Thermochimica Acta, 189 (1991) 351–355
Elsevier Science Publishers B.V., Amsterdam

Note

Tellurites in the triple systems $ZnSO_4$–Na_2TeO_3–H_2O at 25 °C and $Zn(CH_3COO)_2$–Na_2TeO_3–H_2O at 100 °C

G.G. Gospodinov [a] and V.G. Karaivanova [b]

[a] *Department of Inorganic Chemistry, Higher Institute of Chemical Technology, Burgas (Bulgaria)*

[b] *Department of Inorganic Chemistry, Faculty of Pharmacy, Academy of Medicine, Sofia (Bulgaria)*

(Received 4 February 1991)

The earliest data concerning zinc tellurites are those of Berzelius [1] who obtained $ZnTeO_3$ in the form of a white amorphous powder by means of sedimentary reactions. Markovskii and Pron [2] also obtained $ZnTeO_3$ as a white amorphous powder by mixing 0.5 N solutions of $ZnSO_4$ and Na_2TeO_3.

Another study [3] showed that $ZnTeO_3$ can be obtained by the interaction of ZnO–TeO_2 and TeO_2. By investigating the system ZnO–TeO_2 in the range 50–100 mol.% TeO_2, Marinov and Kozhuharov [4] have determined the presence of two compounds in this concentration interval, $ZnTeO_3$ and $Zn_2Te_3O_8$, melting incongruously at 695 and 642 °C, respectively. The present study investigates the phase state of the tellurites in the systems $ZnSO_4$–Na_2TeO_3–H_2O at 25 °C and $Zn(CH_3COO)_2$–Na_2TeO_3–H_2O at 100 °C, in order to determine a method for the preparation of crystalline zinc tellurites.

The thermolysis of the tellurites thus obtained has also been examined.

EXPERIMENTAL

The starting materials $ZnSO_4$, $Zn(CH_3COO)_2$ and $Na_2TeO_3 \cdot 5H_2O$, all with p.a. qualification, were used for the examination of the $ZnSO_4$–Na_2TeO_3–H_2O system at 25 °C and of the $Zn(CH_3COO)_2$–Na_2TeO_3–H_2O system at 100 °C. The charging of the systems and the investigation of the equilibrium kinetics are reported in ref. 5. After equilibrium had been reached, the liquid phases were separated from the solids at the temperature of the experiment and were subjected to analysis.

The equilibrium solutions and the solid phases were analysed complexometrically for the Zn^{2+} ions [6]; the tellurite ions were analysed by the bichromatic method; and elemental tellurium was determined gravimetrically [7].

0040-6031/91/$03.50

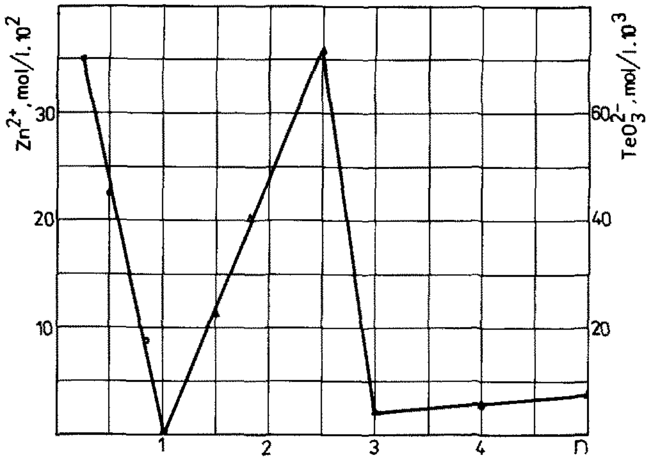

Fig. 1. Solubility of the $Zn(CH_3COO)_2$–Na_2TeO_3–H_2O system at 100 °C.

The method of "residual concentrations", according to Tananaev and Mzaurechvili [8] was used to construct the solubility isotherm.

pH-metric examinations were carried out using a laboratory digital pH meter, LP-17. Derivatographic examinations took place using a Hungarian MOM Company derivatograph, type OD-102. Crystalo-optical examinations were carried out on a Dokuval microscope (F.R.G.). The X-ray analysis was carried out on a DRON-3 apparatus with Cu and Kα radiation.

The composition of the compounds was established by solubility isotherms, by a chemical preparatory method and, after their isolation in a pure state, by chemical and X-ray phase analyses. The solubility isotherm data of the $ZnSO_4$–Na_2TeO_3–H_2O system at 25 °C at concentrations $n = 0.5$, 1, 2 and 3, can produce only one $ZnTeO_3$ phase. The tellurite thus produced was generally separated in a colloidal state. The deposit is strongly solvated; for a complete separation of the adsorbed ions, a longer washing period is necessary. The X-ray phase analysis confirmed the visual observation that $ZnTeO_3$ separates in an amorphous state.

The results of the solubility isotherm studies of the $Zn(CH_3COO)_2$–Na_2TeO_3–H_2O system at 100 °C (Fig. 1) indicate that the phases $ZnTeO_3$ and $Zn_2Te_3O_8$ were formed. In addition, between $n = 0.2$ and 0.25, some phases of variable composition were formed between $ZnTeO_3$ and $Zn(CH_3COO)_2$. The X-ray phase analysis (Fig. 2) and the pH dependence on the mole ratio of the reagents, n, (Fig. 3) confirm the presence of three such phases.

The solubility isotherm shows that the $ZnTeO_3$ solubility in the mother solution is considerable; in our opinion, this indicates the complex interactions between the deposit and the mother solution. The fact that at 25 °C only amorphous $ZnTeO_3$ occurs over the entire concentration range studied, and that three crystalline phases were obtained at 100 °C, shows that there

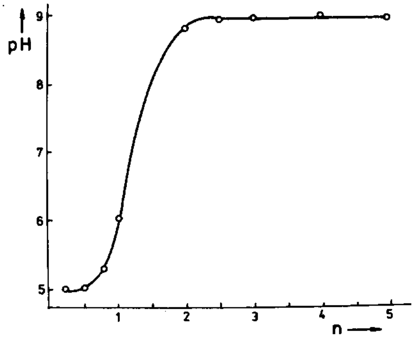

Fig. 2. pH dependence of the molar ratio $Na_2TeO_3 : Zn(CH_3COO)_2$.

are two types of processes taking place: physical aging of the deposit which is in contact with the mother solution and chemical aging of the deposit following interaction with the mother solution. In the first, the X-ray-amorphous $ZnTeO_3$ deposit becomes crystalline under the influence of various factors, such as high temperature and time. During aging of the deposit, all types of irreversible structural changes have been observed: recrystallisation of the primary fractions and the formation of agglomerates; Oswald ripping or growth of the larger fractions, with simultaneous dissolution of the smaller fractions; and thermal aging or formation of more perfect structures due to ion thermal movement.

Significant changes take place as a result of the chemical aging of the deposit. Hydrolysis and chemical interaction leading to the formation of pyrotellurite ($Zn_2Te_3O_8$) takes place between the initially formed $ZnTeO_3$ and the mother solution containing dissolved Na_2TeO_3.

The elementary cell parameters of the two compounds already obtained were measured: normal zinc tellurite, $ZnTeO_3$, crystallises orthorhombically

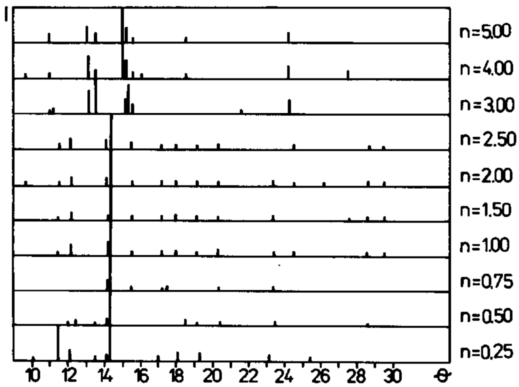

Fig. 3. X-ray pattern of the solid phases of the system $Zn(CH_3COO)_2$–Na_2TeO_3–H_2O at 100 °C ($n = TeO_3^{2-} : Zn^{2+}$).

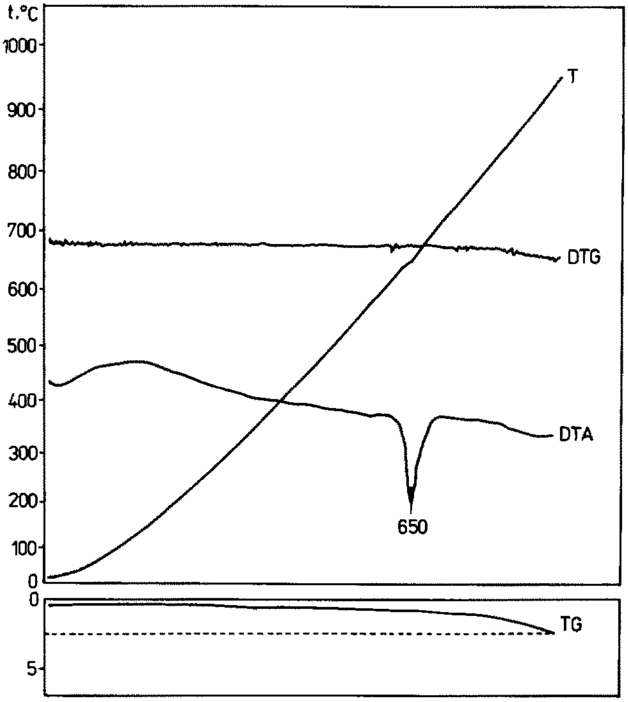

Fig. 4. Derivatogram of $ZnTeO_3$.

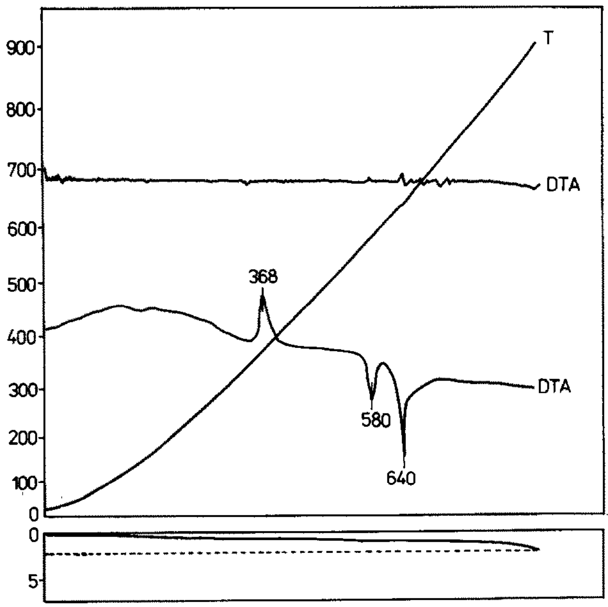

Fig. 5. Derivatogram of $Zn_2Te_3O_8$.

with cell parameters $a = 7.365$ Å, $b = 6.378$ Å and $c = 12.323$ Å (± 0.002 Å); zinc pyrotellurite, $Zn_2Te_3O_8$, crystallises with cell parameters $a_0 = 12.713 \pm 0.001$ Å, $b = 5.212 \pm 0.001$ Å, $c = 11.818 \pm 0.002$ Å and $\beta = 100.0°$.

Figure 4 shows the thermogram of $ZnTeO_3$; the zinc tellurite melts at 650 ° C and the effect is reversible. A chemical analysis of a sample heated to this temperature (ZnO, 33.66%; TeO_2, 66.38%) indicates that it has no connection with the change in the tellurite composition. The thermogravimetric analysis shows that the tellurite is thermo-resistant to 900 ° C. The change in sample weight due to its thermal dissolution and the formation of gaseous TeO_2 at 950 ° C (the upper limit of the thermal treatment) is only 1.5%.

Figure 5 shows the thermogram of $Zn_2Te_3O_8$ with a fixed exoeffect at 368 ° C due to a partial crystallisation of the pyrotellurite. The endoeffect at 580 ° C is due to a polymorphic transformation of α-$Zn_2Te_3O_8$ to β-$Zn_2Te_3O_8$; this is confirmed by the XRD patterns of samples heated to 500 ° C and to 620 ° C. The endoeffect at 640 ° C corresponds to melting of the compound; this effect is reversible and is not connected with any weight change of the pyrotellurite; moreover, visual examination in a furnace confirms that the sample melts at 640 ° C. As can be seen from the TG curve, the weight change in pyrotellurite due to the temperature dissolution of ZnO and TeO_2 and the transformation of TeO_2 to a gas at 900 ° C, is only 1%.

REFERENCES

1 J.J. Berzelius, Ann. Phys. Chem., 32 (1834) 599.
2 L.Ia. Markovskii and G.F. Pron, J. Neorg. Chim., 13 (1968) 2640.
3 R.I. Smirnova, G.F. Pron and L. Ia. Markovskii, Sb. Nauch. Issled. Rab. Chim. Technol. Luminiforov (1963) 1.
4 M.R. Marinov and V.S. Kozhuharov, C. R. Acad. Bulg. Sci., 25 (N3) (1972) 329.
5 G.G. Gospodinov, Thermochim. Acta, 99 (1986) 373.
6 G. Scharlo, Metody Analiticeskoi Chimii, Verlag Chimia, Moscow, 1963.
7 W.F. Hillebrand, G.F. Lundell, H.A. Bright and D.I. Hofman, Applied Inorganic Analysis, John Wiley and Sons Inc., New York, Chapman and Hall Ltd., London, 1953.
8 I.V. Tananaev and N.V. Mzaurechvili, J. Neorg. Chim., 1 (N10) (1956) 2216, 2231.