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Note

Determination of some thermal constants of the tellurites of the 2s elements of the periodic system

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INTRODUCTION

Information about the phase state of the tellurites of 2s elements is rather scarce. Over a narrow concentration interval by means of DTA and X-ray analysis a T–X projection of the diagrams of state of the systems $MO–TeO_2$ (where M = Mg, Ca, Sr, Ba) [1–9] has been studied and built.

The aim of this work is to specify the separate phases of the triple system M–Te–O and their temperatures of fusion, to confirm some polymorphous transformations and to determine the enthalpies and enthropies of the known phase transformations of the investigated tellurites.

EXPERIMENTAL, RESULTS AND DISCUSSION

Barium and magnesium tellurites were synthesised in quartz ampules from the corresponding oxides (purity > 99.99). In view of the instability of the calcium, strontium and barium oxides, the synthesis of the tellurites of these metals was done from the corresponding carbonates and TeO_2 (with the same purity). In each of the last three cases the synthesis was done three times in a platinum vessel in an inert medium. Completion of the reaction and the purity of the phase obtained was tested by chemical analysis and X-ray spectroscopy.

The chemical analysis of MO was performed complexometrically [10]; TeO_2 was analysed jodometrically [11] and gravimetrically [12]. The results for MO and TeO_2 are shown in Table 1.

The X-ray analysis used DRON-2 apparatus with Cu anode and $K\alpha$ emission and a nickel filter for β radiation.

The thermal curves were obtained on an OD-derivatograph (MOM Company, Budapest) under the following conditions: heating rate

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TABLE 1

Chemical analysis of the tellurites

Compound	Theoretical content (%)		Chemical analysis data (%)	
	MO	TeO_2	MO	TeO_2
$MgTeO_3$	20.16	79.84	20.07; 20.12; 20.18	80.01; 80.10; 79.81
$MgTe_2O_5$	11.21	88.79	11.40; 11.20; 11.18	88.81; 88.77; 88.79
$Mg_2Te_3O_8$	14.41	85.96	14.39; 14.48; 14.40	85.60; 85.55; 85.70
$MgTe_6O_{13}$	4.04	95.96	4.10; 4.02; 4.07	95.89; 95.95; 95.79
$CaTeO_3$	26.00	74.00	26.13; 26.02; 25.92	74.13; 73.99; 73.83
$CaTe_2O_5$	14.93	85.07	14.90; 15.00; 14.87	85.13; 85.02; 85.10
$SrTeO_3$	39.37	60.63	39.32; 39.41; 39.40	60.59; 60.68; 60.64
$SrTe_2O_5$	24.50	75.50	24.60; 24.42; 24.52	75.52; 75.43; 75.40
$BaTeO_3$	49.00	51.00	49.05; 49.13; 48.97	80.93; 50.98; 51.12
$BaTe_2O_5$	32.45	67.55	32.27; 32.51; 32.40	67.59; 67.52; 67.50
$BaTe_4O_9$	19.37	80.63	19.40; 19.33; 19.29	80.70; 80.65; 80.61

10°C min^{-1}; initial weight of samples 400 ± 0.5 mg; medium nitrogen; sample flow-rate 17 l h^{-1}; inert substance Al_2O_3 (heated); corundum crucible.

All of the substances obtained by the two methods were thoroughly ground in an agate mortar and put through a sieve of dimensions

TABLE 2

Values obtained for the temperature (T), enthalpy (ΔH) and entropy (ΔS) of phase transitions of the tellurites

Compound	T (K)		ΔH (kcal mol^{-1})	ΔS (cal K^{-1} mol^{-1})
	From DTA	Lit. value		
$MgTeO_3$	1123 (fusion)	–	11.4	10.2
$MgTe_2O_5$	1113 (fusion)	1103	18.1	16.3
$Mg_2Te_3O_8$	1123 (fusion)	–	42.2	37.6
$MgTe_6O_{13}$	993 (fusion)	–	47.4	47.8
$CaTeO_3$	1148 (polym. tr.)	1118	3.8	3.3
$CaTeO_3$	1352 (fusion)	1318	6.7	4.9
$CaTe_2O_5$	1093 (polym. tr.)	1068	0.36	0.2
$CaTe_2O_5$	1143 (fusion)	1123	13.8	12.0
$SrTeO_3$	1053 (fusion)	–	55.5	53.0
$SrTe_2O_5$	883 (polym. tr.)	888	2.9	2.3
$SrTe_2O_5$	963 (polym. tr.)	–	2.3	2.4
$SrTe_2O_5$	1078 (fusion)	1103	9.8	9.1
$BaTeO_3$	1043 (polym. tr.)	–	1.1	1.1
$BaTeO_3$	1183 (fusion)	1203	4.7	4.0
$BaTe_2O_5$	838 (polym. tr.)	–	3.7	4.4
$BaTe_4O_9$	873 (fusion)	873	36.8	42.2

0.25 mm^2. The samples obtained were poured into a corundum crucible and heated in the derivatograph. For each of the tellurites four or five determinations were made and the results combined.

The thermal effects of phase transformations on the DTA curve peaks were determined. For calibration according to temperature, chemically pure standard substances K_2SO_4, KCl, NaCl and SnS were used (phase transformations at 590, 770, 801, and 880°C respectively).

For calibration according to enthalpy of transformation, NaCl p.a. (pure of analysis) was used (heat of fusion 7.22 kcal mol^{-1} [13]).

The enthalpy of each phase transformation was determined throughout the range of the corresponding transition on the DTA curve by a weight method (Table 2). The enthalpies of the transformations were calculated in the conventional thermodynamic way (Table 2).

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