Liquidus Diagram for the Sodium Orthophosphate–Lead Orthophosphate System*

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The Na_3PO_4–$Pb_3(PO_4)_2$ system was studied by thermal analysis, high-temperature microscopy, and X-ray diffraction powder methods. The compound $NaPbPO_4$ melts congruently at 1117°C. An unidentified phase occurs in the vicinity of 10 mole% $Pb_3(PO_4)_2$. The system has eutectics at 44.5 and 96 mole% $Pb_3(PO_4)_2$, melting at 1074 and 1004°C, respectively. The respective melting points of Na_3PO_4 and $Pb_3(PO_4)_2$ are 1512 and 1015°C.

Introduction

A variety of compounds of the general formula $A^IB^{II}PO_4$ have been reported. In the known examples the univalent cations include Li^+, Na^+, K^+, and Rb^+, and the divalent include Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}, and Pb^{+2}. Interest in these compounds stems from luminescent properties and from crystallographic relationships to $A^{II}B^{II}SiO_4$ and $A^IB^ISO_4$ compounds.

The $A^IB^{II}PO_4$ compounds occur in the A_2^IO–$2A^IPO_3$–$B^{II}(PO_3)_2$–$B^{II}O$ quaternary systems at the intersection of the $A_3^IPO_4$–$B^{II}(PO_4)_2$ and the A^IPO_3–$B^{II}O$ sections. Phase diagrams have been determined for surprisingly few of these sections. Of the latter type, the $NaPO_3$–PbO, $NaPO_3$–MnO, and $NaPO_3$–CdO systems have been studied (*1*), as well as the $NaPO_3$–MgO and $NaPO_3$–ZnO systems (*2*). Of the mixed orthophosphate systems, only part of one has been reported, $NaCaPO_4$–$Ca_3(PO_4)_2$ (*3, 4*). The 25 and 50°C isotherms of the Na_3PO_4–$Cu_3(PO_4)_2$–H_2O system show the occurrence of $NaCuPO_4$ (*5*).

Experimental

Because of uncertainties in the composition of commercial trisodium phosphate hydrates (*6, 7*), Na_3PO_4 was prepared from Na_2CO_3 and Na_2HPO_4 (*8*). Appropriate mixtures of Na_3PO_4

and reagent grade $Pb_3(PO_4)_2$ were ground, heated at 1200°C for 3–4 min, cooled, reground, and annealed at 800°C for 4 hr. Heating at 1200°C provided a liquid phase in almost all the samples to increase homogeneity. Possible shifts of sample composition through volatility prevented longer heating or the use of a higher temperature. Crystallinity was improved by annealing at 800°C.

From 30 to 100% $Pb_3(PO_4)_2$ phase changes were determined by thermal analysis and by high-temperature microscopy (*9*). Only the hot stage was used at lower lead phosphate levels because of the temperatures involved. Calibration points were K_2SO_4 tr. 583°C, m. 1069°C; NaCl m. 800°C; and CaF_2 m. 1330°C. Thermal analyses were carried out at 10°C per min on 0.9-g samples using a bare 95Pt5Rh–80Pt20Rh thermocouple in the sample. In almost every case the cooling curve and a second heating curve were determined in addition to the original heating curve. The reported temperatures below 1300°C are felt to be ±5°; those above 1300°C have larger uncertainties due to composition changes resulting from partial volatilization of the sample.

Results and Discussion

X-ray diffraction powder patterns for successive samples across the system showed the occurrence of four phases. The pattern for the

first phase, Na_3PO_4, was sharply reduced in intensity at 3% $Pb_3(PO_4)_2$ and indetectable at ⩾5% $Pb_3(PO_4)_2$. The pattern for the second phase peaked in intensity at about 10% $Pb_3(PO_4)_2$ and vanished beyond 50% $Pb_3(PO_4)_2$. With principal lines at the following d values (I/I_0), it could not be matched with any pattern in the ASTM file or otherwise available to us: 3.97 (80), 2.84 (100), 2.78 (90), 2.28 (30), 1.99 (45). The pattern for the third phase showed maximum intensity at about 50% $Pb_3(PO_4)_2$ and was attributed to $NaPbPO_4$. The final phase was $Pb_3(PO_4)_2$; its pattern was detectable only at >50% of that component.

Temperatures at which phase changes were observed are shown in Fig. 1 for each composition studied. For the compounds Na_3PO_4, $NaPbPO_4$, and $Pb_3(PO_4)_2$ the respective melting points are 1512, 1117, and 1015°C. Melting point values of 1014 (10) and 1015°C (11) have previously been reported for $Pb_3(PO_4)_2$. A transition was observed at 340°C for Na_3PO_4.

The $NaPbPO_4$–$Pb_3(PO_4)_2$ eutectic occurs at 1004°C and 96% $Pb_3(PO_4)_2$. A reversible transition at 800°C was attributed to $NaPbPO_4$ on the basis of the dependence on composition of the strength of the accompanying thermal effect. Although such a transition is typical of $A^IB^{II}PO_4$ compounds, $NaPbPO_4$ has previously been reported to be an exception, showing only what should be the high-temperature form (12). It has been shown, however, that the high-temperature

phase of an $A^IB^{II}PO_4$ compound can be stabilized at ordinary temperatures by the presence of a substance insoluble in the low-temperature phase, such as sodium carbonate (13, 14).

Because of the high temperatures involved, thermal studies in the composition range 0–20% $Pb_3(PO_4)_2$ were limited to hot-stage microscopy. Fogging of the hot stage cover slide and successive decreases in the liquidus temperature on reheating of samples gave evidence of serious composition shifts in the 3–10% $Pb_3(PO_4)_2$ range. For this range Fig. 1 shows the highest liquidus temperature determined on the first heating of several samples at each composition. It is probable that these temperatures are low. If, as suggested by the X-ray data, a compound exists in this composition range, it is probably not congruent melting; the last crystals to disappear during heating on the hot stage appeared to be Na_3PO_4. It is possible that this apparent compound is a ternary solid solution, comparable to the "γ-$Zn_3(PO_4)_2$" observed in the $Zn_3(PO_4)_2$–$Mn_3(PO_4)_2$ system (15). The eutectic between this unidentified phase and $NaPbPO_4$ occurs at 1074°C and 44.5% $Pb_3(PO_4)_2$.

We did not find in this system the previously reported apatite-like compound, $NaPb_4(PO_4)_3$ (16), nor a compound analogous to $Na_2Ca_5(PO_4)_4$ (17). The former compound forms only in the presence of water vapor (12). Since these compounds would occur at 80 and 71 mole% $Pb_3(PO_4)_2$, respectively, and the liquidus shape
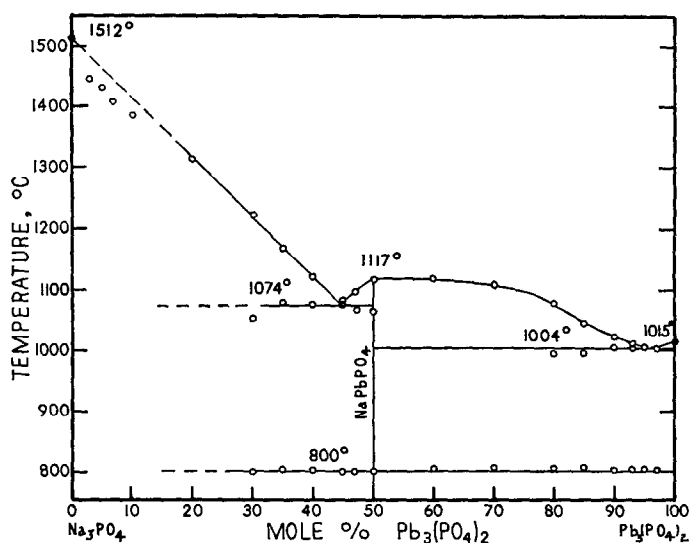

FIG. 1. Na_3PO_4–$Pb_3(PO_4)_2$ system.

is unusual in this region, the samples at 80 and 70% $Pb_3(PO_4)_2$ were additionally heated at 800°C for twelve 22-hr periods, the samples being ground between the heating periods. This extended annealing caused no change in the thermal analyses nor in the X-ray diffraction patterns for these samples. The liquidus shape in this region is attributable, presumably, to quaternary features outside this binary section.

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