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On the composition of the crystal phases in the $PbO–TeO_2$ system

D. STAVRAKIEVA, Y. IVANOVA
Higher Institute of Chemical Technology, 1756 Sofia, Bulgaria

J. PYROV
Scientific Manufacturing Enterprise of Electrothermics, 1870 Sofia, Bulgaria

The phase diagrams and the inconsistencies in the type and composition of the crystal phases in the $PbO–TeO_2$ system reported by different workers are reported. With the help of X-ray microanalysis, X-ray analysis and IR spectroscopy new data about the composition of the crystal phases have been obtained. The data from the X-ray microanalysis were treated by the method of the number of the oxygen atoms, and the chemical formulae of the crystal phases were evaluated. The following phases were established: solid solution from $PbO \cdot 4TeO_2$ in $2PbO \cdot 7TeO_2$, $2PbO \cdot 5TeO_2$, $2PbO \cdot 3TeO_2$, $PbO \cdot TeO_2$ with two polymorphic modifications, a phase with varied composition from $5PbO \cdot 2TeO_2$ to $3PbO \cdot TeO_2$, and $5PbO \cdot TeO_2$. It was assumed that there was polymorphic transformation for the $2PbO \cdot TeO_2$, $3PbO \cdot TeO_2$ and $5PbO \cdot TeO_2$ compositions. Data from X-ray analysis and the IR absorption spectra are presented. On the basis of the new data for the composition of the crystal phases and the data from the investigations of different workers a corrected phase picture of the $PbO–TeO_2$ system is built up.

1. Introduction

The $PbO–TeO_2$ system has been the object of a number of investigations. The thermal resistance of $PbTeO_3$ and $PbTeO_4$ was investigated by Tananaeva and Novoselova [1]. The polymorphic transformation of $PbO \cdot TeO_2$ compound, melting with decomposition at 560° C and forming a phase richer in lead (Pb/Te = 1.08), was determined. The system was investigated by Marinov *et al.* [2] in the range from 0 to 50 mol % PbO. Crystal phases with $PbO \cdot 4TeO_2$, $PbO \cdot 2TeO_2$, $2PbO \cdot 3TeO_2$ and $PbO \cdot TeO_2$ composition were established and the polymorphic transformation of $PbO \cdot TeO_2$ was confirmed. The morphological characteristics were described and the interplanar spacings were determined. A phase picture of the $PbO–TeO_2$ system in the concentration range from 0 to 50 mol % PbO (Fig. 1) was built up. Later, Robertson *et al.* [3] confirmed the $PbO \cdot 3TeO_2$ phase, but they did not verify the formation of $PbO \cdot TeO_2$. They determined $3PbO \cdot TeO_2$ and $6PbO \cdot TeO_2$ phases and constructed the phase picture of the system for the range from 0 to 100 mol % PbO (Fig. 2). The same workers [3] presented the phase diagram of the $PbO–TeO_2$ system after Cole and Douglas (Fig. 3) which was not previously reported. The investigations of Young [4] in the same system in an atmosphere of argon in the range 40 to 75 mol % PbO showed a different course of the liquidus line (Fig. 4). It was confirmed that there was formation of $2PbO \cdot 3TeO_2$ and $PbO \cdot TeO_2$ with polymorphic transformation at 665 ± 2° C, melting incongruently at 690 ± 3° C. Kosse and collaborators [5, 6] have synthesized $PbO \cdot TeO_2$ (tetrahedral),

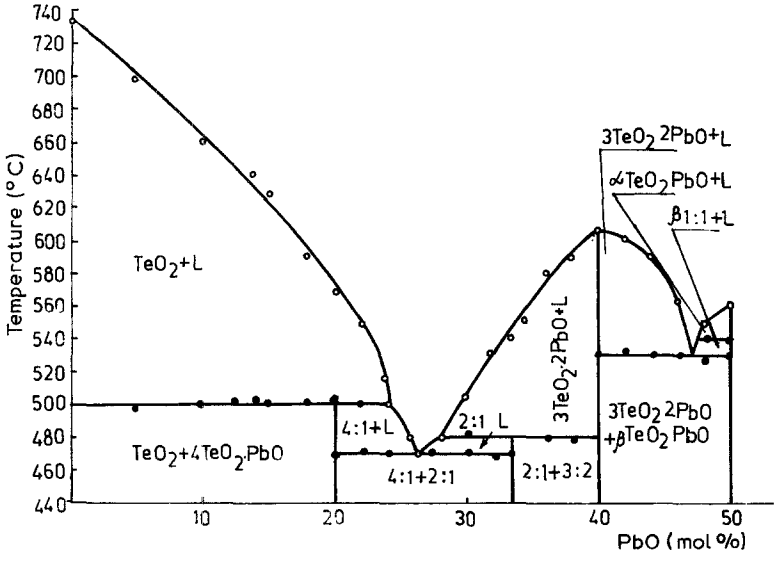

Figure 1 Phase diagram of the $PbO–TeO_2$ system after Marinov *et al.* [2]. L = liquid.

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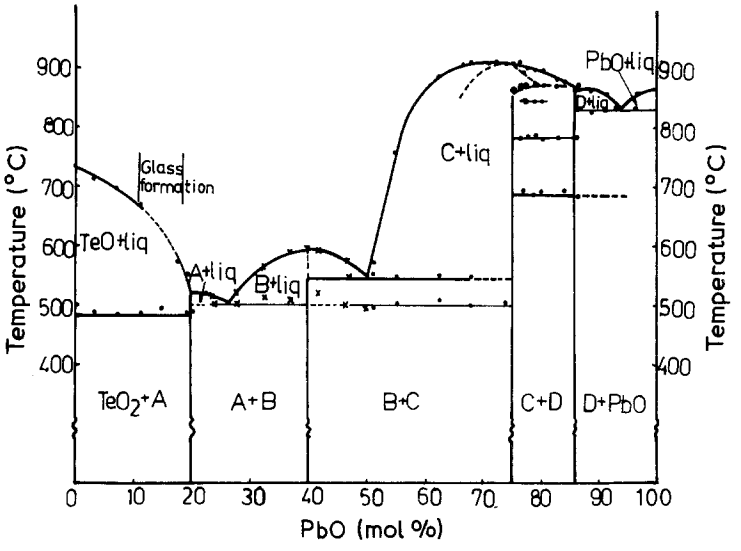
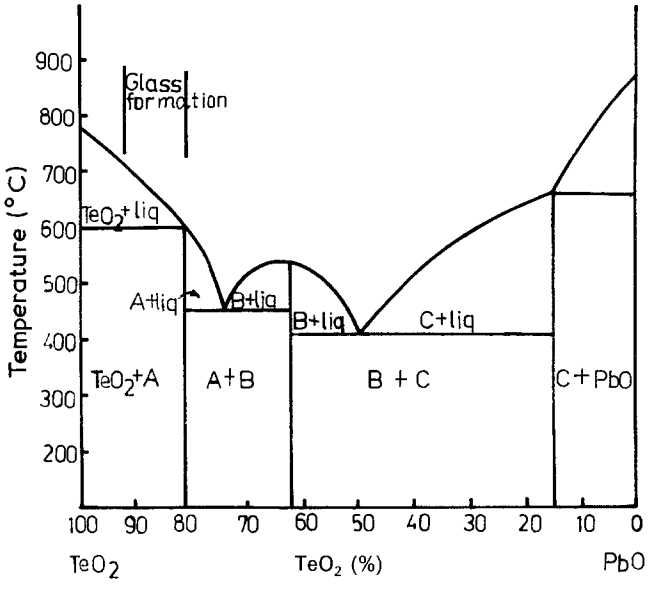


Figure 2 Phase diagram of the PbO–TeO_2 system after Robertson *et al.* [3]. A = PbO · $4TeO_2$, B = 2PbO · $3TeO_2$, C = 3PbO · TeO_2 or 8PbO · $3TeO_2$, and D = 6PbO · TeO_2.

Figure 3 Phase diagram of the PbO–TeO_2 system after Cole and Douglas (1964, unpublished) from Robertson *et al.* [2]. A = $4TeO_2$ · PbO, B = $3TeO_2$ · 2PbO and C = TeO_2 · 4PbO.



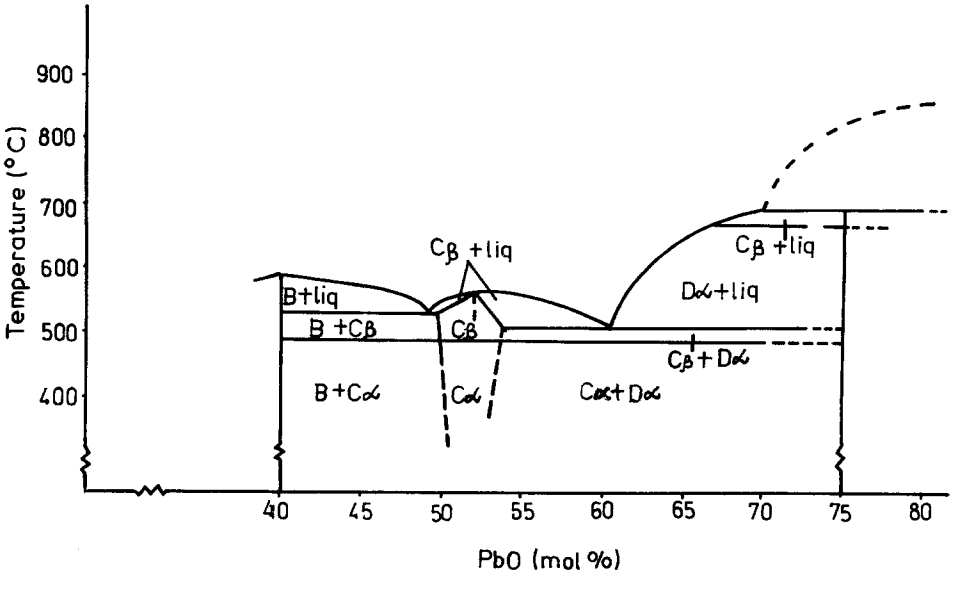


Figure 4 Central part of the PbO–TeO_2 system after Young [4]. B = $Pb_2Te_3O_3$, C = $PbTeO_3$, D = Pb_3TeO_3.

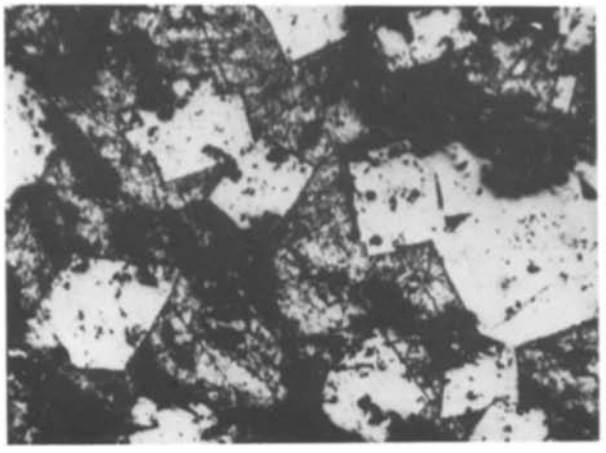


Figure 5 Idiomorphic crystals of $PbO \cdot 4TeO_2$. Reflected light. Crystals etched by dilute HCl. Magnification 139×.

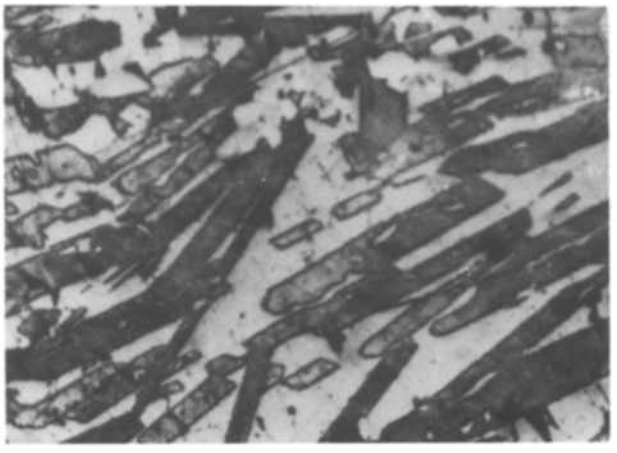


Figure 7 Elongated rhombic sections of $2PbO \cdot 3TeO_2$. Reflected light. Etched by dilute HCl. Magnification 139×.

Pb_3TeO_5 and Pb_3TeO_6 by slow cooling of the melt and single crystals of $PbTeO_3$ (monoclinic) as well as $Pb_2Te_3O_8$ by the method of Chochralsky, and they have examined their dielectric properties. They confirmed that $PbTeO_3$ (tetrahedral) and Pb_3TeO_6 had undergone reversible phase transformations at 530 and 490 K, respectively, and at the temperature of the phase transformation they were in a spontaneously polarized state, determining them as ferroelectrics.

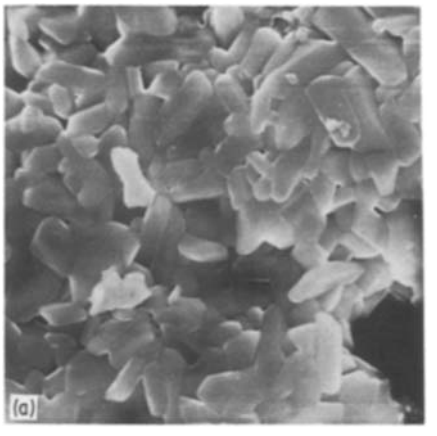
The aim of the present work is to explain the composition of the newly forming crystal phases in the system PbO–TeO_2 because of the contradictions in the investigations by the workers mentioned above.

2. Experimental procedure

Samples corresponding to the stoichiometric ratios of $PbO \cdot 4TeO_2$, $PbO \cdot 2TeO_2$, $2PbO \cdot 3TeO_2$, $PbO \cdot TeO_2$, $2PbO \cdot TeO_2$, $3PbO \cdot TeO_2$, $4PbO \cdot TeO_2$ and $6PbO \cdot TeO_2$ were synthesized by crystallization at temperatures above the solidus temperatures (in the range between solidus and liquidus). The operating conditions are presented in Table I. The thermal treatment of the samples was performed in air. The synthesis was followed by the X-ray technique (apparatus by DRON, powder samples, Cu$K\alpha$ radiation). The IR spectra were taken on a Karl Zeiss Jena UR-10 spectrometer (1400 to 700 cm^{-1} with NaCl prism, 700 to 400 cm^{-1} with KBr prism). The samples were prepared as tablets with KBr. TeO_2 (USSR) and Pb_3O_4 were used as starting materials. The composition of the crystal phases was determined with the help of an X-ray microanalyser (Philips). In order to avoid casual mistakes the analyses were performed at points on at least 5 to 6 different crystal specimens, as well as on the glassy state. The data obtained were treated with a microprocessor.

3. Results and discussion

In Figs 5 to 12 the morphologies of the crystal phases at the analysed points are given. The results of the chemical analyses by using electron microscopy were used to derive crystallochemical formulae based on the number of oxygen atoms. In Table I the compositions in accordance with the data from X-ray



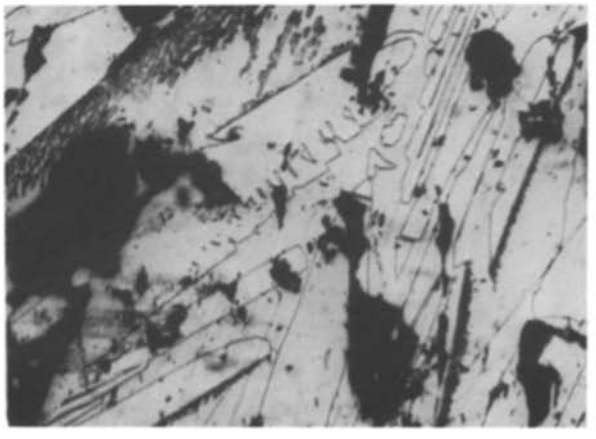


Figure 6 Prismatic crystals of $2PbO \cdot 5TeO_2$. Reflected light. Magnification 139×.

Figure 8 Single crystals of the $PbO \cdot TeO_2$ phase: (a) scanning electron microscopy, 310×; (b) reflected light, 139×.

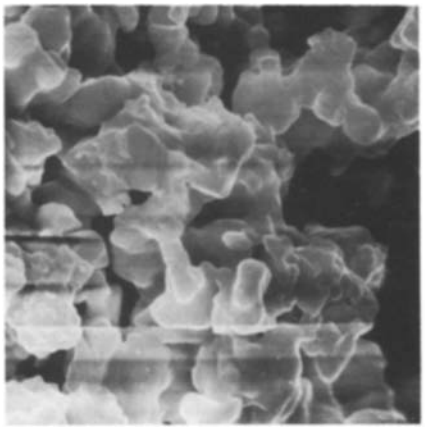


Figure 9 Mass crystallization of crystals of $2PbO \cdot TeO_2$. Scanning electron microscopy. Magnification 310×.

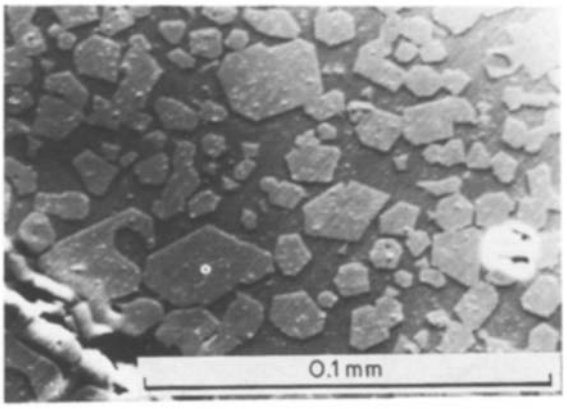


Figure 11 Analysed crystals of the $3PbO \cdot TeO_2$ phase from $4PbO \cdot TeO_2$ composition. Scanning electron microscopy. Magnification 485×.

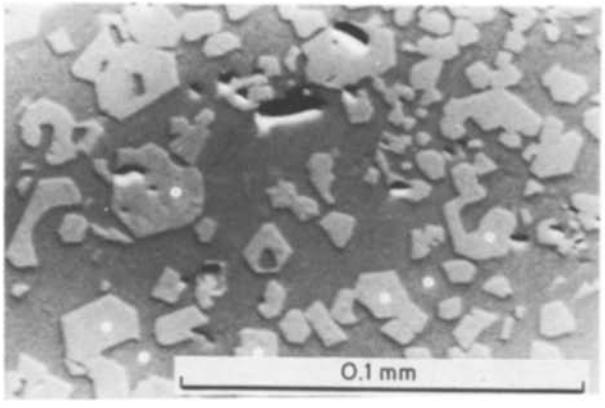


Figure 10 Analysed crystals of the $3PbO \cdot TeO_2$ phase. Magnification 485×. Scanning electron microscopy.

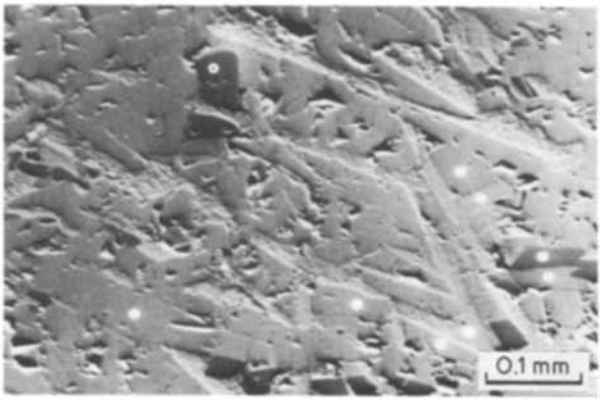


Figure 12 Analysed crystals of the $5PbO \cdot TeO_2$ phase from $6PbO \cdot TeO_2$ composition. Electron scanning microscopy. Magnification 115×.

microanalysis are presented. Data from X-ray microanalysis in the investigated concentration range confirm the formation of phases with $3PbO \cdot 2TeO_2$ composition. New crystal phases with $2PbO \cdot TeO_2$ and $5PbO \cdot TeO_2$ composition were determined. The existence of polymorphic forms of the $5PbO \cdot TeO_2$ phase was assumed. Samples with a stoichiometric ratio $3PbO \cdot TeO_2$ correspond to a phase with variable composition from $5PbO \cdot 2TeO_2$ to $3PbO \cdot TeO_2$ (from 61.5 to 75 mol % PbO, respectively), probably with polymorphic transformation. For samples corresponding to the stoichiometric ratio $PbO \cdot 2TeO_2$, thermally treated above 470° C, we identified a $2PbO \cdot 3TeO_2$ phase, and below the above-mentioned temperature crystal phases of the $2PbO \cdot 5TeO_2$ and $2PbO \cdot 3TeO_2$ type were both present. Consequently, the X-ray data given by Marinov *et al.* [2] for $PbO \cdot 2TeO_2$ composition correspond to a crystal phase with composition $2PbO \cdot 5TeO_2$ composition.

At $PbO \cdot 4TeO_2$ stoichiometric ratio the identified crystal phase has a variable composition from 20 to 22.2 mol % PbO, corresponding to $4TeO_2 \cdot PbO$ to $7TeO_2 \cdot 2PbO$, respectively, and X-ray data given by Marinov *et al.* [2] correspond to this phase. On the basis of the results from X-ray microanalysis the interplanar spacings of the crystal phases are as summarized in Table II.

The characteristic IR absorption spectra of the

TABLE I Composition of crystal phases in the $PbO-TeO_2$ system

Phase No.	Given stoichiometric composition	Composition of the crystal phases from X-ray microanalysis data	Figure	Temperature of crystallization (° C)
1	$PbO \cdot 4TeO_2$	($2PbO \cdot 7TeO_2$ to $PbO \cdot 3TeO_2$) solid solution + $2PbO \cdot 5TeO_2$	5	480
2	$PbO \cdot 2TeO_2$	$2PbO \cdot 5TeO_2$ + $2PbO \cdot 3TeO_2$ $2PbO \cdot 3TeO_2$ + glassy phase	6	Below 470 Above 470 (crystallization from the melt)
3	$2PbO \cdot 3TeO_2$	$2PbO \cdot 3TeO_2$	7	580
4	$PbO \cdot TeO_2$	$PbO \cdot TeO_2$	8	540
5	$2PbO \cdot TeO_2$	$2PbO \cdot TeO_2$	9	550
6	$3PbO \cdot TeO_2$	($3PbO \cdot TeO_2$ to $5PbO \cdot 2TeO_2$) solid solutions	10	670
7	$4PbO \cdot TeO_2$	$3PbO \cdot TeO_2$	11	670
8	$6PbO \cdot TeO_2$	$5PbO \cdot TeO_2$	12	840

TABLE II X-ray data for the phases in $PbO-TeO_2$

$PbO \cdot 4TeO_2$ to $2PbO \cdot 7TeO_2$ (s.s.) Orthorhombic [2]*		$2PbO \cdot 5TeO_2$ Monoclinic [2]*		$2PbO \cdot 3TeO_2$ Orthorhombic [3] $a = 0.714$ nm, $b = 1.877$ nm, $c = 1.945$ nm Interplanar spacings [2, 4]*			$PbO \cdot TeO_2$ Monoclinic [2, 4] $a = 2.759$ nm, $b = 0.461$ nm, $c = 1.797$ nm, $\beta = 112.90°$ [4] Interplanar spacings [1, 2, 4]*			$PbO \cdot TeO_2$ Tetragonal [4] $a = 0.533$ nm, $c = 1.188$ nm, [4]; $a = 0.5323 \pm 0.0002$ nm, $c = 1.1950 \pm 0.0008$ nm, $I4_1md$ [5] Interplanar spacings [1, 2, 4, 5]*			$2PbO \cdot TeO_2$†		β-$3PbO \cdot TeO_2$ (s.s)† Monoclinic (?)		α-$5PbO \cdot 2TeO_2$ to $3PbO \cdot TeO_2$(s.s)† Orthorhombic [6] $a = 0.55$ nm, $b = 0.66$ nm, $c = 1.15$ nm [6]		$5PbO \cdot TeO_2$†	
I	d (nm)	I	d (nm)	I	d (nm)	hkl	I	d (nm)	hkl	I	d (nm)	hkl	I	d (nm)	I	d (nm)	I	d (nm)	I	d (nm)
35	0.339	5	0.342	m	0.979	002	w	0.839	002	5	0.4864	101	4	0.507	10	0.374	9	0.375	4	0.444
100	0.324	70	0.317	vw	0.545	211	w	0.635	402	100	0.3184	112	33	0.313	11	0.342	11	0.342	3	0.355
20	0.310	100	0.307	w	0.488	004	w	0.355	013	16	0.2987	004	100	0.306	6	0.339	53	0.323	5	0.348
70	0.298	5	0.294	w	0.470	400	w	0.347	413	90	0.2658	200	68	0.300	48	0.322	5	0.313	7	0.340
20	0.280	3	0.288	w	0.431	204	vw	0.331	$\bar{7}01$	4	0.2338	211	32	0.285	51	0.304	27	0.305	62	0.320
12	0.239	2	0.270			213			$\bar{6}02$	2	0.2180	105	1	0.271	100	0.298	100	0.299	22	0.310
15	0.1985	2	0.252	vw	0.385	411	s	0.323	314	3	0.2042	213	19	0.218	83	0.295	100	0.296	100	0.3046
20	0.1866	2	0.240	vw	0.350	120	s	0.311	705	26	0.1987	204	31	0.2108	11	0.283	11	0.284	16	0.293
23	0.1692	2	0.230	s	0.330	122	s	0.300	406	12	0.1881	220	3	0.2088	18	0.279	17	0.280	23	0.278
6	0.1650	2	0.218	s	0.322	215			901	12	0.1759	116	20	0.1806	5	0.272	2	0.265	5	0.2724
2	0.1555	3	0.2005	vs	0.311	320	mw	0.286	$\bar{7}10$	1	0.1684	215	21	0.1768	2	0.265	3	0.255	6	0.2513
4	0.1509	5	0.1825	s	0.300	602	mw	0.273	811	29	0.1619	312	14	0.1733	5	0.255	13	0.218	4	0.2409
2	0.1486	2	0.1788			315	w	0.266	806	17	0.1591	224	21	0.1684	2	0.253	32	0.210	3	0.2377
10	0.1473	2	0.1765	mw	0.284	420	mw	0.253	$\bar{2}06$	3	0.1491	008	20	0.1675	3	0.241	5	0.203	13	0.2184
		5	0.1702			611	ms	0.230	020	4	0.1391	217	6	0.1565	21	0.218	5	0.1996	9	0.2145
		3	0.1690			124	mw	0.226	$\bar{4}06$	6	0.1333	400	16	0.1530	5	0.214	6	0.1966	14	0.2128
		5	0.1578	s	0.276	224	mw	0.221	617	10	0.1303	208	10	0.1501	6	0.212	6	0.1939	10	0.1974
		2	0.1553	vw	0.260	017	vw	0.218	$\bar{8}04$	19	0.1285	316	4	0.1428	31	0.210	2	0.1840	29	0.1959
				m	0.253	515	ms	0.211	017				9	0.1382	6	0.203	8	0.1768	4	0.1890
				vw	0.241	317	ms	0.186	824				8	0.1371	6	0.1993	8	0.1760	8	0.1877
				vw	0.234	131	m	0.182	426				8	0.1367	5	0.1986	2	0.1730	14	0.1859
				w	0.228	417	m	0.179	$\bar{4}08$				9	0.1346	6	0.1965	14	0.1715	6	0.1842
				w	0.223	033	w	0.177	1022				5	0.1330	5	0.1934	8	0.1691	6	0.1813
				vw	0.215	720	mw	0.173	10010				3	0.1290	6	0.1859	8	0.1621	12	0.1763
				s	0.210	333	mw	0.168	127						5	0.1839	6	0.1616	27	0.1742
				s	0.202	219									8	0.1764	6	0.1480	6	0.1722
				s	0.194	0010									11	0.1758	4	0.1464	18	0.1677
				m	0.180	920									8	0.1741			26	0.1666
				m	0.178	140									15	0.1712			17	0.1601
				m	0.169	808									6	0.1688			9	0.1578
				s	0.165	3210									10	0.1641			5	0.1527
				m	0.161	540									5	0.1616				
				w	0.157	542														
				w	0.152	1017														

*Interplanar spacings from corresponding reference.
†Interplanar spacings from current work.

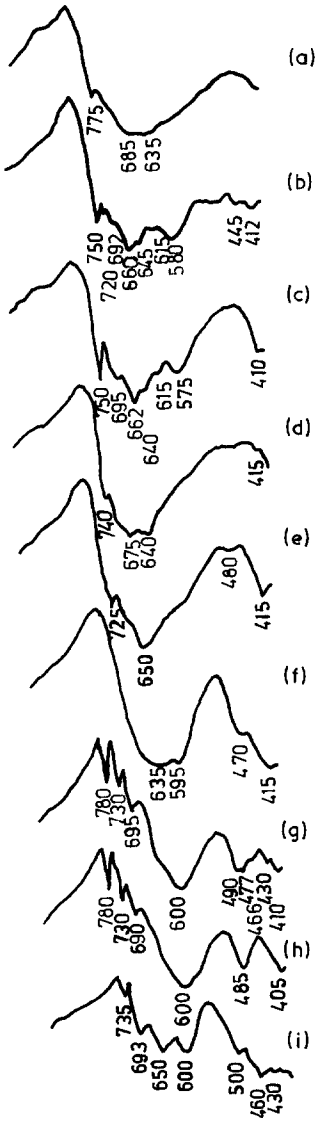


Figure 13 Infrared absorption spectra (cm^{-1}) of crystal phases from the PbO–TeO_2 system: (a) PbO · $4TeO_2$, (b) 2PbO · $5TeO_2$, (c) 2PbO · $3TeO_2$, (d) β-PbO · TeO_2, (e) α-PbO · TeO_2, (f) 2PbO · TeO_2, (g) β-3PbO · TeO_2, (h) α-3PbO · TeO_2 and (i) 5PbO · TeO_2.

crystal phases in the PbO–TeO_2 system are shown in Fig. 13. The results obtained could be used for characterization of their structure.

4. Conclusion

With the help of X-ray microanalysis the composition of the newly forming phases in the binary PbO–TeO_2 system was examined. The formation of phases with 2PbO · $3TeO_2$ composition was confirmed, and the phase $5TeO_2$ · 2PbO corresponds to the phase $2TeO_2$ · PbO. The formation of new phases with chemical composition 2PbO · TeO_2, 5PbO · TeO_2 and two phases with variable composition $4TeO_2$ · PbO to $7TeO_2$ · 2PbO (from 20 to 22.2 mol % PbO) and 5PbO · $2TeO_2$ (from 61.5 to 75 mol % PbO) was established. Based on the results for the chemical compositions of the crystal phases obtained by us and with respect to those reported by other workers, especially by Robertson and Young on temperature data in the range 50 to 100 mol % PbO for the course of the liquidus–solidus lines, a corrected phase diagram for the PbO–TeO_2 system (Fig. 14) was constructed.

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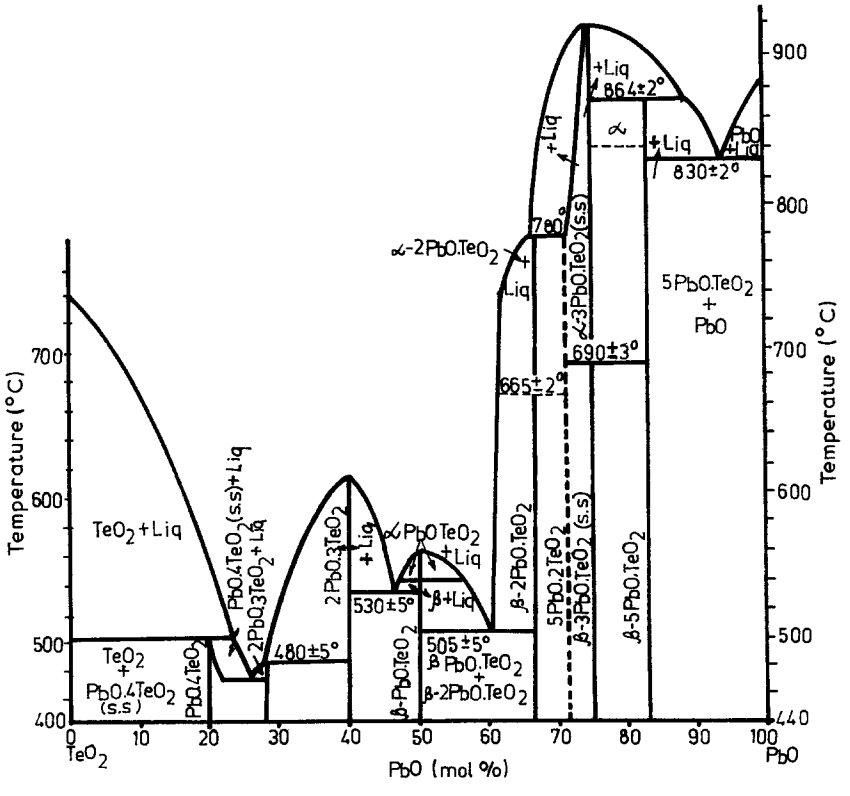

Figure 14 Phase diagram of the PbO–TeO_2 system from the current work.