Journal of Thermal Analysis and Calorimetry, Vol. 65 (2001) 983–987

Short Communication

ENTHALPIES AND ENTROPIES OF MELTING OF THE TELLURITES OF THE RARE-EARTH ELEMENTS FROM THE YTTRIUM GROUP

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(Received in revised form January 5, 2001)

Abstract

A derivatograph (MOM, Hungary) was used to determine the temperatures, enthalpies and entropies of melting of the tellurites of the rare-earth elements from the yttrium group (Gd, Tb, Dy, Ho, Er, Tm, Yb, Ln and Y). The necessary normal tellurites of type $Ln_2(TeO_3)_3$ and tetratellurites of type $Ln_2Te_4O_{11}$ were synthesized in two ways. The melting temperatures of each sub-group were found to undergo non-monotonous changes as the ionic radii of the corresponding elements changed. The progressive filling of the 4*f* sublayers with electrons resulted in non-significant changes in melting temperature, as expected.

Keywords: enthalpies and entropies of melting, tellurites, temperatures, thermal analysis

Introduction

Enthalpies and entropies of melting are of great importance in modern thermodynamic analysis. They characterize the intermolecular interactions in the corresponding phases [1] and can be used to calculate theoretical state diagrams when this is impossible experimentally for some reason [2].

Determination of the nature of the enthalpy of melting and its separate components is directly related to the problem of crystal growth and the formation of ideal structures [3]. The value of the entropy of melting is a criterion for one mechanism of crystal growth to change into another [4, 5]. Thus, the kinetics and morphology of the

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

growth of crystals with different physicomechanical characteristics, as confirmed in [6], are substantially determined by the entropy of melting.

The entropy of a phase transition is particularly important as a criterion for the stability of the phases with a definite degree of disorder [7–9], as in the case, for example, when new glass-like semiconductors are developed for the needs of the electronics industry. It is known that in this case the entropies of melting of the separate components reveal the presence or absence of areas of glass formation in the complex semiconductor systems.

Only a few data are available concerning the tellurites of rare-earth elements reported during recent decades. These data are related to the study of *T–x* projections of state diagrams for the systems Ln_2O_3–TeO_2 [10–12]. The solubility isotherm of the system $La(NO_3)$–Na_2TeO_3–H_2O at room temperature was earlier constituted, and thereby the possibility of preparation of tellurites under these conditions was studied [13–14]. Regardless of the amount of precipitant used, normal tellurite with an amorphous structure, $Ln_2Te_4O_{11}$, was obtained [14]. This was confirmed by other authors [15, 16]. The second group of tellurites, $Ln_2Te_4O_{11}$, has been obtained and investigated [17–19]. Studies on the physical and chemical properties, including the thermal stabilities of these compounds, have also been reported. However, no data relating to the enthalpies and entropies of the phase transitions of the tellurites of the rare-earth elements have been published so far. This fact aroused our interest in these systems.

Experimental, results and discussion

In order to determine the thermodynamic parameters, all the necessary tellurites were synthesized.

The normal tellurites, $Ln_2(TeO_3)_3$, were synthesized by hydrothermal technology in a steel autoclave with a teflon coating, at 250°C for 96 h. The tetratellurites were obtained by solid-phase synthesis from well-homogenized mechanical mixtures of Ln_2O_3 and TeO_2 corresponding to the stoichiometry of the tellurites. The temperatures of tempering were determined by preliminary thermal analysis.

In order to synthesize $Ln_2Te_4O_{11}$, the processes were carried out in the following sequence: heating the samples for 48 h at a temperature 50°C lower than the melting temperatures of the corresponding tellurites, grinding, homogenisation, and repeated vacuum synthesis at the same temperature and for the same time.

The compositions of the compounds were checked by chemical analysis, and the completeness of synthesis was checked by X-ray phase analysis. The metal oxide content in each tellurite was determined by direct complexometric titration [20] and the TeO_2 content iodometrically and gravimetrically [21] (Table 1).

Since some published X-ray data are available, the syntheses of the tellurites were considered to be complete if the measured relative intensities and interplanar distance coincided with those in the literature. In the cases when no such data are available, the completeness of the synthesis was determined by the absence of bands corresponding to the initial metal oxide and tellurium oxide in the X-ray patterns of the synthesized compounds. The parameters and the volumes of the elementary cells

of a number of tellurites were calculated from the measured X-ray data and by using the method of analogy.

Table 1 Chemical analyses of the tellurites

Compound	Theoretical content/%		Chemical analysis/%	
	Metal oxide	TeO_2	Metal oxide	TeO_2
$Gd_2(TeO_3)_3$	43.09	56.91	43.12; 43.06; 43.10	57.00; 56.88; 56.93
$Gd_2Te_4O_{11}$	36.22	63.78	36.19; 36.22; 36.20	63.81; 63.75; 63.79
$Tb_2(TeO_3)_3$	43.31	59.69	43.33; 43.29; 43.30	56.70; 56.73; 56.78
$Tb_2Te_4O_{11}$	36.43	63.57	36.44; 36.40; 36.44	63.60; 63.55; 63.57
$Dy_2(TeO_3)_3$	43.79	56.21	43.80; 43.81; 43.78	56.20; 56.23; 56.21
$Dy_2Te_4O_{11}$	36.88	63.12	36.92; 36.85; 36.88	63.08; 63.10; 63.15
$Ho_2(TeO_3)_3$	44.11	55.89	44.10; 44.09; 44.12	55.90; 55.91; 55.88
$Ho_2Te_4O_{11}$	37.18	62.82	37.21; 37.17; 37.18	62.80; 62.84; 62.82
$Er_2(TeO_3)_3$	44.41	55.59	44.40; 44.42; 44.41	55.62; 55.56; 55.60
$Er_2Te_4O_{11}$	37.43	62.53	37.48; 37.39; 37.47	62.55; 62.50; 62.53
$Tm_2(TeO_3)_3$	44.68	55.37	44.60; 44.64; 44.62	55.40; 55.38; 55.35
$Tm_2Te_4O_{11}$	37.67	62.33	37.71; 37.68; 37.66	62.35; 62.33; 62.28
$Yb_2(TeO_3)_3$	45.15	54.85	45.18; 45.15; 45.14	54.80; 54.88; 54.84
$Yb_2Te_4O_{11}$	38.17	61.83	38.20; 38.16; 38.18	61.69; 61.77; 61.85
$Ln_2(TeO_3)_3$	45.39	54.61	45.40; 45.38; 45.41	54.63; 54.61; 54.60
$Y_2(TeO_3)_3$	32.04	67.96	32.13; 32.11; 32.06	68.00; 67.95; 67.92
$Y_2Te_4O_{11}$	26.13	73.87	26.09; 26.15; 26.14	73.75; 73.83; 73.88

The temperatures, enthalpies and entropies of melting of the synthesized tellurites were determined with a derivatograph (MOM, Hungary). The operating conditions were: temperature, from 20 to 1100°C; heating rate, 10°C min^{-1}; sample mass 200–300 mg; thermocouple, Pt/PtRh; standard substance Al_2O_3; in a medium of chemically pure nitrogen, with metalloceramic crucibles. For temperature calibrations, chemically pure samples of K_2SO_4, KCl, NaCl and SnS were used, which have phase transformations at 590, 770, 801 and 880°C, respectively. Calibration was also carried out by using the enthalpy of melting of chemically pure NaCl [22–24]. The enthalpies of all the phase transitions were determined from the areas of the transitions in the DTA curves (Fig. 1), via a weight method. Five determinations of the enthalpy of each tellurite were made and the results were averaged. The values obtained and the known thermochemical dependences were utilized to calculate the entropies of the corresponding transitions (Table 2).

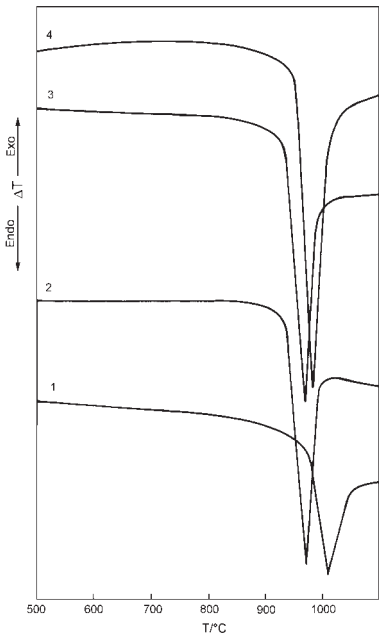

Fig. 1 DTA curves of some normal and tetratellurites of rare-earth elements from the yttrium group: 1 – $Ho_2(TeO_3)_3$; 2 – $Ho_2Te_4O_{11}$; 3 – $Er_2(TeO_3)_3$; 4 – $Er_2Te_4O_{11}$

Table 2 Values obtained for the temperatures (T), enthalpies (ΔH) and entropies (ΔS) of melting of the tellurites

Compound	T/K	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
$Gd_2(TeO_3)_3$	1263	52	41
$Gd_2Te_4O_{11}$	1243	122	98
$Tb_2(TeO_3)_3$	1328	40	29
$Tb_2Te_4O_{11}$	1278	113	89
$Dy_2(TeO_3)_3$	1313	67	51
$Dy_2Te_4O_{11}$	1243	59	47
$Ho_2(TeO_3)_3$	1283	100	78
$Ho_2Te_4O_{11}$	1248	208	167
$Er_2(TeO_3)_3$	1248	173	139
$Er_2Te_4O_{11}$	1253	272	217
$Tm_2(TeO_3)_3$	1188	148	125
$Tm_2Te_4O_{11}$	1168	56	48
$Yb_2(TeO_3)_3$	1238	204	165
$Yb_2Te_4O_{11}$	1213	87	72
$Ln_2(TeO_3)_3$	1283	347	270
$Y_2(TeO_3)_3$	1243	139	111
$Y_2Te_4O_{11}$	1263	144	114

Conclusions

1. The melting temperatures and related thermodynamic parameters such as the enthalpies and entropies of the tellurites of the rare-earth elements from the yttrium group were obtained.
2. The melting temperatures in each subgroup were found to undergo non-monotonous changes as the ionic radii of the corresponding elements changed.
3. The progressive filling of the 4*f* sublayers with electrons resulted in non-significant changes in the melting temperatures, as expected.
4. Thorough study of the tellurites of these rare-earth elements indicates that the results obtained allow theoretical calculations of the state diagrams of similar two-component systems. Other thermodynamic calculations can also be performed.

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