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DETERMINATION OF STANDARD ENTHALPIES OF FORMATION OF THE TELLURITES OF THE RARE EARTHS Y, La, Ce AND Pr BY DSC METHOD

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Abstract

The standard enthalpies of tellurites of Y, La, Ce and Pr were determined by differential scanning calorimetric (DSC) method. The completeness of the chemical reactions between the metal oxides and tellurous oxide were checked by DSC and X-ray powder diffraction methods. The calculated standard enthalpies are presented.

Keywords: calorimetry, enthalpies of formation, rare earth, tellurites, thermodynamic data, X-ray analysis

Introduction

There are random literature data about the tellurites under study and they are mainly concerned with their synthesis [1–6] and oxidation [7]. The authors synthesized and experimentally determined the standard enthalpies of formation of a number of tellurites [8, 9]. Data concerning the standard enthalpies of formation of the rare earths studied in the present work are not available. These functions are particularly necessary to develop rational technologies for their synthesis as well as to operate laser and semiconductor apparatuses based on them. Filling this gap was the aim of the present study.

Experimental

Materials

The initial metal tellurites were obtained from high purity (99.999%) metal oxides and tellurous oxide.

The metal oxides used to determine the standard enthalpy of formation were subjected to X-ray analysis and X-ray patterns were obtained. It was established that Y_2O_3 crystallizes in a cubic crystal system of a Mn_2O_3 structure type. The parameters of the elementary cell for Y_2O_3 was found to be a=10.606 Å. La_2O_3 crystallizes in a hexagonal lattice, the parameters of the elementary cell being a=3.9392 and c=6.1273 Å. Cerium diox-

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ide crystallizes in a face centered cubic crystal lattice of a CaF_2 structure type. The parameter of the elementary cell is a=5.3938 Å. The obtained parameters of the elementary cells are in good agreement with ICDD reference tables.

Mixtures were prepared and homogenized thoroughly. The degree of homogenization was checked chemically and by X-ray analyses.

Chemical analysis

The chemical analysis for metal ions was made complexometrically [10]. The tellurite ions were analyzed bichromatically or gravimetrically [11]. The data obtained (Table 1) show that mechanical mixtures were homogenized and their composition corresponds to the stoichiometry of the compounds under study.

Table 1 Results from the chemical analysis of the mechanical mixture of a metal oxide and tellurous oxide coresponding to the stoichiometry of the compound

Compound	Calculated/%		Found/%	
	Metal oxide	Tellurous oxide	Metal oxide	Tellurous oxide
$Y_2(TeO_3)_3$	32.04	67.96	32.13, 32.11, 32.03	68.00, 67.95, 67.92
$Y_2Te_4O_{11}$	26.13	73.87	26.09, 26.15, 26.14	73.75, 73.85, 73.88
$La_2(TeO_3)_3$	40.49	59.51	40.53, 40.44, 40.49	59.49, 59.53, 59.57
$La_2Te_4O_{11}$	33.79	66.21	33.84, 33.77, 33.87	66.22, 66.19, 66.21
$Ce(TeO_3)_2$	35.03	64.97	35.00, 35.07, 35.01	65.01, 64.96, 64.96
$CeTe_3O_8$	26.44	73.56	26.41, 26.48, 26.44	73.51, 73.57, 73.56
$Pr(TeO_3)_2$	35.14	64.86	35.11, 35.19, 35.15	64.88, 64.79, 64.86
$PrTe_3O_8$	26.53	73.47	26.48, 26.55, 26.51	73.51, 73.46, 73.48

X-ray phase analysis

Part of the mechanical mixtures were sealed in vacuum quartz ampoules. Solid phase synthesis was carried out at a temperature which was 50°C lower than the melting temperatures of the corresponding tellurites. X-ray patterns were made using a URD-6 apparatus (Germany) with Cu anode and K_α-emission and a nickel filter for β-emission. The samples were considered to be homogeneous if the interplanar distances and the intensity of all peaks on the X-ray patterns corresponded to the tellurites under study. When no X-ray data of the corresponding tellurite are available, the mixtures were assumed to be homogeneous if the X-ray patterns showed no bands characteristic of the starting metal oxides and tellurous oxide.

The DSC measurements were carried out by a DSC-111 calorimeter (Setaram, France). α-Al_2O_3 (saphire) was used as a standard substance. The samples (50–100 mg) were sealed in platinium crucibles which were inactive with respect to metal oxides, tellurous oxide and the synthesized tellurites. Scanning rate was 1°C min^{-1} in the temperature interval 20–860 K.

In order to determine the temperature interval of the DSC curves, a preliminary derivatograph analysis was also made on an OD-102 apparatus (MOM, Hungary). The operating conditions were: temperature, from 20 to 1300°C; heating rate, 10 min^{-1}; sample mass, 200–300 mg; thermocouple, Pt/PtRh; standard substance, α-Al_2O_3; in a medium of chemically pure nitrogen, with metalloceramic crucibles. 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.

Results and discussion

DSC curves were used to determine the enthalpies of the reactions. By summing up the data obtained and the enthalpies of formation of metal oxides [12–16] and tellurous oxide [13, 14, 17, 18] and taking into consideration their mol ratios, the standard enthalpies of formation of metal tellurites were calculated by the equations:

$$\text{for } Me_2(TeO_3)_3 \quad \Delta H^0_{298} = \Delta H^0_{298\,Me_2O_3} + 3\Delta H^0_{298\,TeO_2} + \Delta H_{reac}$$

$$\text{for } Me(TeO_3)_2 \quad \Delta H^0_{298} = \Delta H^0_{298\,MeO_2} + 2\Delta H^0_{298\,TeO_2} + \Delta H_{reac}$$

The accuracy of determining the standard enthalpies of formation is particularly important and it depends on the accuracy of determining the enthalpies of the chemical reactions [19].

The completeness of the chemical reactions between metal oxides and tellurous dioxides and the accurate determination of the standard enthalpies of formation of metal tellurites were checked by two methods: repeated DSC analyses and X-ray phase analysis. The lack of exothermal peaks on the repeated DSC curves shows that the reactions were completed. The area of the exothermal peaks provides accurate quantitative characteristics of the enthalpies of the chemical reactions between the initial metal oxides and tellurous oxide. The second method involves making a X-ray phase analysis of the products of the interaction between metal oxides and tellurous oxide. The lack of peaks on X-ray patterns corresponding to the initial oxides is indicative of the completion of the chemical reactions and the accuracy of the data obtained. The data obtained from the chemical analysis of the products taken out of the ampoules after finishing the experiment show that their composition exactly corresponds to the stoichiometry of the tellurites presented in Table 1. The X-ray analysis data for the same samples show that their peaks and relative intensities completely agree with the data for these tellurites published in ICDD by the present authors.

The DSC curves of all compounds only contained exothermal peaks corresponding to the combination of the metal oxides and tellurium dioxide, and the formation of the corresponding tellurite. No endothermal peaks were observed on the DSC curves since all the tellurites melted at temperatures over 1000 K. The DSC curves show that the formation of a number of tellurites takes place at several stages, which indicates that intermediate oxotellurates are formed (Table 2, compounds: $PrO_2 \cdot 2TeO_2$;

$PrO_2\cdot 3TeO_2$). This phenomenon is not observed only in the cases when temperatures of the chemical interaction between two oxotellurates of the same element are very close (Table 2, compounds: $Y_2O_3\cdot 3TeO_2$; $Y_2O_3\cdot 4TeO_2$). Five determinations were made for each tellurite and the values were averaged.

Table 2 Heats of formation of some metal tellurites. ΔH values are given in kJ mol^{-1}

Compound	Literature data		Present data		
	$-\Delta H^0_{form}$ of metal oxide	$-\Delta H^0_{form}$ of TeO_2	$-\Delta H$ of reaction	Transition temperature/K	$-\Delta H_{form}$ of metal tellurites
$Y_2O_3\cdot 3TeO_2$	1905.31	966.63	92.91	820.5, 899	2964.85
$Y_2O_3\cdot 4TeO_2$	1905.31	1288.84	100.98	823, 903	3295.13
$La_2O_3\cdot 3TeO_2$	1793.70	966.63	26.33	912	2786.66
$La_2O_3\cdot 4TeO_2$	1793.70	1288.84	25.32	843	3107.86
$CeO_2\cdot 2TeO_2$	1088.68	644.42	10.79	904, 946.5	1743.89
$CeO_2\cdot 3TeO_2$	1088.68	966.63	10.26	902, 921	2065.57
$PrO_2\cdot 2TeO_2$	949.35	644.42	50.89	838, 857	1644.66
$PrO_2\cdot 3TeO_2$	949.35	966.63	73.65	839, 857, 874	1989.63

The results obtained for the enthalpies of the chemical reactions, the literature data available concerning the standard enthalpies of metal oxides and tellurous oxide, as well as the standard enthalpies of formation of the metal tellurites under study obtained by the authors are presented in Table 2.

By using the same apparatus and procedures, data concerning a number of metal tellurites were determined and published [20, 21].

The reliability of the results obtained by the authors is highly assessed in reference [22].

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