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The central region of the PbO/TeO$_2$ phase diagram

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This work constitutes a closer investigation of part of the system, PbO/TeO$_2$, with particular attention to the existence and nature of a 1:1 molar ratio compound, following inconsistencies in previous publications. Observations on previous attempts to pull crystals from the melt are reconsidered in the light of the current work.

1. Introduction

In the three known versions of the phase diagram of the system PbO/TeO$_2$, there are a number of differences. The versions due to Cole and Douglas [1] and Robertson *et al.* [2] do not show the presence of a 1:1 molar ratio compound. The partial phase diagram of Tananaeva and Novoselova [3] shows the relationship between a compound PbTeO$_3$ and PbO, the preparation of PbTeO$_3$ being outlined, with references to four other authors who have prepared a similar compound. The clarification of these inconsistencies formed the basis of the work recorded below, with the establishment of the effect of the gas ambient during heating of the samples.

2. Experimental details

Techniques used included, differential thermal analysis (DTA), X-ray powder photography (Debye–Scherrer), precession single crystal photography and thermogravimetric analysis. In order to re-investigate the phase diagram in this region and to determine more accurately the shape of the liquidus, samples were made up at 2 mol % intervals, instead of the previously used 5 mol % [2, 3]. As previous work [2] had been performed in air, it was decided that any preheating of samples should be done under argon and the results compared. Mixtures of PbO and TeO$_2$, vacuum dried at 120° C, from 40 to 60 mol % PbO were fired for 16 h under flowing argon at 530° C, and one sample of 50 mol % PbO was heated at 530° C for 64 h. As the X-ray powder patterns obtained after 16 and 64 h firing were identical and did not correspond to a mixture of PbO and TeO$_2$, it was therefore concluded that firing for 16 h was sufficient to produce the compound by sintering of the starting materials. Each fired sample was subjected to repeated heating and cooling in a DTA system under flowing argon (15 ml min^{-1}). Samples of precipitated PbTeO$_3$.xH$_2$O, obtained commercially* were also subjected to similar sintering and DTA cycling in addition to thermogravimetric analysis. Single crystal precession X-ray photographs were taken of fragments of crystalline material grown from a melt of 50 mol % PbO by the Czochralski method, and the cell parameters obtained were used for powder photograph indexing.

3. Results

3.1. General observations on the phase diagram

One feature noted in this work was that the position of the liquidus in the phase diagram (Fig. 1), with a mol % PbO, 50 to about 75, was found to be different from that observed in the original set of experiments which were performed in air [2]. Careful visual observations of melting in air showed that though mixtures appeared to melt at one temperature, a cloudy surface appeared almost immediately which did not disappear until a somewhat higher temperature was reached: on

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* Obtained from BDH Chemicals Ltd., Poole, Dorset, UK.

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heating the samples in argon, no such effect was observed. Samples with a mol%PbO greater than 52, show a decrease in the liquidus temperature to a eutectic at 60% PbO. This is at variance with Tananaeva and Novoselova [3], but may be due to a confusion of the phase change and solidus line in this earlier work. The liquidus for samples of 70 to 80 mol%PbO has been drawn as a dotted line, as the melting temperature was recorded by visual observation, the DTA peaks being indistinct. The horizontal line at 665° C from about 67 to 80 mol%PbO is believed to be a phase transformation in $3PbO.TeO_2$.

The liquidus temperature of 52 to 49 mol%PbO shows a decrease to a eutectic temperature of 527° C at 49 mol%PbO, whereafter it rises to 500° C at the congruent point of $Pb_2Te_3O_8$. The horizontal line from 40 to 75 mol%PbO at 485° C is attributed to the $\alpha \rightarrow \beta$ phase transition in the compound labelled C in Fig. 1.

This region of the phase diagram as plotted from DTA cycles, in argon, differs from the same region as done in air [2], primarily, as mentioned, in the shape of the liquidus with a mol%PbO greater than 50, including a previously unobserved maximum melting point at 52 mol%PbO. The region 50 mol%PbO upwards also differs from that published by Tananaeva and Novoselova [2], in the position of the eutectic, and also in the value of the melting point of $3PbO.TeO_2$.

3.2. DTA results

As previously noted, all DTA runs were performed on presintered samples, and no reaction peaks were observed. It was noted that samples with 40 to 50 mol%PbO all apparently melt about the same temperature, approximately the melting point of $Pb_2Te_3O_8$, on their first DTA cycle, but on reheating will melt at a lower temperature, the actual differences, 10 to 20° C, depending on the amount of PbO present. Upon subsequent recycling the samples will repeatedly melt at this lower temperature.

The maximum melting point composition, with its single melting and solidification peak occurs at 52 mol%PbO, there being a doublet melting peak associated with 50 mol%PbO. Samples with a mole % PbO greater than 52, showed no anomalous behaviour on repeated DTA cycling, the results being as shown in Fig. 1.

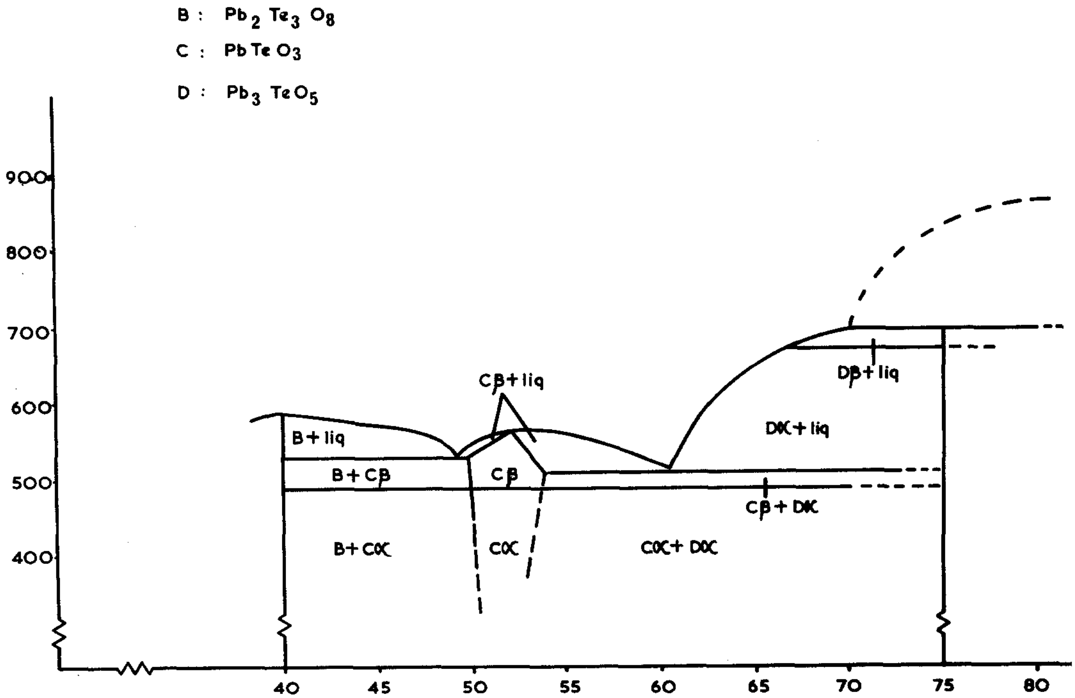

Figure 1 Region of the phase diagram of PbO/TeO_2 containing 40 to 75 mol%PbO. 40 mol%PbO, 500 ± 3° C congruent point. 49 mol%PbO, 527 ± 3° C eutectic point. 52 mol%PbO, 560 ± 3° C maximum melting point. $PbTeO_3$ phase change 485 ± 3° C. 60.5 mol%PbO, 505 ± 3° C eutectic point. 70 mol%PbO, 690 ± 3° C incongruent melting $3PbO.TeO_2$. $3PbO.TeO_2$ phase change 665 ± 2° C.

3.3. X-ray results

3.3.1. Sintered samples

All the sintering of samples for this work, was done in argon, and the X-ray powder photographs obtained for sintered material, differed from the corresponding X-ray powder photographs after DTA for all samples with greater than 44 mol % PbO. The powder photographs of sintered samples of 40 to 48 mol % PbO are almost indistinguishable from that obtained for $Pb_2Te_3O_8$ [2]; the powder photograph of 50 mol % sintered PbO, shows extra lines apart from those attributable to $Pb_2Te_3O_8$. The powder photograph of 52 mol % PbO sintered sample is quite different from 50 mol % and can be indexed on a monoclinic cell ($a = 27.59$ Å, $b = 4.61$ Å, $c = 17.97$ Å, $\beta = 112.90°$) [7, 8], as recorded in Table I. This set of d spacings does not correspond to any set listed previously [3, 6]. As the mol % PbO increases from 52, the lines corresponding to $3PbO.TeO_2$ become predominant.

There seems little doubt, from the indexing of the powder photograph of 50 mol % PbO, (Table II), that the sintering of powders at 530° C in argon does not produce a single phase, which is supported by the doublet melting peak observed on the DTA trace during this work. The nature of the phase or phases other than $Pb_2Te_3O_8$, producing lines in the 50 mol % powder photograph has not been completely established. The extra lines do not fit PbO as might at first be suspected; they could, however, fit with those corresponding to $PbTeO_4$ [3] (Table II). In order for this system to balance chemically, the presence of free lead has to be envisaged, which may have been the cause of the slight grey appearance of sintered samples of 46 to 50 mol % PbO; however, no other evidence, chemical or X-ray, was obtained to support this idea.

3.3.2. Samples after DTA

The X-ray powder photographs of the 40 to 75 mol % PbO samples, after melting and solidification, show a more normal trend than those of the sintered samples, a simple pattern of lines being predominant in the region of 46 to 56 mol % PbO, other lines becoming more apparent, the further the PbO:TeO_2 ratio moves from 1:1. These additional lines correspond to $Pb_2Te_3O_8$ for mol % PbO less than 46, and to $3PbO.TeO_2$ for mol % PbO greater than 56. The predominant set

TABLE I Interplanar spacings measured for materials produced during current work, with same calculated spacings

$PbTeO_3$ (monoclinic)				$PbTeO_3$ (tetragonal)				$PbTeO_3$ (precipitate)	
I	d_{obs}	$h\ k\ l$	d_{calc}	I	d_{obs}	$h\ k\ l$	d_{calc}	I	d_{obs}
w	8.39	0 0 2	8.33	m	4.88	1 0 1	4.86	vw	10.46
w	6.35	4 0 2	6.35	vs	3.19	1 1 2	3.18	m	5.04
w	3.55	0 1 3	3.55	s	2.98	0 0 4	2.98	m	4.73
w	3.47	4 1 3	3.47	s	2.66	2 0 0	2.66	vw	4.05
vw	3.31	$\bar{7}$ 0 1 $\bar{6}$ 0 2	3.32	m	2.33	2 1 1	2.33	vw	3.78
				m	2.18	1 0 5	2.18	vw	3.60
s	3.23	3 1 4	3.21	w	2.04	2 1 3	2.04	vw	3.44
s	3.11	7 0 5	3.11	s	1.99	2 0 4	1.99	vs	3.26
s	3.00	4 0 6 9 0 1	2.99	s	1.88	2 2 0	1.88	vs	3.15
				s	1.76	1 1 6	1.76	ms	3.00
mw	2.86	$\bar{7}$ 1 0	2.86	vw	1.68	2 1 5	1.69	ms	2.79
mw	2.73	8 1 1	2.73	s	1.62	3 1 2	1.62	m	2.57
w	2.66	8 0 6	2.64	s	1.59	2 2 4	1.59	w	2.37
mw	2.53	$\bar{2}$ 0 6	2.52	w	1.49	0 0 8	1.49	w	2.18
ms	2.30	0 2 0	2.30	vw	1.39	2 1 7	1.39	m	2.06
mw	2.26	$\bar{4}$ 0 6	2.26	w	1.33	4 0 0	1.33	s	1.93
mw	2.21	6 1 7	2.21	m	1.30	2 0 8	1.30	m	1.85
vw	2.18	$\bar{8}$ 0 4	2.17	ms	1.28	3 1 6	1.28	ms	1.78
ms	2.11	0 1 7	2.11	m	1.23	3 3 2	1.23	mw	1.75
ms	1.86	8 2 4	1.87	m	1.21	4 0 4	1.21		
m	1.82	4 2 6	1.83	m	1.19	4 2 0	1.19		
m	1.79	$\bar{4}$ 0 8	1.79	m	1.17	2 2 8	1.17		
w	1.77	10 2 2	1.77	m	1.14	1 1 10	1.14		
mw	1.73	10 0 10	1.72						
mw	1.68	1 2 7	1.68						

of lines in the region 46 to 56 mol % PbO, as observed in this work and previous work [2], can be indexed on a tetragonal cell ($a = 5.33$ Å, $c = 11.88$ Å) (Table I). This set of lines corresponds to the d spacings for $PbTeO_3$ published by Tananaeva and Novoselova [3].

3.4. Observations on precipitated material

A DTA trace of lead tellurite, prepared by precipitation and unfired, shows a small peak about 200° C, presumably associated with dehydration, an endothermic peak at 485° C and a doublet melting peak, about 550° C.

X-ray powder photographs of samples prepared after Berchenko and Belyaev [6] and also Tananaeva and Novoselova [3], were taken before and after firing, and after DTA. The precipitated material obtained by these two methods was

TABLE II Comparison of interplanar spacings for 50 mol % PbO with spacings for $Pb_2Te_3O_8$ [2] and $PbTeO_4$ [3]

$Pb_2Te_3O_8$ orthorhombic [2]				50 mol % fired		$PbTeO_4$ [3]	
I	d_{obs}	$h\ k\ l$	d_{calc}	I	d_{obs}	I	d_{obs}
m	9.79	0 0 2	9.74	ms	9.77		
vw	5.45	2 1 1	5.46				
w	4.88	0 0 4	4.88				
w	4.70	4 0 0	4.70				
w	4.30	2 0 4	4.32				
		2 1 3	4.28				
vw	3.85	4 1 1	3.85			vs	3.61
vw	3.50	1 2 0	3.51			m	3.49
s	3.30	1 2 2	3.30	ms	3.35		
s	3.22	2 1 5	3.21	s	3.22		
vs	3.11	3 2 0	3.10	s	3.13		
s	3.00	6 0 2	3.00	s	3.07		
		3 1 5	3.00	s	3.00		
mw	2.84	4 2 0	2.84	ms	2.85	vw	2.86
		6 1 1	2.84				
		1 2 4	2.85				
s	2.76	2 2 4	2.76	ms	2.76	s	2.77
vw	2.60	0 1 7	2.59				
m	2.53	5 1 5	2.53	m	2.53	m	2.57
vw	2.41	3 1 7	2.40			w	2.41
vw	2.34	1 3 1	2.34				
w	2.28	4 1 7	2.27			vw	2.29
w	2.23	0 3 3	2.23				
vw	2.15	7 2 0	2.15	m	2.18		
s	2.10	3 3 3	2.11	s	2.11		
s	2.02	2 1 9	2.02	m	2.02	m	2.03
s	1.94	0 0 10	1.95	m	1.95	s	1.97
m	1.80	9 2 0	1.80	ms	1.81	vs	1.87
m	1.78	1 4 0	1.78	ms	1.77	s	1.74
m	1.69	8 0 8	1.69	m	1.73		
s	1.65	3 2 10	1.65	w	1.70	mw	1.70
m	1.61	5 4 0	1.61	mw	1.68		
w	1.57	5 4 2	1.57	m	1.65	m	1.62
w	1.52	10 1 7	1.52	mw	1.57	w	1.60
				w	1.50	s	1.49

shown to be crystalline and gave a powder photograph different to any previously obtained in this work (Table I), but fitting well with the *d* spacings reported by Tananaeva and Novoselova [3] and Berchenko and Belyaev [6] for hydrated lead tellurite. After firing these samples at 400° C for 20 h under flowing argon, the powder photograph obtained was that of the $PbTeO_3$ tetragonal phase (Table I). The powder photograph of precipitated material after DTA, is similar to that before DTA, i.e. the tetragonal phase. It is interesting to note that precipitated material fired at 400° C produced the tetragonal phase, whereas mixed oxide powders fired produced the monoclinic phase. This is presumably a consequence of the structural relationship between the hydrated form and the tetragonal form.

The phase change in $PbTeO_3$ at 485° C was shown to be irreversible from the following observations: A sample of precipitated material is totally molten by 550° C and crystallizes on cooling at 470° C. An X-ray powder photograph of the resulting material shows the simpler line pattern (Table I), which can be indexed on the tetragonal cell. If this sample is reheated, it shows an endothermic peak at 485 ± 3° C in addition to the melting peaks. Only one peak is observed on cooling, i.e. solidification at 470° C. If this sample is heated to 510° C, through the first endothermic peak and cooled without melting, the resulting powder photograph is that of the monoclinic phase (Table I). If this sample is reheated, no DTA peak is observed until melting. Thus it has been shown, that if a sample of tetragonal material is heated to melting, a phase change will be observed at 485 ± 3° C; but if a sample of monoclinic material is heated to melting, no phase change is observed. It is concluded that the tetragonal form is the stable low temperature form and the monoclinic form the high temperature form, metastable at room temperature. Further, if a tetragonal sample is heated above the phase transition and cooled, without melting, the monoclinic phase is obtained, implying that the phase change is irreversible. This is supported by the observation that if the melt is seeded, i.e. if crystallization is induced above 485° C, the material remains in the monoclinic phase at room temperature. Thus the phase change in $PbTeO_3$ is irreversible in the solid state, and conversion can only be effected from the tetragonal to the monoclinic phase. At this point, it is worth noting that it is, therefore, impossible to grow a crystal of the tetragonal phase, using the Czochralski technique.

3.5. TGA on selected samples

As there is some disagreement between authors [3, 6] as to the amount of bonded water ($\frac{1}{3}$ mole or $\frac{2}{3}$ mole), a sample of precipitated material, having been dried at about 120° C was subjected to thermogravimetric analysis (TGA) in air and argon. This did not show a weight loss large enough to be consistent with even $\frac{1}{3}$ mole water. Another experiment on samples of precipitated material, heating to constant weight at 300° C showed a typical weight loss of $\frac{1}{12}$ mole. The results of TGA runs on precipitated material and mixed oxides are shown in Table III. The initial weight loss of the precipitated material is attributable to the loss of bonded water, but is not

TABLE III TGA results on selected samples

Sample	Wt. change (air) ± 0.02%	Wt. change (argon) ± 0.02%
$PbTeO_3$ (ppt)	200–400° C 0.41% loss	200–400° C 0.51% loss
	500–700° C 0.54% gain	500–700° C 0.11% gain
	~ 730° C start of weight loss	
	~ 850° C change rate loss	~ 830° C start of weight loss
52 mol% PbO	450–720° C 0.44% gain	no loss below 650° C
	~ 730° C start increasing loss	~ 650° C start gradual loss
		~ 770° C loss rate increasing
75 mol% PbO	370–730° C 0.48% gain	250–630° C 0.08% gain
	~ 755° C 0.20% loss	~ 700° C start increasing loss
	~ 800° C start increasing loss	
80 mol% PbO	500–580° C 0.30% loss	nothing until 740° C
	590–720° C 0.60% loss	
	720–760° C 0.35% loss	~ 740° C start increasing loss
	~ 790° C start increasing loss	

consistent with any previously predicted amount of bonded water. The magnitude of the weight loss in the region 200 to 400° C is less when heated in air, than when heated in argon, there being a reduction in weight loss at about 320° C when heated in air. In the region 500 to 700° C when heated in air, there is a noticeable weight gain, followed by the onset of a weight loss at about 730° C, increasing in rate at about 850° C. In argon, heating in the region 500 to 700° C causes a slight weight gain followed by an increasing loss above 830° C. This latter observation is caused by the loss of TeO_2 when heating in air or argon.

There was no weight gain in the 52 mol % PbO sample when heated in argon, only a loss above 770° C due to TeO_2 being evolved. This sample, however, did show a weight gain at 450 to 720° C when heated in air followed by a subsequent weight loss.

The 75 mol % PbO sample showed some weight gain when heated in air (400 to 700° C), comparable with weight gains of the previous samples in the same region. The 80 mol % PbO sample shows no weight increase when heated in air or argon, but did show an unusually large weight loss below 800° C when heated in air.

4. Discussion

From the current work, it appears that the phase diagram is considerably more complex than envisaged by any previous workers, particularly in the central region, where the maximum melting point composition occurs at 52 mol % PbO. The system can be further complicated by its dependence upon the ambient atmosphere, as demonstrated in the results obtained, where a section of the liquidus has a different shape if the DTA is run in air. As some Te(VI) has been observed in air-fired samples of $PbTeO_3$ [3], the system should perhaps be regarded as a three-oxide system if the ambient is air. Yamada and Iwasaki [4] have shown that if a melt of $SrTeO_3$ is exposed to oxygen, a solid crust is formed due to oxidation of the melt surface to a higher melting point compound. In studying the thermal stability of $NiTeO_3$, Kolar *et al.* [5] showed that this compound is so unstable during heating, that it never melts as $NiTeO_3$, but converts rapidly to $Ni_2Te_3O_8$, which subsequently oxidizes at a higher temperature to Ni_3TeO_6. Thus, it may be envisaged, that melts of PbO and TeO_2, containing greater than 50 mol % PbO if heated in air will melt with accompanying surface oxidation, this solid not melting or dissolving until a higher temperature is attained. Even in argon though, single crystal growth from the melt is not a viable proposition in the 50 mol % PbO region, by virtue of the nature of the phase diagram. Previous attempts [2] to grow crystals from a 50 mol % melt showed the material to be always lead-rich, in keeping with the phase diagram (Fig. 1).

The anomalous behaviour of samples of 42 to 50 mol % PbO, when subjected to DTA, coupled with the abrupt changes in powder photograph line patterns, are consistent with the idea that mixed powders of PbO and TeO_2 containing from 40 to 50 mol % PbO sintered at 530° C will initially produce $Pb_2Te_3O_8$, presumably kinetically favourable, plus some other phase not detectable in the photographs of 42 to 48 mol % PbO. Not until the mixtures are heated above the melting point of $Pb_2Te_3O_8$, does the system rearrange to produce tetragonal $PbTeO_3$ and $Pb_2Te_3O_8$ in a ratio proportional to the original starting compositions.

The TGA results on precipitated $PbTeO_3$ and 52 mol % PbO fired in air and argon, are consistent with some oxidation of the samples when heated in air, followed by the subsequent breakdown of the tellurate formed, at a temperature of about 730° C. As previously noted, the increasing loss of material above 830° C is attributable to loss of TeO_2 from the melt. The initial weight loss of the precipitated material, in air or in argon is due to dehydration. The 75 mol % PbO sample shows a similar gain, followed by a loss, below 830° C consistent with some oxidation of tellurite (Te(IV)) to tellurate, followed by decomposition above 730° C. The 80 mol % PbO sample shows no weight gain in air, only a loss at 500 to 760° C, which is not observed in argon. The effect of heating is presumably more complex here as the results are not consistent with the simple oxidation theory developed above.

This work has also confirmed the existence of a compound, nominally $PbTeO_3$, and two polymeric forms have been identified. The interconversion of these two forms has been studied and the phase change from tetragonal to monoclinic shown to be irreversible in the solid state. The work has, in addition, verified the existence of a hydrated form of the 1:1 molar ratio compound showing how it behaves on dehydration, producing the tetragonal phase, not the monoclinic phase as with sintered oxides. The exact composition of the hydrated form was not determined. The reason for the lack of success in the attempts to grow crystals from 50 and 75 mol % PbO melts, has also become apparent from the nature of the revised phase diagram.

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