

BRIEF COMMUNICATION

Experimental Determination of the Enthalpies of Formation of the Tellurites of Er, Nd, Sm, Ho, and Eu

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By means of DSC-111 (Setaram, France) the heats of synthesis reactions of Me_2O_3 and TeO_2 are determined. These values are summarized with the heats of formation of metal oxides and the heats of formation of TeO_2 , and in this way the heats of formation of tellurites of Er, Nd, Sm, Ho, and Eu are obtained. © 1995

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INTRODUCTION

The tellurites of a number of rare metals can be used as new materials in laser devices. Their dielectric properties render them useful in electronic components. Due to their beautiful color they can be used for coloring ceramic glasses, enamels, etc. (1). These tellurites may be turned into tellurides of stoichiometric composition by reduction with hydrogen or carbon monoxide.

The aim of this research is to determine the thermodynamic functions of these compounds. The results obtained may be of particular practical interest in synthetic chemistry, chemical technology, the semiconductor industry, etc.

EXPERIMENTAL, RESULTS, AND DISCUSSION

High-purity (class B-5) metal oxides and tellurous oxide were used to determine the enthalpies of formation of the tellurites of Er, Nd, Sm, Ho, and Eu. Their standard enthalpies of formation were determined by differential scanning calorimetry and the results obtained are given in Table I. For this purpose, mixtures were prepared and homogenized thoroughly. The degree of homogenization was checked chemically and by X-ray analysis.

Chemical analysis. The chemical analysis for metal ions were performed complexometrically (2). The tellurite ions were analyzed bichromatically or gravimetrically (3).

X-ray analysis. Part of the mechanical mixtures were sealed in vacuum quartz ampules. Solid-phase synthesis was carried out at a temperature which was 50°C lower than the melting temperature of the corresponding tellurites. X-ray patterns were made using a "TURM" apparatus with Cu anode, 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 the peaks in the X-ray patterns corresponded to the tellurites under study. Where no X-ray data of the tellurites were 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.

In order to determine the standard enthalpies of formation, mixtures of metal oxides and tellurous oxide, corresponding to the stoichiometry of the tellurites, were sealed in ampules which were inert to metal oxides, tellurous oxide, and the synthesized tellurites. DSC curves were obtained on a DSC-111 calorimeter (Setaram, France); standard DSC capsules of iron were employed. Preliminary derivatograph analysis was also made. DSC curves were used to determine the enthalpies of the reactions. A scan rate of 2°C/min was used; the measurements are independent of scan rates in the range 1–5°C/min; the baseline is also stable in this range. The reproducibility was on the order of $\pm 0.5\%$. By summing up the data obtained and the enthalpies of formation of the metal oxides and tellurous oxide, the standard enthalpies of formation of metal tellurites were calculated. Their molar ratios were taken into consideration in these calculations. Since the accuracy of the standard enthalpies of the chemical reactions was determined by us, this problem was dealt with carefully.

TABLE 1
Enthalpy of Formation (kJ mol^{-1}) of Some Metal Tellurites

Compound	Literature data		Experimental data	
	$-\Delta H_f^\circ$ of metal oxide (4)	$-\Delta H_f^\circ$ of TeO_2 (5)	$-\Delta H_f^\circ$ of reaction	$-\Delta H_f^\circ$ of metal tellurite
$\text{Er}_2(\text{TeO}_3)_3$	1899.13	965.89	62.84	2927.87
$\text{Er}_2\text{Te}_4\text{O}_{11}$	1899.13	1287.86	102.87	3289.86
$\text{Nd}_2(\text{TeO}_3)_3$	1809.33	965.89	47.48	2822.70
$\text{Nd}_2\text{Te}_4\text{O}_{11}$	1809.33	1287.86	92.70	3189.88
$\text{Sm}_2(\text{TeO}_3)_3$	1816.61	965.89	97.09	2879.60
$\text{Sm}_2\text{Te}_4\text{O}_{11}$	1816.61	1287.86	122.76	3227.23
$\text{Ho}_2(\text{TeO}_3)_3$	1882.18	965.89	106.01	2954.08
$\text{Ho}_2\text{Te}_4\text{O}_{11}$	1882.18	1287.86	107.85	3277.89
$\text{Eu}_2(\text{TeO}_3)_3$	1829.63	965.89	53.76	2849.28
$\text{Eu}_2\text{Te}_4\text{O}_{11}$	1829.63	1287.86	31.74	3149.23

Chemical and X-ray phase analyses were made and DSC determinations were repeated in order to check the progress of synthesis of the tellurites. The lack of exothermic peaks on the DSC curves shows that the reactions were complete, i.e., the starting metal oxides and tellurous oxide were completely turned into the corresponding tellurites.

The standard enthalpies of formation of metal tellurites and the ΔH_f° of metal oxides and tellurous oxide are presented in Table 1.

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