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Note

Three-component compounds in the system Ge–Te–O and some of their properties

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INTRODUCTION

Attempts to obtain tellurites of germanium in an aqueous medium have not been described so far. Studying the temperature composition projection of the state diagram of the system GeO_2–TeO_2 [1], it was found that no compounds were formed in the system. In ref. 2, however, it is reported that germanium tellurite with composition $Ge(TeO_3)_2$ has been synthesized. Therefore the question of the existence of tellurites of germanium still stands open. This work presents the results of a study of the interactions in the three-component system $GeCl_4$–Na_2TeO_3–H_2O at 100 °C by the solubility method [3] and by measuring pH [4].

EXPERIMENTAL

The concentration of $GeCl_4$ in the initial solutions was 0.025 mol l^{-1}. The titre of these solutions was determined by means of mannitol using the technique from ref. 5. The concentration of Na_2TeO_3 in the precipitating solutions, determined by the bichromatic method [6], in each sample was such that the molar ratio between the concentration of TeO_3^{2-} and Ge^{4+} ranged from 0 to 5.

The samples were prepared by adding 50 ml of a solution of Na_2TeO_3 to 50 ml of a solution of $GeCl_4$. They were thermostatted at 25 °C for 24 h, then they were placed in "Razotherm" glass ampoules, sealed and kept in an air thermostat at 100 ± 0.1 °C until they had attained equilibrium.

The time needed to attain chemical and crystallo-optical equilibrium was studied as in ref. 7. The experimental technique used to perform X-ray phase analysis, pH-metric, crystallo-optical and thermal analyses has also been described in ref. 7.

The concentration of Ge^{4+} and TeO_3^{2-} ions in the equilibrium solutions was determined, and the solubility isotherm was drawn. The equilibrium solutions were also used to determine pH and to draw a plot with coordinates pH–n. The composition of the solid phases was determined (a) by the

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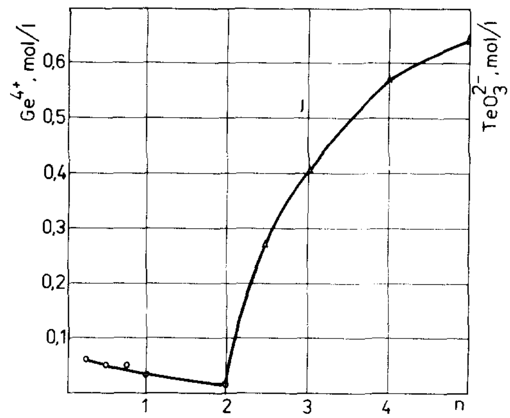

Fig. 1. Solubility for the $GeCl_4$–Na_2TeO_3–H_2O system at 100 °C.

solubility isotherm and the dependence of pH on the mole ratio of TeO_3^{2-} to Ge^{4+}, (b) using the concentration of the unreacted ions in the mother solutions, (c) by chemical preparative analyses of the unwashed solid phases [8] and (d) by chemical, crystallo-optical and X-ray phase analyses of the washed and dried solid phases.

In studying the system $GeCl_4$–Na_2TeO_3–H_2O at 100 °C, it was found that the residual concentration curves had a minimum at $n = 2$ (Fig. 1). Chemical preparative, chemical and crystallo-optical analyses showed that at $n = 0.2$–2 crystals of germanium tellurite with composition $Ge(TeO_3)_2$ are obtained, containing 24.58% GeO_2 and 75.43% TeO_2 (calculated: GeO_2 24.68%; TeO_2 75.32%). The presence of that compound was proved also by recording the pH of the equilibrium solutions as a function of the mole ratio between the components ($n = TeO_3^{2-}$: Ge^{4+}) (Fig. 2). Furthermore, using the above methods, we found that another compound with composition $Ge(TeO_3)_2 \cdot 0.5H_2O$ was formed at $n > 2$. Chemical analysis showed that the

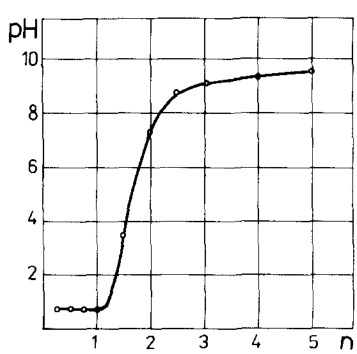

Fig. 2. pH dependence of the molar ratio Na_2TeO_3: $GeCl_4$.

TABLE 1

X-ray data of germanium tellurites

No.	$Ge(TeO_3)_2$		$Ge(TeO_3)_2 \cdot 0.5H_2O$	
	I/I_1	d (Å)	I/I_1	d (Å)
1	9	8.5880	9	7.6280
2	48	5.2154	100	5.6802
3	12	4.1713	14	5.0107
4	13	3.7697	2	3.8667
5	7	3.7078	95	3.3022
6	67	3.4796	4	2.6905
7	30	3.3264	3	2.4422
8	21	3.2318	45	2.2064
9	25	3.1754	2	1.9729
10	100	3.0480	3	1.8554
11	7	2.5707	3	1.7217
12	16	2.4358	3	1.6556
13	23	2.1609	2	1.5166
14	12	1.9217		
15	70	1.8953		
16	47	1.8589		
17	12	1.7127		
18	28	1.6751		
19	12	1.5302		
20	18	1.5055		
21	18	1.4924		

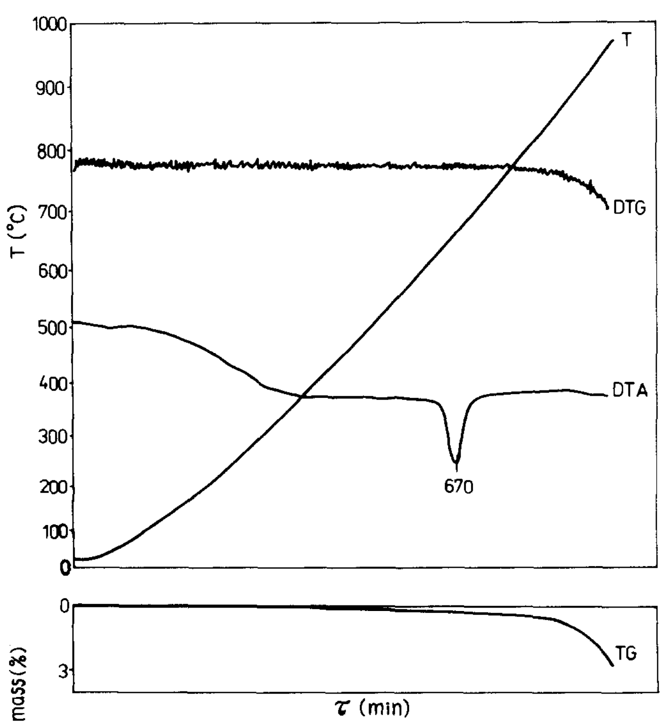

Fig. 3. Derivatogram for $Ge(TeO_3)_2$.

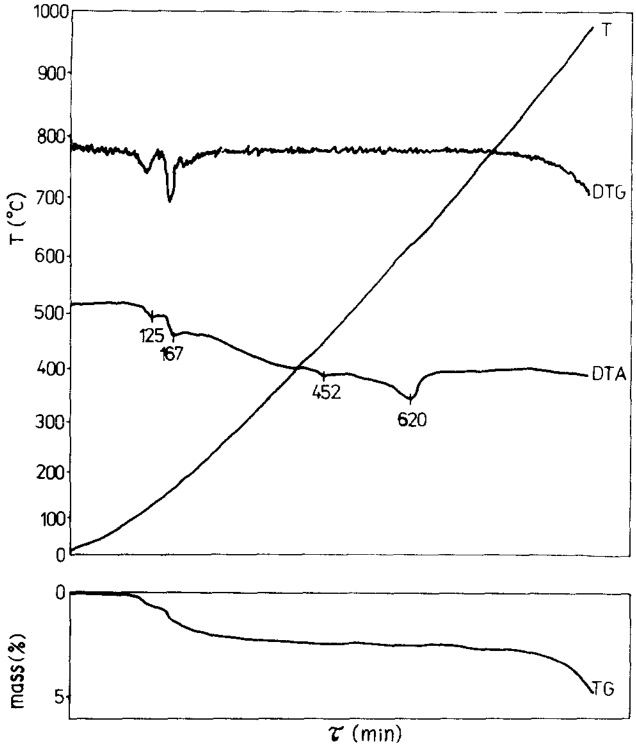

Fig. 4. Derivatogram for $Ge(TeO_3)_3 \cdot 0.5H_2O$.

compound contains 24.21% GeO_2, 73.68% TeO_2 and 2.12% H_2O (calculated: GeO_2 24.17%, TeO_2 73.75% and H_2O 2.08%).

The synthesis of $Ge(TeO_3)_2$ at a mole ratio n of the components from 0 to 2 and the synthesis of $Ge(TeO_3)_2 \cdot 0.5H_2O$ at a ratio n of TeO_3^{2-} : Ge^{4+} where $n > 2$ were also confirmed by X-ray analysis (Table 1).

The thermogram of $Ge(TeO_3)_2$ (Fig. 3) has one endothermic peak at 670 °C. The peak is reversible and visual observation shows that it is due to melting of the compound. Thermal decomposition begins at 780 °C but is insignificant. At 980 °C (the highest temperature to which $Ge(TeO_3)_2$ was heated) the weight loss due to decomposition is about 2.5%.

Figure 4 shows the thermogram of $Ge(TeO_3)_2 \cdot 0.5H_2O$. Dehydration takes place in two stages, at 125 °C and 167 °C. According to chemical analysis data, the product after heating to 200 °C contains 24.72% GeO_2 and 75.29% TeO_2. This composition corresponds to anhydrous $Ge(TeO_3)_2$. The endothermal effect at 452 °C is due to the monotropic polymorphous transition of α-$Ge(TeO_3)_2$ into high temperature β-$Ge(TeO_3)_2$. The β-$Ge(TeO_3)_2$ melts at 620 °C (this corresponds to the last endothermic peak) and begins to decompose slightly at 840 °C. At 980 °C (the final heating temperature) only 2–2.5% of the tellurite is decomposed.

REFERENCES

1 Y. Dimitriew, E. Kaschieva and E. Gurov, Mater. Res. Bull., 11 (1976) 1397.
2 O.K. Chtanov, V.P. Zlomanov and L.L. Doudkin, Khimiya i Fizika Chalkogenidov, Naukova Dumka, Kiev, 1977, p. 82.
3 I.V. Tananaev, Izv. Sekt. Fiz.-Khim. Anal. Inst. Obshch. Neorg. Khim., Akad. Nauk SSSR, 20 (1950) 227, 277.
4 I.V. Tananaev and N.V. Mzaurechvili, Zh. Neorg. Khim., 1 (1956) 2216, 2231.
5 G. Schwarzenbach and H. Flaschka, Kompleksonometricheskoe Titrovanie, Khimiya, Moscow, 1970.
6 S.Yu. Fainberg and N.A. Filippova, Analiz Rud Zvetnich Metalov, Metalurgizdat, Moscow, 1963.
7 G.G. Gospodinov, Thermochim. Acta, 91 (1985) 357.
8 E.V. Margoulis, E.D. Meletina and L.I. Beisekeeva, Zh. Neorg. Khim., 10 (1965) 1481.