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Some properties of zinc tellurates

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Abstract

The solubility isotherm of the system $ZnSO_4$–$K_2H_4TeO_6$–H_2O was studied and the conditions of synthesis of zinc tellurates were determined. The thermal and thermodynamic properties of the compounds obtained were determined.

INTRODUCTION

The tellurates of a number of metals can be used as new materials in semiconductors.

Data concerning zinc tellurates are scarce [1, 2]. In ref. 1, three zinc tellurates, $3ZnO \cdot ZnTeO_4 \cdot 4H_2O$, $4ZnO \cdot TeO_3$ and $ZnTeO_4$, were synthesized by mixing aqueous solutions of zinc sulphate and potassium tellurate. In ref. 2, mixing the same aqueous solutions gave $Zn_2H_2TeO_6 \cdot 2H_2O$ and Zn_3TeO_6. However, the problem of which zinc tellurates are possible remains unresolved, nor are data available concerning the properties of zinc tellurates.

EXPERIMENTAL

Reliable information concerning the composition of all the possible zinc tellurates of the system $ZnSO_4$–$Na_2H_4TeO_6$–H_2O was obtained by studying and drawing its solubility isotherm at 100°C. The Tananaev method of residual concentrations was used. The unwashed solid phases were analysed by a chemico-preparative method [3]. The liquid phases and the washed and dried solid phases were subjected to chemical analysis. In both cases, the metal ions were determined complexometrically [4]. The tellurate ions were analysed iodometrically and gravimetrically [5].

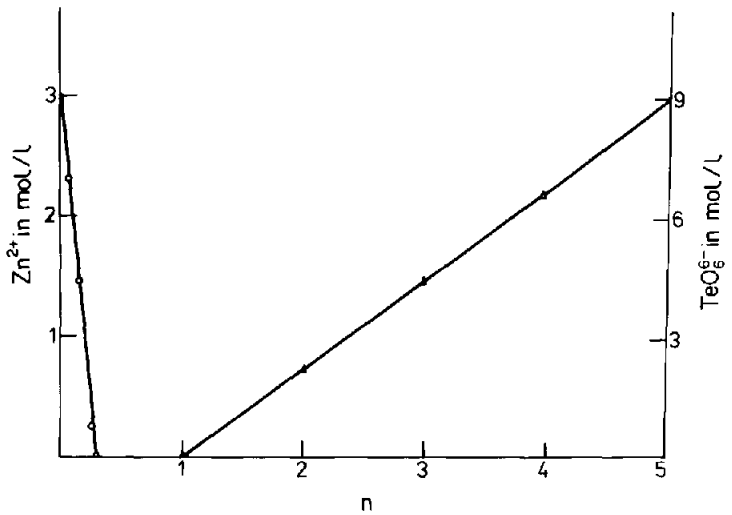

Fig. 1. Solubility for the $ZnSO_4$–$Na_2H_4TeO_6$–H_2O system at 100°C ($n = TeO_6^{6-}:Zn^{2+}$).

Thermal analysis was made with a MOM OD-102 apparatus (Hungary). X-ray phase analysis was carried out using a TURM-61 M apparatus with a copper anode and Kα emission and a nickel filter for β-emission.

RESULTS AND DISCUSSION

The isotherm of the system $ZnSO_4$–$Na_2H_4TeO_6$–H_2O (Fig. 1) indicates that $ZnSO_4$ and $Na_2H_4TeO_6$ interact in three stages.

First, at $n = 0$–0.33, where n is $TeO_6^{6-}:Zn^{2+}$, the normal salt is obtained by the reaction

$$3ZnSO_4 + K_2H_4TeO_6 = Zn_3TeO_6 + K_2SO_4 + 2H_2SO_4$$

The pH changes in this system show that at $n = 0$–0.33, $n = 0.5$ and $n = 1$–5 the acidity of the solution obtained is higher than those of the initial solutions.

At $n = 0.5$ the reaction between the solutions is

$$2ZnSO_4 + Na_2H_4TeO_6 = Zn_2H_2TeO_6 + Na_2SO_4 + H_2SO_4$$

This equation could account for the minimum on the curves for the residual concentrations of Zn^{2+} and TeO_6^{6-}. However, a slight decrease in acidity is observed on the pH curve (Fig. 2).

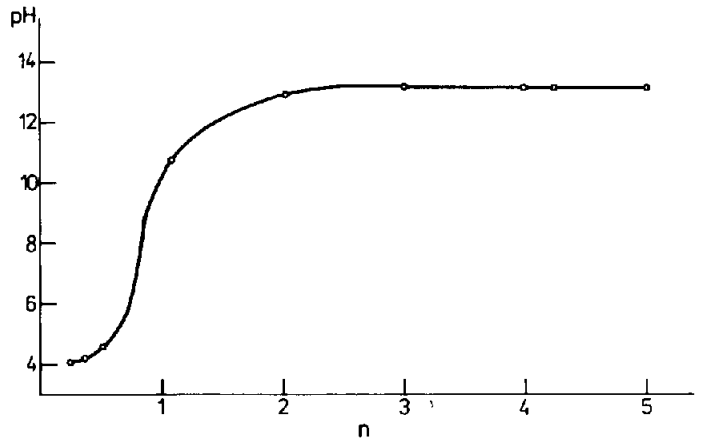

Fig. 2. pH dependence of the molar ratio $Na_2H_4TeO_6$:$ZnSO_4$.

At $n = 1$–5, zinc tetrahydrogen orthotellurate is obtained

$$ZnSO_4 + Na_2H_4TeO_6 = ZnH_4TeO_6 + Na_2SO_4$$

This reaction accounts for the abrupt increase in pH, which is 13 at $n = 3$. The data obtained by the preparative method of analysis of the unwashed solid phases, chemical analysis of the washed and dried phases, and X-ray hatched patterns (Fig. 3) of all the phases confirm the synthesis of three definite compounds in the system. These X-ray patterns differ from those of the starting compounds in peak intensity and interplanar distances. The

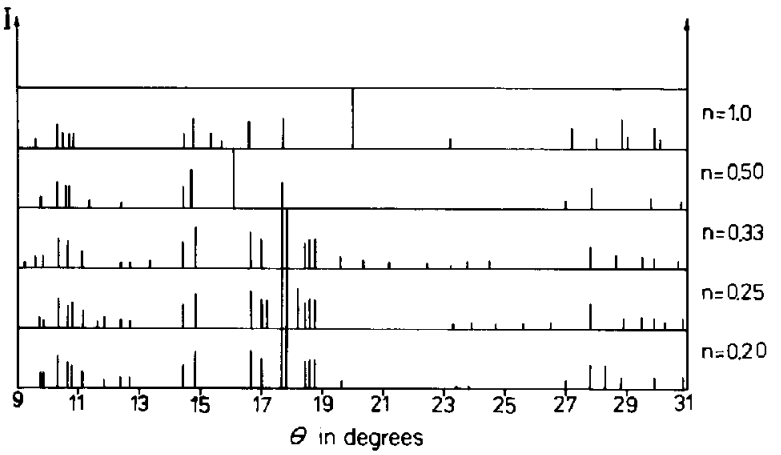

Fig. 3. X-ray patterns of the solid phases of the system $ZnSO_4$–$Na_2H_4TeO_6$–H_2O at 100°C ($n = TeO_6^{6-}$:Zn^{2+}).

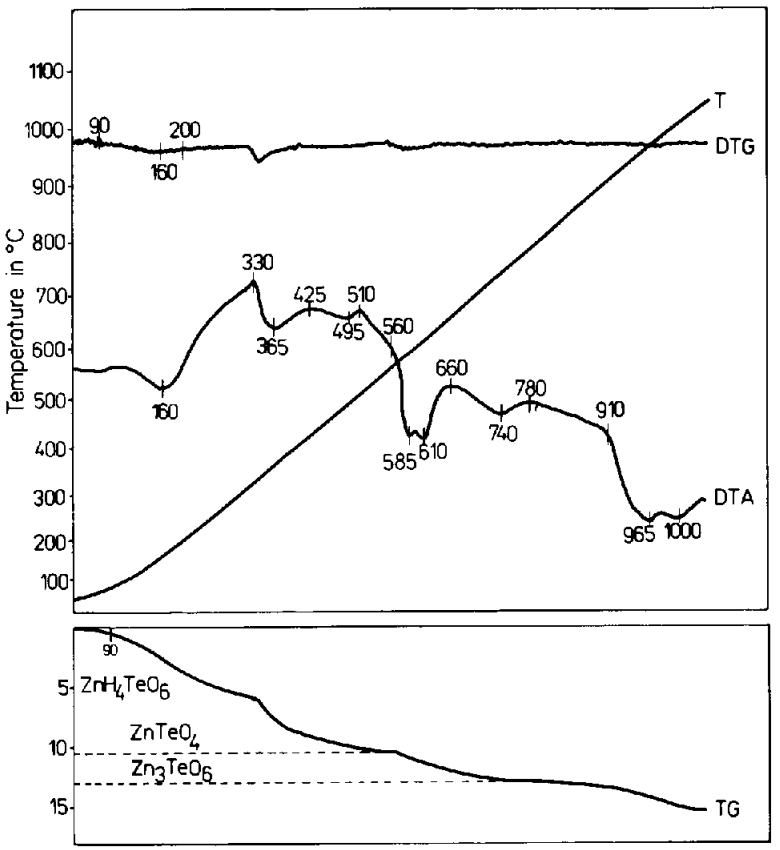

Fig. 4. Derivatogram of ZnH_4TeO_6.

X-ray patterns can be divided into three groups corresponding to the synthesis of three different compounds.

Unlike copper and silver tellurates, hydrogen tellurates and the normal salt are crystalline.

The thermal stability and the thermolysis mechanism of ZnH_4TeO_6 and $ZnTeO_4$ were studied. The derivatogram of Znh_4TeO_6 in Fig. 4 shows that zinc tetrahydrogen orthotellurate starts losing constitutional water at temperatures above 100°C. Dehydration takes place in two stages by the reaction

$$ZnH_4TeO_6 \xrightarrow{-H_2O} ZnH_2TeO_5 \xrightarrow{-H_2O} ZnTeO_4$$

The first molecule of water is liberated at 100–330°C. At 330–425°C, the second molecule of water is liberated and zinc metatellurate is produced.

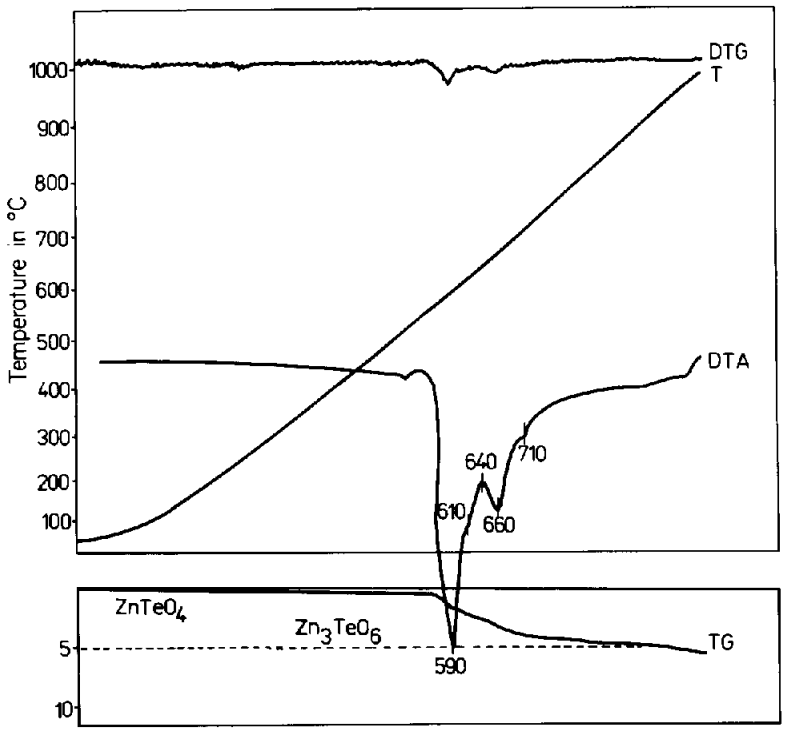

Fig. 5. Derivatogram of $ZnTeO_4$.

The minima on the derivatogram are at 160 and 365°C, respectively. In addition, the derivatogram shows exothermic peaks corresponding to crystallization of the amorphous phases obtained by dehydration. Zinc metatellurate tempered at 510–530°C has a distinct X-ray pattern. Chemical analysis gave the concentration of ZnO as 31.65%, and that of TeO_3 as 68.42%. These data are in good agreement with the theoretical calculations. Zinc metatellurate is a white crystalline substance. It is insoluble in water and soluble in mineral acids.

The derivatogram of $ZnTeO_4$ (Fig. 5) shows that it is thermally stable to 540°C. Above this temperature it starts to decompose, liberating oxygen by the reaction

$$3ZnTeO_4 \rightarrow Zn_3TeO_6 + 2TeO_2 + O_2$$

X-ray phase analysis indicated that this decomposition takes place in stages corresponding to the endothermic peaks at 590, 610 and 710°C on the derivatogram. The X-ray patterns confirm the syntheses of Zn_3TeO_6 and the high-temperature phase TeO_2. Beginning at 770°C, a slight decrease in weight is visible on the curve for the change in weight (TG). This is due to transformation of TeO_2 into the gaseous phase. These results confirm the

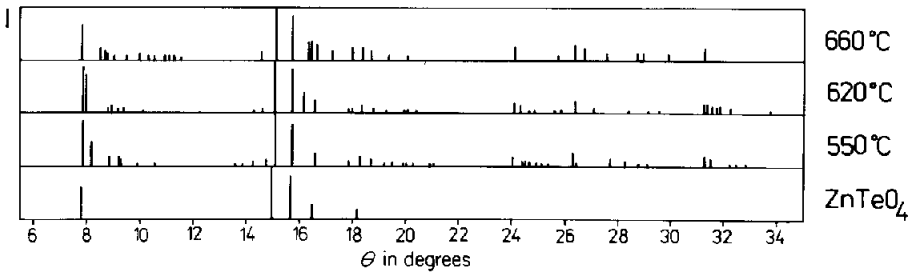

Fig. 6. X-ray patterns of the products of the thermal decomposition of $ZnTeO_4$ at different temperatures.

high thermal stability of Zn_3TeO at 980°C, i.e. the temperature at which the initial product was heated.

The X-ray patterns (Fig. 6) confirm the decomposition mechanism of $ZnTeO_4$ and the accumulation of Zn_2TeO_6 in the decomposition product. The temperature dependence of the molar heat capacity C_p of zinc metatellurate was measured at 390–550 K with a calorimeter (Seteram, France) at a heating rate of 1 K min^{-1}.

The results obtained (Table 1) were used to determine the equation for the temperature dependence of the heat capacity

$$C_{p_T}/\mathrm{J\,K^{-1}\,mol^{-1}} = -1.0480 \times 10^2 + 2.7102 \times 10^{-1} T + 2.4216 \times 10^7 T^{-2}$$

$$10^2 \frac{\delta C_p}{C_p} = 1.8$$

The values of S_T, $H_T - H_0$ and the Gibbs function Φ'' were calculated using this equation and $S^{\ominus}_{298}$ (Table 2).

TABLE 1

Experimental values of the heat capacities of $ZnTeO_4$

T/K	C_p/J mol^{-1} K^{-1}	T/K	C_p/J mol^{-1} K^{-1}
403	149.14	473	129.15
413	154.48	483	131.53
423	148.78	493	133.17
433	142.75	503	129.91
443	135.15	513	126.64
453	132.70	523	124.60
463	130.92	533	122.80

TABLE 2

Thermodynamic functions of $ZnTeO_4$

T/ K	C_{p_T}/ J mol^{-1} K^{-1}	S_T/ J mol^{-1} K^{-1}	$H - H_0$/ J mol^{-1}	Φ''/ J mol^{-1} K^{-1}
298	213.27	142.67	0.00	142.67
300	211.81	144.09	425.08	142.67
310	204.68	150.92	2507.29	142.83
320	197.86	157.31	4519.73	143.19
330	191.34	163.30	6465.46	143.71
340	185.13	168.92	8347.55	144.36
350	179.22	174.20	10169.06	145.14
360	173.62	179.17	11933.03	146.02
370	168.33	183.85	13642.54	146.98
380	163.34	188.27	16300.64	148.01
390	158.66	192.45	16910.39	149.09
400	154.28	196.42	18474.85	150.23
410	150.21	200.17	19997.07	151.40
420	146.45	203.75	21480.12	152.61
430	142.99	207.15	22927.06	153.83
440	139.84	210.40	24340.94	155.08
450	136.99	213.51	25724.83	156.35
460	134.45	216.50	27081.78	157.62
470	132.22	219.36	28414.85	158.91
480	130.29	222.13	29727.11	160.20
490	128.66	224.80	31021.60	161.49
500	127.35	227.38	32301.39	162.78
510	126.33	229.89	33569.54	164.07
520	125.63	232.34	34829.11	165.36
530	125.23	234.73	36083.16	166.65
540	125.14	237.07	37334.74	167.93
550	125.35	239.36	38586.91	169.21
560	125.87	241.63	39842.74	170.48
570	126.69	243.86	41105.28	171.75
580	127.82	246.07	42377.60	173.01
590	129.26	248.27	43662.74	174.27
600	131.00	250.46	44963.77	175.52
610	133.05	252.64	46283.76	176.76
620	135.40	254.82	47625.75	178.01
630	138.06	257.01	48992.80	179.24
640	141.03	259.21	50387.99	180.48
650	144.30	261.42	51814.36	181.70
660	147.88	263.65	53274.97	182.93
670	151.76	265.90	54772.89	184.15
680	155.95	268.18	56311.16	185.37
690	160.44	270.18	57892.86	186.59
700	165.24	272.83	59521.04	187.80
710	170.35	275.21	61198.76	189.02

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