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Note

Thermodynamic investigations of the phase transformations of the tellurites of the d elements from groups I and IIB of the periodic system

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The thermodynamic constants of the metal tellurites are very important in resolving a number of theoretical and practical problems: in the theoretical construction of the T–X section of state diagrams of MeO–TeO_2 systems; in obtaining monocrystals from these compounds; and in deciding problems associated with the metallurgical extraction of tellurium from its raw material by pyrometallurgical treatment, etc. [1–3].

The present paper gives the enthalpy and entropy of fusion, and the enthalpy and entropy of the polymorphic transformations and crystallizations of the amorphous phases of the metal tellurites. The studied tellurites are those of the d elements from groups I and IIB of the periodic system. They were prepared by two basic methods:

I. By sedimentary reactions, using our earlier investigations on the phase equilibrium of the triple system, metal salt–Na_2TeO_3 (K_2TeO_3)–H_2O. The results obtained for Ag_2TeO_3 are published in ref. 4 and results for the tellurites of Cu, Zn and Cd in ref. 5.

II. By solid state syntheses (except for tellurites of silver) from a metal oxide and tellurium dioxide. A mixture (5 g) of the metal oxide and tellurium dioxide, corresponding to the stoichiometry of the compound, was thoroughly homogenized in an agate mortar. The mixture was then transferred to a quartz ampoule, which was sealed under a vacuum and kept at specified temperatures (40–50°C lower than the temperatures of fusion) [5–7]. After the first heat treatment, the ampoules were opened, and the contents were ground carefully and homogenized. The samples were treated three times in this manner.

The identification of the tellurites synthesized by the two methods was carried out by chemical and X-ray analyses, and the type of crystal system and elementary cell parameters were determined.

The metal oxide content in the Cu, Zn and Cd tellurites was determined by direct (indicator xylenol orange) or reverse (indicator Eriochrome black

TABLE 1

Chemical analyses of the tellurites

Compound	Theoret. content		Chemical analysis	
	Metal oxide (%)	TeO_2 (%)	Metal oxide (%)	TeO_2 (%)
$CuTeO_3$	33.26	66.74	33.31, 33.28, 33.40	66.79, 66.73, 66.76
$CuTe_2O_5$	19.95	80.05	20.01, 19.93, 19.90	80.12, 80.07, 80.09
Ag_2TeO_3	59.22	40.78	59.28, 59.22, 59.30	40.72, 40.80, 40.71
$ZnTeO_3$	33.77	66.23	33.80, 33.72, 33.76	66.21, 66.28, 66.25
$Zn_2Te_3O_8$	28.37	74.63	25.42, 25.36, 25.38	74.60, 74.66, 74.61
$CdTeO_3$	44.58	55.42	44.51, 44.55, 44.57	55.50, 55.44, 55.48
$CdTe_2O_5$	28.69	71.31	28.72, 28.63, 28.70	71.29, 71.38, 71.34

T) complexometric titration [8]. The silver oxide content in silver tellurite was determined by Felhard's method [9]. The TeO_2 content in the tellurites was determined iodometrically and gravimetrically [10].

Table 1 gives the results of the chemical analyses of the tested tellurites together with the calculated values.

The X-ray analysis and investigations were carried out on a DRON-2 apparatus with a copper anode and K_α emission. The X-ray data were gathered on an IBM PC-TX computer and a Brother recorder; the elementary cell parameters were calculated. The results obtained are presented in Table 2.

A derivatographic analysis was carried out in order to determine the heat of the phase transition of the metal tellurites. A MOM derivatograph OD-IO2 was used for the DTA, TG and DTG measurements. For temperature calibrations, chemically pure samples of K_2SO_4, KCl, NaCl and SnS were used, having phase transformations at 590, 770, 801, and 880°C, respectively. A calibration was also carried out using the enthalpy of

TABLE 2

Elementary cell parameters of some tellurites of the d elements from groups I and IIB of the periodic system

Compound	Crystal system	Parameters of the elementary cell (Å)			
		a	*b*	*c*	*β*
$CuTeO_3$	Orthorhombic	7.607	12.704	5.838	–
$CuTe_2O_5$	Monoclinic	6.870	9.322	7.640	109°
Ag_2TeO_3	Monoclinic	7.002	10.530	4.912	51°49′
$ZnTeO_3$	Orthorhombic	7.365	6.384	12.318	
$Zn_2Te_3O_3$	Monoclinic	12.719	5.213	11.827	100°10′
$CdTeO_3$	Cubic	5.345	–	–	–
$CdTe_2O_5$	Monoclinic	9.323	3.854	3.862	106°6′

TABLE 3

Values obtained for the temperatures (T), enthalpies (ΔH) and entropies (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 K^{-1} mol^{-1})
$CuTeO_3$	Crystallization	753	6.5	8.6
	Fusion	918	2.3	2.5
$CuTe_2O_5$	Polymorphic transform.	823	1.7	2.1
	Fusion	903	25.7	28.5
Ag_2TeO_3	Fusion	868	13.3	15.3
$ZnTeO_3$	Fusion	923	15.8	17.1
$Zn_2Te_3O_8$	Crystallization	641	18.8	29.3
	Polymorphic transform.	853	11.9	14.0
	Fusion	913	47.3	51.8
$CdTeO_3$	Polymorphic transform.	883	1.4	2.7
	Fusion	1023	10.9	10.7
$CdTe_2O_5$	Fusion	883	21.7	23.8

transformation of chemically pure NaCl, which has a heat of fusion of 7.22 kcal mol^{-1} [11].

The enthalpies of all the phase transitions were determined from the areas of the transitions on the DTA curves using a weight method, see Table 3. The entropies of the tellurites were calculated in the conventional way (Table 3).

The data presented here have not been previously obtained.

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