Thermochimica Acta, 195 (1992) 395–397
Elsevier Science Publishers B.V., Amsterdam

Note

Derivatographic investigation on the temperature enthalpy and entropy of the phase transformations of the tellurites of the p-elements from groups IIIA–VA of the periodic system

G.G. Gospodinov and K.M. Gurova

Department of Inorganic Chemistry and Central Research Laboratory, Technical University of Bourgas, 8010 Bourgas (Bulgaria)

(Received 10 May 1991)

Derivatographic analysis (DTA, TG, DTG) is widely used in the investigation of the phase composition of substances by physical and chemical processes during heating and cooling. Moreover, it is a preferable method, which gives the answer to a number of theoretical and practical problems [1,2].

In the present paper the enthalpy and entropy of polymorphic transformations and crystallization of the X-ray amorphous phases, as well as the enthalpy and entropy of fusion, are determined by means of derivatographic methods. The studied tellurites are those of the elements from groups IIIA–VA of the periodic system. They are synthesized by two methods, from aqueous solutions of the metal salt of alkaline tellurite and by a dry route from metal oxide and tellurium dioxide. In the first method the synthesis has been made on the basis of our investigations on a phase equilibrium in the systems metal salt–alkaline tellurite–water [3–5]. In the second method for preparation of the metal tellurites, stoichiometric amounts of metal oxide and tellurium dioxide, corresponding to the compositions of the relevant tellurite, are thoroughly homogenized. These mechanical mixtures are transferred in to quartz ampoules, which are sealed under vacuum and kept at certain temperatures about 50 °C lower than the temperatures of fusion). The ampoules are opened after 72 h treatment and the product is subjected to a second homogenization. The processes of solid state synthesis and homogenization are repeated three times. The identification of the reaction products is carried out by chemical and X-ray analysis. The type of crystal system and the elementary cell parameters of the obtained tellurites are determined. The chemical analysis of the metal ions (except for Ge^{4+}) is carried out either by (indicator xylenol orange) or reverse (indicator eryochrome black T) complexometric titration [6]. The

TABLE 1
Chemical analysis of the tellurites

Compound	Theoretical content (%)		Chemical analysis data (%)	
	Metal oxide	TeO_2	Metal oxide	TeO_2
$Al_2(TeO_3)_3$	17.98	82.02	18.03, 17.96, 17.99	82.05, 82.0, 82.07
$Ga_2(TeO_3)_3$	28.13	71.87	28.18, 28.08, 28.17	71.80, 71.90, 71.86
$Ge(TeO_3)_2$	24.68	75.32	24.72, 24.65, 24.67	75.31, 75.30, 75.33
$SnTe_3O_8$	23.94	76.06	24.01, 23.94, 23.98	76.10, 76.08, 76.04
$PbTeO_3$	58.31	41.69	58.33, 58.40, 58.30	41.67, 41.72, 41.70
$Pb_2Te_3O_8$	48.25	51.75	48.32, 48.28, 48.23	51.72, 51.74, 51.78
$Bi_{16}Te_5O_{34}$	82.37	17.63	82.40, 82.36, 82.39	17.70, 17.62, 17.65

determination of Ge^{4+} is carried out by volumetric titration with manite [7] and TeO_3^{2-} iodometrically [8] and gravimetrically [9] (Table 1).

X-ray analyses are made on a DRON-2 apparatus with a copper anode and CuK_α emission. The data obtained from X-ray analysis are processed using an IBM RS-TH computer and Brother recorder. The calculated results for the crystal system type and of the parameters of the elementary cell are presented in Table 2.

The thermal analysis measurements are carried out with a derivatograph F. Paulik, J. Paulik, L. Erdey (MOM) under the following conditions: temperature range, 20–1000 °C; heating rate, 10 deg min^{-1}, initial mass of samples, 200–600 ± 1 mg; medium, air (static); inert substance, Al_2O_3 (heated); cone-like corundum crucible, diameter 9.5 mm; thermocouple, Pt/PtRh.

All of the studied substances, obtained from the two methods, are homogenized by grinding in an agate mortar and are sieved through a mesh with dimensions of 0.25 mm^2. The obtained samples are poured into a corundum crucible and heated in a derivatograph.

The values of the enthalpy of the phase transitions, given by the DTA curves have been calculated. Each of the tellurites is heated three or four

TABLE 2
Parameters of the elementary cell of some tellurites of the p-elements from groups IVA and VA of the periodic system

Compound	Symmetry	Parameters of the elementary cell (Å)		
		a	*b*	*c*
$SnTe_3O_8$	Cubic	11.122	–	–
α-$PbTeO_3$	Orthorhombic	4.110	4.905	4.759
β-$PbTeO_3$	Tetragonal	5.321	–	5.951
$Pb_2Te_3O_3$	Orthorhombic	7.143	18.769	19.494
$Bi_{16}Te_5O_{34}$	Tetragonal	5.493		5.639

TABLE 3
Values obtained for the temperatures (T), enthalpies (ΔH) and enthropies (ΔS) of the phase transitions of the studied tellurites by means of thermal analysis

Compound	Type of transformation	T (K)	ΔH (kcal mol^{-1})	ΔS (cal deg^{-1} mol^{-1})
$Al_2(TeO_3)_3$	Fusion	883	5.2	5.9
$Ga_2(TeO_3)_3$	Fusion	1153	76.8	66.6
$Ge(TeO)_3)_2$	Fusion	943	24.4	25.9
$SnTe_3O_8$	Fusion	1178	30.5	25.9
$PbTeO_3$	Polymorphic	763	3.1	4.1
	Fusion	813	11.5	13.9
$Pb_2Te_3O_8$	Fusion	1033	7.7	7.5
$Bi_{16}Te_5O_{34}$	Fusion	1193	31.2	26.2

times. Temperature calibration is carried out using chemically pure substances, K_2SO_4, KCl, NaCl, SnS, with phase transformations at 590 °C, 770 °C, 801 °C and 880 °C respectively. As a reference substance for enthalpy measurements pure NaCl is used, with heat of fusion of 7.22 kcal mol^{-1} [10].

The enthalpies of all the phase transitions are determined through areas of the transitions, registered on the DTA curves by a weight method. The results are presented in Table 3 with the entropies of the tellurites, calculated in a conventional way for comparison.

REFERENCES

1 W.W. Wendlandt, Thermal Methods of Analysis, Wiley–Interscience, New York, 1978, p. 288.
2 V.I. Miheeva, Method Fiziko-Chimitcheskovo analisa v neorganitcheskom sinteze, Nauka, Moscow, 1977.
3 G.G. Gospodinov, Thermochim. Acta, 91 (1985) 351.
4 G.G. Gospodinov, Thermochim. Acta, 91 (1985) 357.
5 G.G. Gospodinov, Thermochim. Acta, 98 (1986) 373.
6 V. Umlaud, A. Janssen, D. Tierg and C. Winsch, Theorie und practische Anwendung von Complexbildnern, Dechema, Frankfurt am Main, 1971.
7 G. Charlot, in Masson et al. (Eds.), Les Methodes de la Chimie Analytique (Analyse Quantitative Minerale), Paris, 1961, p. 734.
8 I. Nazarenko and E.I. Ermakov, Analiticheskaja Chimia Selena, Nauka, Moskow, 1974, p. 22.
9 J.U. Fainberg and N.A. Filipova, Analis Rud Tsvetnyh Metalov, Moskow, 1963.
10 Thermicheskie konstanti vechestva, Spravotchnik, in N.P. Gluchko (Ed.), Moskow, VINITI, 1970.