STRUCTURAL, THERMAL AND THERMODYNAMIC INVESTIGATION OF THE TELLURITES OF RARE-EARTH ELEMENTS FROM CERIUM GROUP

G. G. Gospodinov[1]*, N. I. Ilieva*[1] *and Z. M. Dimitrova*[2]

[1]Department of Inorganic Chemistry, Prof. Assen Zlatarov University, 8010 Bourgas, Bulgaria
[2]Department of Physics, Prof. Assen Zlatarov University, 8010 Bourgas, Bulgaria

Abstract

Thirteen tellurites of rare-earth elements from cerium group (Sc, La, Ce, Pr, Nd, Sm, Eu) have been synthesized and characterized by chemical, X-ray and thermal analyses. The space group, crystal systems and parameters of the elementary cells of most of the tellurites have been established. The temperatures, enthalpies and entropies of melting were measured. The change of melting temperatures *vs*. ion radius occurs gradually in a uniform mode with some exceptions.

Introduction

Enthalpies and entropies of melting are of great importance in thermodynamic analysis. They can be used to calculate theoretical state diagrams when this is impossible experimentally for some reason [1, 2]. They are also made use of in evaluating segregation coefficients [3] and the numerous kinetic parameters of melts [4]. The value of the entropy of melting is a criterion for changing one mechanism of crystal grown into another [5, 6] and for the stability of the phases with a definite degree of disorder [7–9] as in the case, for example, when new glasslike semiconductors are developed for the needs of electronic industry.

Only a few data are available concerning the tellurites of rare-earth elements reported during resent decades. These data are related to the study of $T–x$ projections of state diagrams for the $Ln_2O_3–TeO_2$ systems [10–12]. The solubility isotherm of the system $Ln(NO_3)–Na_2TeO_3–H_2O$ 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, $Ln_2(TeO_3)_3$ was obtained [14]. This was confirmed by other authors [15, 16]. The second group of tellurites, $Ln_2Te_4O_{11}$, has been obtained and studies on the physical and chemical properties, including the thermal stabilities of these compounds, have also been reported [17–19].

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

Materials

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

Synthesis of normal tellurites of the $Ln_2(TeO_3)_3$ type involves blending equimolar amounts of hot aqueous solutions containing nitrates of the cerium group with sodium tellurite. The amorphous tellurite tetrahydrate thus obtained can be separated from the mother liquor by filtration, rinsing and subsequent drying procedures. The following thermal treatment for 72 h at 800°C in an inert medium results in dehydration and crystallization of the product.

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

Methods

The compositions of the compounds were checked by chemical analysis, and the completeness of synthesis was checked by X-ray phase analysis. X-ray patterns were made by using a URD-6 (Germany) apparatus with Cu anode, K_α emission, and nickel filter for β-emission. The metal oxide content in each tellurite was determined by direct complexometric titration [20] and the TeO_2 content-iodometrically and gravimetrically [21, 22] (Table 1).

The temperatures, enthalpies and entropies of melting of the synthesized tellurites were determined with a derivatograph (MOM, Hungary) in following conditions: temperature from 20 to 1100°C; heating rate, 10°C min^{-1}; sample mass, 100–400±0.5 mg; in a medium of chemically pure nitrogen. For temperature calibration, 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 [23, 24].

Results and discussion

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

Table 1 Results from the chemical analyses of the metal tellurites

Compound	Calculated/mass%		Observed/mass%	
	metal oxide	TeO_2	metal oxide	TeO_2
$Sc_2(TeO_3)_3$	22.36	77.64	22.37±0.02	77.64±0.02
$La_2(TeO_3)_3$	40.49	59.51	40.50±0.02	59.50±0.02
$La_2Te_4O_{11}$	33.79	66.21	33.80±0.01	66.22±0.02
$Ce_2(TeO_3)_3$	40.67	59.33	40.68±0.02	59.32±0.02
$CeTe_3O_8$	26.44	73.56	26.45±0.02	73.56±0.01
$Pr(TeO_3)_2$	35.14	64.86	35.12±0.02	64.86±0.02
$PrTe_3O_8$	26.53	73.47	26.54±0.01	73.47±0.03
$Nd_2(TeO_3)_3$	41.27	58.73	41.27±0.02	58.75±0.02
$Nd_2Te_4O_{11}$	34.52	65.48	34.52±0.03	65.47±0.03
$Sm_2(TeO_3)_3$	42.15	57.85	42.15±0.02	57.86±0.02
$Sm_2Te_4O_{11}$	35.33	64.67	35.33±0.02	64.68±0.03
$Eu_2(TeO_3)_3$	42.36	57.64	42.37±0.02	57.64±0.04
$Eu_2Te_4O_{11}$	35.54	64.46	35.54±0.01	64.47±0.03

Table 2 Parameters of the elementary cell of the tellurites studies

Compound	Space group	Parameters of the elementary cell (Å)				$Z^{\bullet}$
		a	b	c	β	
$Sc_2(TeO_3)_3$	P2$_1$/c	16.85833	9.99014	11.77419	102°91'	8
$La_2(TeO_3)_3$	P2$_1$/m	13.8269	6.8683	7.9437	89°09'	4
$La_2Te_4O_{11}$	P2/m	12.2562	5.1314	15.8341	107°37'	4
$Ce_2(TeO_3)_3$	P2$_1$/m	13.2200	6.9493	6.9493	96°30'	4
$CeTe_3O_8$	–	–	–	–	–	–
$Pr(TeO_3)_2$	–	–	–	–	–	–
$PrTe_3O_8$	P2/m	12.4108	4.9112	16.1113	104°80'	2
$Nd_2(TeO_3)_3$	P2$_1$/m	13.8871	6.9873	8.0152	90°46'	4
$Nd_2Te_4O_{11}$	C2/c	12.600	5.216	16.270	106°00'	4
$Sm_2(TeO_3)_3$	P2$_1$/c	16.88525	9.83632	11.86666	106°57'	8
$Sm_2Te_4O_{11}$	C2/c	12.560	5.174	16.190	106°00'	4
$Eu_2(TeO_3)_3$	P2/m	15.8141	9.1876	9.3914	115°61'	4
$Eu_2Te_4O_{11}$	C2/c	12.601	5.121	16.198	105°81'	4

$^{\bullet}$Number of formula units

Since some published X-ray data are available, the syntheses of tellurites were considered to be complete if the measured relative intensities and interplanar distance coincided with those in literature. In cases when no such data are available, the com-

pleteness 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 space groups, crystal systems and parameters 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 2). The results show, that the investigated tellurites are of the monoclinic crystal system.

Table 3 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}
$Sc_2(TeO_3)_3$	1123	5.5	5.0
$La_2(TeO_3)_3$	1218	26.0	21.5
$La_2Te_4O_{11}$	1198	62.5	52.0
$Ce_2(TeO_3)_3$	1283	23.0	18.0
$CeTe_3O_8$	1078	49.0	45.0
$Pr(TeO_3)_2$	1198	30.5	25.5
$PrTe_3O_8$	1223	52.5	43.0
$Nd_2(TeO_3)_3$	1203	53.0	44.6
$Nd_2Te_4O_{11}$	1203	61.0	51.0
$Sm_2(TeO_3)_3$	1143	60.0	53.0
$Sm_2Te_4O_{11}$	1233	100.0	81.0
$Eu_2(TeO_3)_3$	1283	50.0	39.0
$Eu_2Te_4O_{11}$	1243	29.0	23.5

The melting temperatures of the tellurites are obtained from DTA curves (Fig. 1) and they vary from 850 to 1010°C (Table 3). The change of the melting temperatures, *vs*. ion radius occurs gradually in a uniform mode, with the exception of Ln (*d*-element) and Pr (oxidation state Pr^{4+}). Some discrepancies, concerning Eu^{3+} can be explained by the particular stability of f^7 orbitals, i.e. the highest unoccupied and fully occupied f^7 orbitals are known to be stable.

On the basis of the areas of the endotherm peaks on DTA curves the entropies of melting are calculated, via a mass method [23]. 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 3).

The data presented here were not obtained previously. Thorough the study of tellurites of rare-earth elements from the cerium group indicates that the results obtained allow theoretical calculations of the state diagrams of similar two-component systems. Other thermodynamic calculations can also be performed.
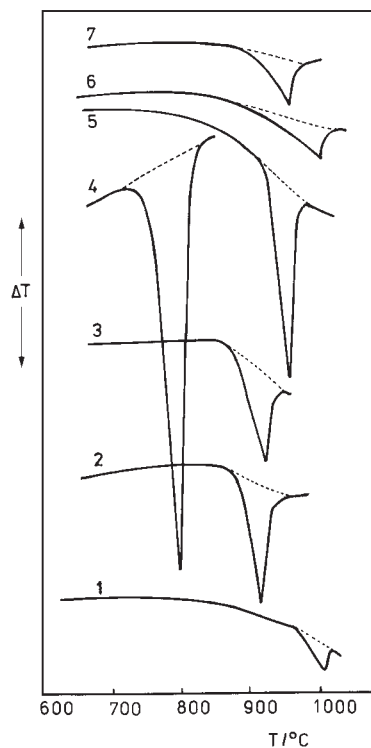
Fig. 1 DTA curves – peaks of melting of NaCl (standard) and of the tellurites:
1 – Ce(TeO$_3$)$_3$ – 120 mg; 2 – Pr(TeO$_3$)$_2$ – 300 mg; 3 – Nd$_2$(TeO$_3$)$_3$ – 400 mg;
4 – NaCl – 200 mg; 5 – Sm$_2$Te$_4$O$_{11}$ – 400 mg; 6 – Eu$_2$(TeO$_3$)$_3$ – 200 mg;
7 – Eu$_2$Te$_4$O$_{11}$ – 300 mg

Conclusions

- Melting temperatures and related thermodynamic parameters such as enthalpies and entropies of the tellurites of rare-earth elements from cerium group were obtained.
- The space group, crystal systems and parameters of the elementary cells were established.
- The change of the melting temperatures, *vs*. ion radius occurs gradually in a uniform mode, with the exception of Ln (*d*-element) and Pr (oxidation state Pr^{4+}). Some discrepancies, concerning Eu^{3+} can be explained by the particular stability of f^7 orbitals, i.e. the highest unoccupied and fully occupied f^7 orbitals are known to be stable.

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