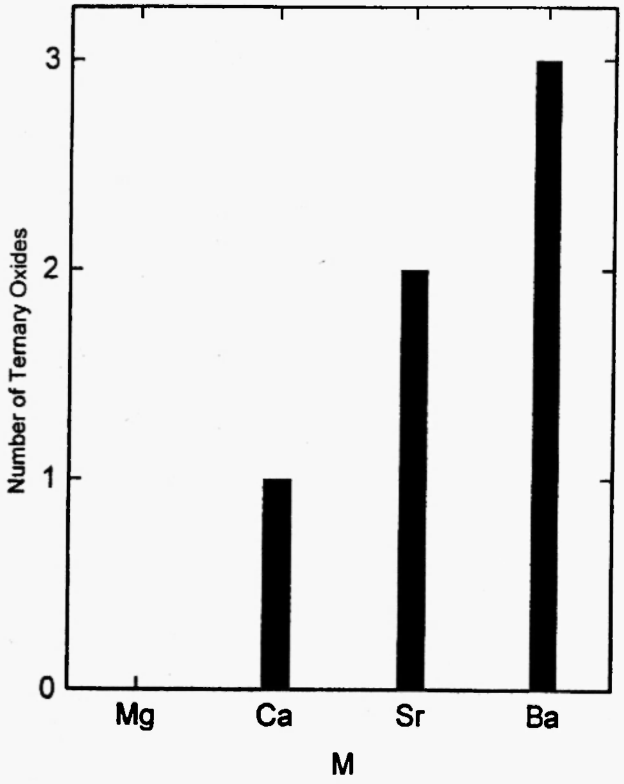

Fig. 2: A bar graph indicating the number of ternary oxides formed in the systems M-Pb-O (M = Mg, Ca, Sr, Ba) at 1100 K.

Table 2
Crystallographic data for M_2PbO_4 and $MPbO_3$ (M = Ca, Sr, Ba)

Ternary oxide	Lattice parameters						Structure / Space group	Ref.
	a (nm)	b (nm)	c (nm)	α	β	γ		
Ca_2PbO_4	0.5836	0.9745	0.3381				Orthorhombic / Pbam	/10/
Sr_2PbO_4	0.6159	1.0080	0.3502				Orthorhombic / Pbam	/10/
Ba_2PbO_4	0.4305		1.3273				Tetragonal / I4/mmm	/11/
$CaPbO_3$	0.5688		1.5328			120	Hexagonal / $R\bar{3}$ or Trigonal	/12/
	0.6074			55.84				
$SrPbO_3$	0.5860	0.5957	0.8325				Orthorhombic / Pbnm	/13/
$BaPbO_3$	0.4265						Cubic / Pm3m	/11/

identified ternary oxide in the system Mg-Pb-O at 1100 K.

It is interesting to interpret the trend in structural stability of M_2PbO_4 and $MPbO_3$ as a function of ionic size of the alkaline-earth element. The compound M_2PbO_4 can be regarded as perovskite-like single $MPbO_3$ layers separated by MO layers of the rock-salt type. The distortion from ideal cubic perovskite structure is represented by a parameter called tolerance factor (t), which is defined for a perovskite oxide with the general formula ABO_3 as:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \tag{1}$$

where r_A, r_B and r_O are the ionic radii of A, B and O ions respectively. The values of ionic radii are chosen according to the valence state and coordination number of the particular ion /8/. For all compounds with perovskite-type structure, the value of t lies between 0.8 and 1. The value of t must be greater than 0.89 for the 'ideal' cubic perovskite structure /9/. The tolerance factor for the compound Mg_2PbO_4 calculated using Shannon's ionic radii /8/ is ($t \approx$) 0.72, well below the perovskite stability limit assuming Sr_2PbO_4-type crystal structure /10/ for Mg_2PbO_4. For the compounds Ca_2PbO_4 and Sr_2PbO_4, a similar estimation of t gives values of 0.8 and 0.85, respectively. The compound Ba_2PbO_4 in the homologous series $Ba_{1+n}Pb_nO_{3n+1}$ (n = 1) has K_2NiF_4-type structure /11/ with $t \approx 0.94$. Thus, structural stability of the ternary oxides of general formula M_2PbO_4 increases from Mg to Ba with tolerance factor.

The oxides $MPbO_3$ (M = Ca, Sr, Ba) have an interesting sequence of crystal structures. High-pressure phase $CaPbO_3$ has been indexed on both trigonal and hexagonal systems /12/. As the size of the alkaline-earth element increases, the crystal structures of $SrPbO_3$ /13/ and $BaPbO_3$ /11/ becomes more symmetric; $SrPbO_3$ is orthorhombic and $BaPbO_3$ is cubic. The perovskite tolerance factor is nearly 0.99 for $BaPbO_3$.

Even though the correlation between tolerance factor and ionic radii of the alkaline-earth metal provides a qualitative explanation in the relative stabilities of M_2PbO_4 and $MPbO_3$, knowledge of their standard Gibbs energies of formation is often beneficial for a quantitative assessment of their thermal stability. In the quaternary system CaO-SrO-PbO-O, no quaternary oxides have been identified /14/. However, there is complete solid solution between Ca_2PbO_4 and Sr_2PbO_4 at 1100 K. The solid solubility of $CaPbO_3$ in $SrPbO_3$ is restricted to 2 mol % at 1100 K. Therefore, phase diagram for similar quaternary systems may be computed in principle from data on binaries and ternaries.

4. THERMODYNAMIC PROPERTIES

The thermodynamic properties of ternary oxides M_2PbO_4 (M = Ca, Sr, Ba) and $MPbO_3$ (M = Sr, Ba) have been measured using solid-state cells based on $(Y_2O_3)ZrO_2$ as the solid electrolyte. A novel three-electrode design of the cell was employed in the recent studies to minimize polarization and improve accuracy of the measured data /5,6,7/. The thermodynamic properties of the compounds M_2PbO_4 were measured using the solid-state cell:

$$\text{Pt, MO + PbO + } M_2PbO_4 \,||\, (Y_2O_3)ZrO_2 \,||\, O_2 \text{ (0.1 MPa), Pt} \tag{I}$$

The standard Gibbs energy of formation of M_2PbO_4 (M = Ca, Sr, Ba) from component binary monoxides and oxygen gas is defined by the reaction:

$$2\,MO + PbO + 1/2\,O_2 \rightarrow M_2PbO_4 \tag{2}$$

Since MO, PbO and M_2PbO_4 are present at unit activities, the standard Gibbs energy change is related to the chemical potential of oxygen corresponding to the three-phase equilibrium /5,6,7/.

$$\Delta_{(2)}G^0 = 1/2\,\Delta\mu_{O_2} = -2\,FE_I \tag{3}$$

where E_I is the emf of cell I and F is the Faraday constant. The standard Gibbs energies of formation of $SrPbO_3$ is determined by combining the measured oxygen chemical potential in the ternary phase field Sr_2PbO_4 + PbO + $SrPbO_3$ with standard Gibbs energies of formation of Sr_2PbO_4 /6/. The cell used can be written as:

$$\text{Pt, } Sr_2PbO_4 + PbO + SrPbO_3 \,||\, (Y_2O_3)ZrO_2 \,||\, O_2 \text{ (0.1 MPa), Pt} \qquad \text{(II)}$$

The standard Gibbs energy of formation of $SrPbO_3$ according to the reaction:

$$SrO + PbO + 1/2\ O_2 \rightarrow SrPbO_3 \qquad (4)$$

is obtained from the emf of the two cells:

$$\Delta_{(4)}G^0 = -\ F(E_I + E_{II}) \qquad (5)$$

In the system Ba-Pb-O, the chemical potentials of oxygen in the three-phase fields Ba_2PbO_4 + PbO + $Ba_4Pb_3O_{10}$ and $Ba_4Pb_3O_{10}$ + PbO + $BaPbO_3$ were also measured /7/.

$$\text{Pt, SS, } Ba_2PbO_4 + PbO + Ba_4Pb_3O_{10} \,||\, (Y_2O_3)ZrO_2 \,||\, O_2\text{, Pt} \qquad \text{(III)}$$

$$\text{Pt, SS, } Ba_4Pb_3O_{10} + PbO + BaPbO_3 \,||\, (Y_2O_3)ZrO_2 \,||\, O_2\text{, Pt} \qquad \text{(IV)}$$

Since Pt lead reacts with BaO, stainless steel (SS) contact was used for the measuring electrode. Combining the emf of three cells (I, III, and IV), incorporating oxide electrolytes, the Gibbs energy of formation of $BaPbO_3$ was obtained /7/.

$$\Delta G^0_{BaPbO_3} / \text{J mol}^{-1} = -165{,}960 + 87.47\ T/\text{K} \ (\pm 200) \qquad (6)$$

Thermodynamic data for $BaPbO_3$ determined from oxide solid-state cells were cross-checked by independently measuring the chemical potential of BaO in the three-phase field $BaPbO_3$ + PbO + O_2 using a solid-state cell based on BaF_2 as the solid electrolyte /7/.

$$\text{SS, } O_2 \text{ (26.2 Pa)} + BaO \,||\, BaF_2 \,||\, BaPbO_3 + PbO + O_2 \text{ (26.2 Pa), SS} \qquad \text{(V)}$$

Temperature dependent expressions for the standard Gibbs energies of formation of ternary oxides M_2PbO_4 (M = Mg, Ca, Sr, Ba) and $MPbO_3$ (M = Ca, Sr, Ba) are presented in Table 3. The standard Gibbs energy of formation of $CaPbO_3$ is estimated from information available in the literature /12, 14/.

Clement *et al.* /12/ reported high-pressure synthesis of $CaPbO_3$ at 693 K and 100 atm pressure of oxygen gas. Below 100 atm pressure, the phases Ca_2PbO_4 and Pb_3O_4 were detected. The corresponding reaction for the formation of $CaPbO_3$ can be written as:

$$3\ Ca_2PbO_4 + Pb_3O_4 + O_2 \rightarrow 6\ CaPbO_3 \qquad (7)$$

Standard Gibbs energy change ($\Delta_{(7)}G^0$) for the above reaction at 693 K is 26,530 J mol^{-1} under the synthesis conditions. Recent electrochemical measurements /5/ provide accurate value for the standard Gibbs energies of formation of Ca_2PbO_4 and Pb_3O_4 from component binary monoxides and oxygen gas as a function of temperature. By combining these thermodynamic data with the estimated value of $\Delta_{(7)}G^0$, standard Gibbs energy of formation of $CaPbO_3$ from component binary oxides and oxygen gas at 693 K is obtained. The average value of standard entropy change for the formation of $SrPbO_3$ and $BaPbO_3$, reported in recent thermodynamic measurements /6,7/, is used to extrapolate the standard Gibbs energy of formation of $CaPbO_3$ from 693 K to 1100 K. The estimated value corresponds to 6.81 kJ mol^{-1} at 1100 K.

The above estimation can be cross-checked using the recently determined phase diagram and thermodynamic data for the system CaO-SrO-PbO-O /14/ at 1100 K. The calcium-rich solid solution, $(Ca_{1-y}Sr_y)_2PbO_4$, characterized by y = 0.255, is in equilibrium with $(Ca_{0.02}Sr_{0.98})PbO_3$. The tie line connecting these compositions is defined by the following intercrystalline ion exchange reaction:

$$Ca_2PbO_4 + 2\ SrPbO_3 \rightarrow Sr_2PbO_4 + 2\ CaPbO_3 \qquad (8)$$

The standard Gibbs energy change for the above reaction is,

$$\Delta_{(8)}G^0 = -RT \ln\left[\frac{a^2_{CaPbO_3} \times a_{Sr_2PbO_4}}{a_{Ca_2PbO_4} \times a^2_{SrPbO_3}}\right] \qquad (9)$$

Activities of components in the solid solution $(Ca_{1-y}Sr_y)_2PbO_4$ have been determined /14/. At 1100 K, activities of the components, Ca_2PbO_4 and Sr_2PbO_4, in the solid solution $(Ca_{1-y}Sr_y)_2PbO_4$ at y = 0.255 are 0.7056 and 0.366, respectively. The activity of $CaPbO_3$ in $SrPbO_3$ at 2 mol % is estimated as 0.06. The activity of solvent $SrPbO_3$ is assumed to be Raoultian, $a_{SrPbO_3} = 0.98$ /14/. The activity coefficient of $CaPbO_3$ at infinite dilution in $SrPbO_3$ is estimated as 3.0 based on systematics of solid solutions in the system Ca-Pb-O. The activity coefficient of CaO in SrO is 8.0, and the activity coefficient of $CaPb_{0.5}O_2$ in $SrPb_{0.5}O_2$ is 4.1, each at infinite dilution at 1100 K /14/. The activity coefficient decreases gradually as the mixing of species Ca and Sr is modulated by the presence of Pb. From the value of $\Delta_{(8)}G^0$ and ΔG^0 for formation reactions of Ca_2PbO_4 /5/, Sr_2PbO_4 /6/ and $SrPbO_3$ /6/ at 1100 K, the standard Gibbs energy of formation of $CaPbO_3$ from component binary oxides and oxygen gas is estimated as 7.94 kJ mol^{-1}. This value is found to be in good agreement with that estimated from high pressure synthesis conditions. The average value, selected to represent the property of $CaPbO_3$, is given in Table 3.

For comparison of the stability of these ternary oxides, standard Gibbs energies of formation of each ternary oxide at 1100 K is plotted as a function of row number of the alkaline-earth element (M) in Figures 3 and 4. Within experimental uncertainty, the variation of standard Gibbs energy of formation is linear for the ternary oxide M_2PbO_4 (M = Ca, Sr, Ba) as evident from Figure 3. From the linear trend, the standard Gibbs energy of formation of Mg_2PbO_4 according to reaction (2) is 13 kJ mol^{-1} at 1100 K. The trend suggests that Mg_2PbO_4 is unstable at 1100 K, although it would become stable at lower temperatures. The compound can be prepared at 1100 K at pressures above 17 atm of oxygen gas. For compounds belonging to the family of $MPbO_3$, the variation of standard Gibbs energy of formation is mildly nonlinear (Figure 4).

The trend in thermodynamic stability of these ternary oxides can be explained in terms of acid-base interactions. According to Lux and Flood, an acid is defined as an oxide ion acceptor and a base as an oxide ion donor /15/. The Lux-Flood definition of acids and bases is particularly useful to study high temperature anhydrous systems involving ceramics and slags. When a given element forms several oxides, the oxide of the element in the highest formal oxidation state (usually the more covalent) is more acidic. The ionic radii of Pb^{2+} and Pb^{4+} are 0.119 and 0.0775 nm respectively /8/. The smaller Pb^{4+} ions will polarize the surrounding oxygen ions and induce greater covalency in Pb-O bonds. This leads to formation of oxyanions of lead which are essentially acidic in character. Thus PbO_2 exhibits strong acidic properties, whereas PbO is a base, as judged from its interaction with known acidic oxides

Table 3

Standard Gibbs energies of formation of ternary oxides M_2PbO_4 (M = Mg, Ca, Sr, Ba) and $MPbO_3$ (M = Ca, Sr, Ba)

Ternary oxide	**ΔG^0 (*T*)/ J mol^{-1}**	**ΔG^0 (1100K) / J mol^{-1}**
$Mg_2PbO_4^{*}$	-90,675 + 94.25 *T* / K	13,000
Ca_2PbO_4	-128,340 + 93.21 *T* / K (±200)	-25,809
Sr_2PbO_4	-168,650 + 97.87 *T* / K (±330)	-60,993
Ba_2PbO_4	-202,640 + 91.67 *T* / K (±400)	-101,803
$CaPbO_3^{**}$	-92,594 + 90.885 *T* / K	7,380
$SrPbO_3$	-141,925 + 94.30 *T* / K (±230)	-38,195
$BaPbO_3$	-165,960 + 87.47 *T* / K (±200)	-69,743

* The value for Mg_2PbO_4 is estimated by linear extrapolation (Figure 3).

** Estimated from high pressure data on synthesis (Clément *et al.* /12/) and phase relations in the system CaO-SrO-PbO-O /14/ as explained in the text.

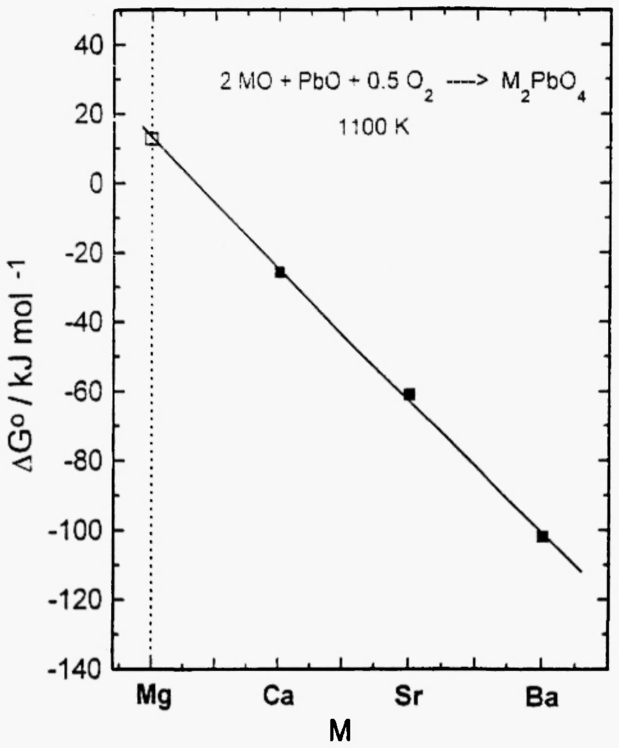

Fig. 3: Comparison of the standard Gibbs energy of formation of M_2PbO_4 (M = Ca, Sr, Ba) at 1100 K. The value for Mg_2PbO_4 can be estimated by linear extrpolation.

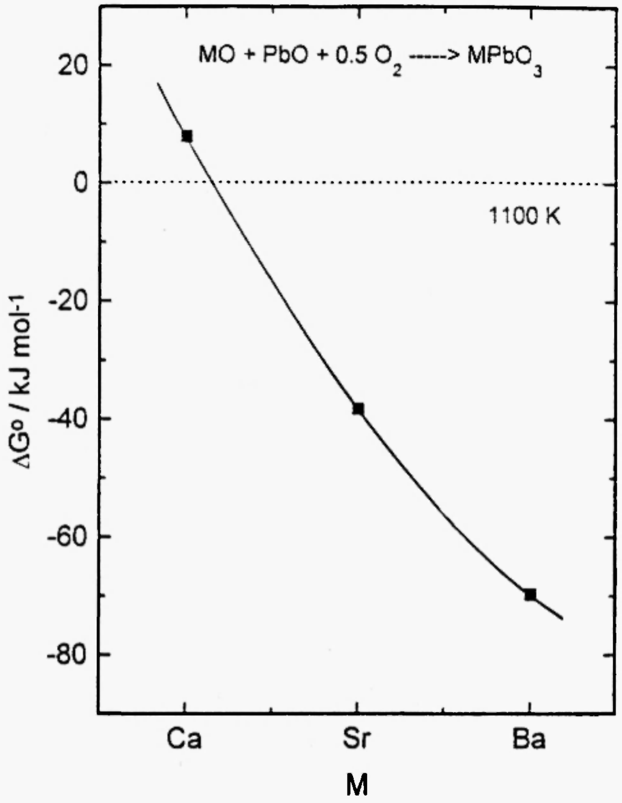

Fig. 4: Comparison of standard Gibbs energy of formation of $MPbO_3$ (M = Ca, Sr, Ba) at 1100 K. The value for $CaPbO_3$ is estimated as explained in the text.

such as SiO_2, B_2O_3 and P_2O_5. The formation of strong compounds in the pseudo-binary MO-PbO_2 (M = Ca, Sr, Ba) and the absence of compounds in the join MO-PbO can be understood in the term of acidic nature of PbO_2 in contrast to the basic character of PbO. Increasing stability of the ternary oxide of a defined stoichiometry with basicity of the alkaline-earth oxide also confirms the acid-base interaction between PbO_2 and MO (M = Ca, Sr, Ba). Similarly, SrO and BaO are known to stabilize Bi^{5+} ions in their ternary oxides with Bi_2O_3 in air or oxygen. The oxides MgO and CaO are not sufficiently basic to stabilize Bi^{5+} ions in ternary oxides at high temperatures /16, 17/. These findings can be generalized to oxides of elements from groups 3 to 5 of the periodic table which exhibit multiple valency. The higher oxidation states of these elements will be stabilized in binary oxides and slags containing oxides which are strongly basic.

5. SCHEMATIC SUBSOLIDUS PHASE DIAGRAM FOR THE REGION BaO-PbO-O

Compared to the ternary oxides in the systems CaO-PbO-O /5/ and SrO-PbO-O /6/, those belonging to BaO-PbO-O system have the highest decomposition temperatures. In this system, there are three ternary oxides, Ba_2PbO_4, $Ba_4Pb_3O_{10}$, and $BaPbO_3$. The highest temperature shown in the schematic three-dimensional sketch (Figure 5) is just above the solid-state decomposition temperature of $Ba_4Pb_3O_{10}$. Among the three ternary compounds in this system, $Ba_4Pb_3O_{10}$ has the lowest thermal stability. It decomposes by a solid state reaction to Ba_2PbO_4 and $BaPbO_3$. The additional ternary phase fields encountered below the decomposition temperature of $Ba_4Pb_3O_{10}$ are $BaPbO_3$ + $Ba_4Pb_3O_{10}$ + liquid and $Ba_4Pb_3O_{10}$ + Ba_2PbO_4 + PbO.

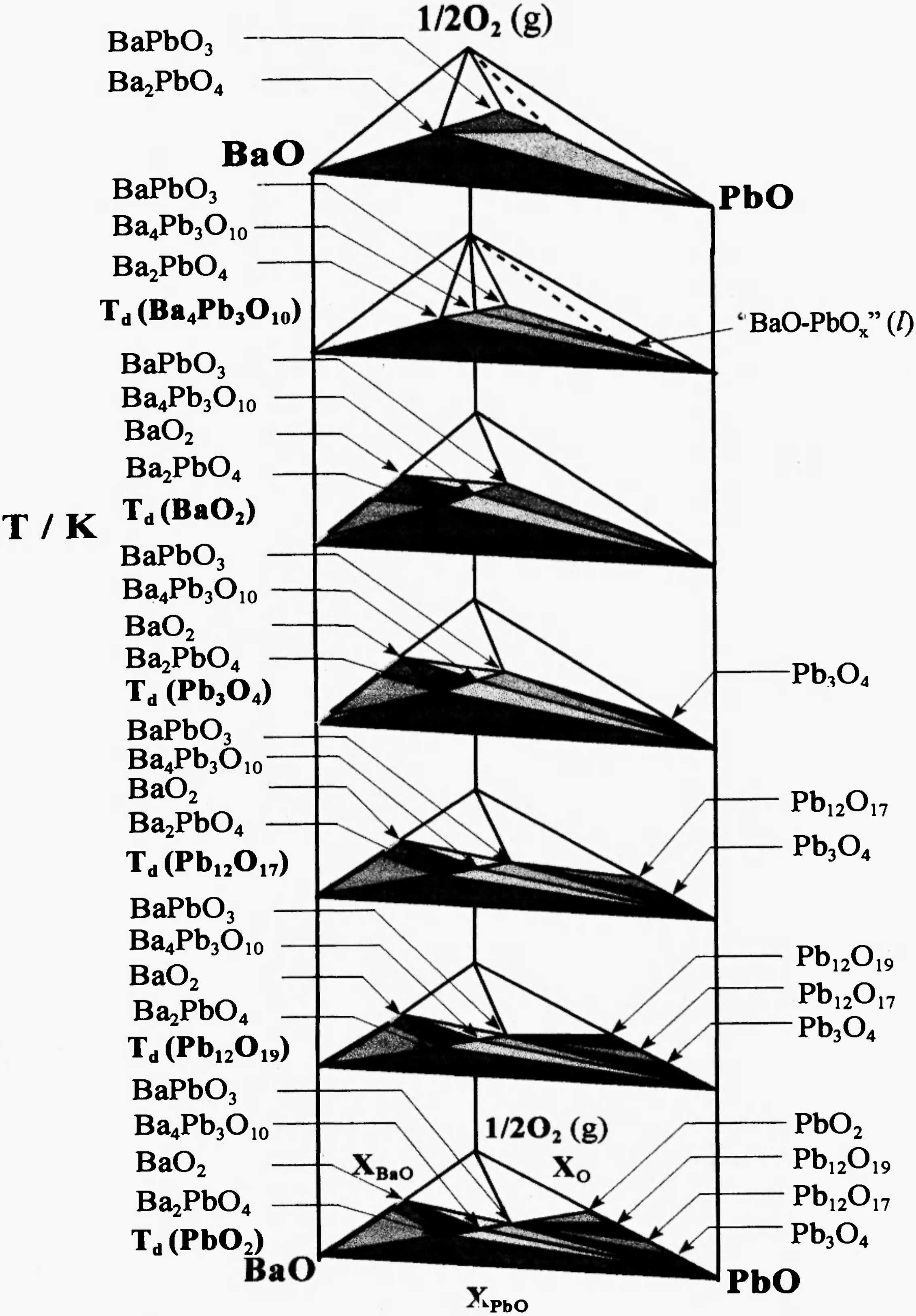

Fig. 5: Schematic subsolidus temperature-composition phase diagram for the system BaO-PbO-O.

On lowering the temperature further, the peroxide phase BaO_2 appears. The peroxide phase, BaO_2, has a very high thermal stability (T_d = 1064 K in pure oxygen) compared to SrO_2 (T_d = 620 K in pure oxygen). Throughout the thermal stability range of the compound BaO_2, the three ternary compounds, Ba_2PbO_4, $Ba_4Pb_3O_{10}$, $BaPbO_3$ are in equilibrium with BaO_2. This results in the generation of additional three-phase fields, $BaO + BaO_2 + Ba_2PbO_4$, $Ba_2PbO_4 + BaO_2 + Ba_4Pb_3O_{10}$ and $Ba_4Pb_3O_{10} + BaO_2 + BaPbO_3$. There is mutual solid solubility between the binary oxides BaO and BaO_2 at high temperature /18/. At a given temperature, the solubility of BaO in BaO_2 is more than that of BaO_2 in BaO. At the highest temperature near to the decomposition of BaO_2 in pure oxygen (P_{O_2} = 1 atm), the mole fraction X_{BaO} in BaO_2 is $\approx$ 0.2 and the solubility of BaO_2 in BaO is (X_{BaO_2}) $\sim$ 0.05.

6. CONCLUSIONS

A comparison of the standard Gibbs energies of formation of M_2PbO_4 (M = Ca, Sr, Ba) and $MPbO_3$ (M = Ca, Sr, Ba) from component binary monoxides and oxygen gas as a function of the position of the alkaline-earth metal in the periodic table shows that as the basicity of alkaline-earth metal increases, the ternary oxides become more stable. Positive Gibbs energy of formation of $CaPbO_3$ /12,14/ from component binary monoxides and oxygen gas at 1100 K confirms the difficulty in synthesizing this ternary oxide. The increasing stability of the ternary oxides, all of which contain tetravalent lead, with the basicity of the alkaline-earth oxide is interpreted in terms of the acidic nature of PbO_2 in contrast to the basic character of PbO. From the observed trends in stability of ternary oxides, an important general principle is deduced. When an element forms several binary oxides, the oxide in which metal is present in its highest oxidation state is more acidic. Hence, they interact with basic oxides such as CaO, SrO and BaO to form ternary phases of high stability. The lower oxides of elements from groups 3 to 5 of the periodic table are more basic than their higher oxides. Thus the lower oxides do not interact strongly with alkaline-earth oxides.

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