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**Note**

# Thermal and structural study of the phase transformations of the tellurites of trivalent iron and chromium

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## INTRODUCTION

The thorough and complete extraction of the basic metals, as well as of the metalloids such as selenium and tellurium, is unthinkable without knowledge of the thermal and structural properties of their respective compounds. Selenium and tellurium are finding ever increasing applications. It is known that they are contained most often in the sulphide minerals, and in the main they are associated with the heavy non-ferrous metals. Selenium and tellurium are concentrated in the intermediate slimes from the electrolysis of copper and nickel or in the wastes from lead–zinc production. Contemporary methods for processing the intermediate slimes involve an oxidative or oxidative–sublimative roasting process with subsequent hydrochemical extraction of the valuable components. Literature reports on the behaviour of the selenides and tellurides (basic selenium- and tellurium-containing compounds in the intermediate slimes) in the roasting process and on the thermal stability of selenites are incomplete, and those on tellurites and tellurates are almost non-existent. For that reason investigation of the thermal behaviour of selenium- and tellurium-containing materials appears to be a pressing problem.

This work is devoted to clarifying one of the questions in this many-sided problem—investigation and calculation of the melting temperatures as well as the enthalpies and entropies of such substances.

## PHASE STATE OF THE TELLURITES

Information on the iron and chrome tellurites is very scanty. The iron tellurite $Fe_2(TeO_3)_3$ is obtained by heating a mechanical mixture of $Fe_2O_3$ and $TeO_2$ exactly corresponding to the stoichiometry of the compound [1].

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A solid-state synthesis is also used to obtain $Fe_2(TeO_3)_3$, $(FeO)_2TeO_3$ and $Fe_2Te_4O_{11}$ [2].

Synthesis of the chrome tellurites has been achieved by means of solid-state thermal treatment of $Cr_2O_3$ and $TeO_2$ [3, 4]. In all cases the processes are carried out in an inert medium (nitrogen).

## EXPERIMENTAL, RESULTS AND DISCUSSION

For the synthesis of the iron and chromium tellurites, high purity oxides (at least 99.99% of the base substance: $Fe_2O_3$, $Cr_2O_3$ and $TeO_2$) were used in an ampoule synthesis. Stoichiometric mixtures of $M_2O_3$ and $TeO_2$ were thoroughly homogenized in an agate mortar, then the mixtures were transferred to quartz ampoules, which were sealed under vacuum and maintained at selected temperatures. In order to establish the optimum conditions for solid-state synthesis, the mechanical mixtures of the relevant oxides were subjected to derivatographic analysis. The temperatures of chemical interaction and the melting temperatures of the compounds were determined from the derivatograms. The synthesis was carried out at temperatures 100°C below the melting temperatures of the compounds. To ensure completion of the solid-state reactions, each of the samples was subjected to threefold heat treatment at the indicated temperature. Each heat treatment was followed by thorough homogenization by grinding and the mixture was transferred into a new quartz ampoule which was sealed under vacuum. The stoichiometry of the substances and the completeness of synthesis were monitored by chemical, X-ray and derivatographic analysis. Chemical analysis of iron(III) was carried out complexometrically using as indicator a 1% ethanolic solution of salicylic acid [5]. Chromium(III) was determined by titration of Cr(II) formed by preliminary treatment with Fe(II), with diphenylaminesulphonate as indicator. Determination of $TeO_3^{2-}$ was made iodometrically [6]

TABLE 1

Chemical analysis of iron and chromium tellurites

| Compound | Theoretical content (%) | | Chemical analysis data (%) | |
|---|---|---|---|---|
| | Metal oxide | $TeO_2$ | Metal oxide | $TeO_2$ |
| $(FeO)_2TeO_3$ | 50.00 | 50.00 | 49.93; 50.02; 50.01 | 50.13; 50.01; 50.03 |
| $Fe_2(TeO_3)_3$ | 25.05 | 74.99 | 25.12; 25.03; 25.00 | 75.03; 75.00; 74.89 |
| $Fe_2Te_4O_{11}$ | 20.01 | 79.99 | 20.07; 19.98; 19.99 | 80.03; 79.98; 79.96 |
| $Cr_2(TeO_3)_2$ | 24.09 | 75.91 | 24.10; 24.05; 24.08 | 76.00; 75.90; 75.93 |
| $Cr_2Te_4O_{11}$ | 19.23 | 80.77 | 19.25; 19.18; 19.20 | 80.79; 80.75; 80.78 |

TABLE 2

Parameters of the elementary cell of the iron tellurites studied

| Compound | Geometry | Parameters of elementary cell (Å) | | | | Z | Space group |
|---|---|---|---|---|---|---|---|
| | | a | b | c | β | | |
| $(FeO)_2TeO_3$ | Monoclinic | 7.663 | 4.937 | 10.817 | 103°13′ | 4 | $P_12/c$ |
| $Fe_2(TeO_3)_3$ | Orthorhombic | 9.510 | 7.512 | 11.03 | – | – | |
| $Fe_2Te_4O_{11}$ | Monoclinic | 11.879 | 6.949 | 14.128 | 123°44′ | 4 | Pbma |

and gravimetrically [7]. Table 1 gives the results from the chemical analysis of the synthesized compounds as well as the theoretically calculated compositions.

X-ray analysis was performed on a DRON-2 apparatus with a Cu anode and K$\alpha$ emission and a nickel filter for $\beta$-radiation. The data obtained by X-ray analysis (Table 2) were evaluated on an IBM-RS-TH computer and a Brother recorder by using an analogue method.

Thermal constants were determined by derivatographic analysis on a type OD-102 instrument (MOM, Budapest) under the following conditions: temperature interval 20–1100 ± 10°C, rate of heating 10°C $min^{-1}$, sample weight 300 ± 1 mg, thermocouple Pt–Pt/Rh, inert substance heated $Al_2O_3$, medium a continuous flow of nitrogen (99.999% purity) at a rate of 17 l $h^{-1}$, and a metal–ceramic crucible.

The substances obtained were submitted to thorough grinding in an agate mortar, and were sifted in a sieve with mesh dimension 0.25 $mm^2$, then poured into crucibles and heated in a derivatograph. Each of the tellurites was heated four or five times and the results were averaged.

From the DTA curve the temperatures and enthalpies of fusion (Table 3) of the tellurites were determined. Calibration was effected with several

TABLE 3

Temperatures $T$, enthalpies $\Delta H$ and entropies $\Delta S$ of fusion of the iron and chromium tellurites studied

| Compound | T (K) | | $\Delta H$ (kcal $mol^{-1}$) | $\Delta S$ (cal $mol^{-1}$ $K^{-1}$) |
|---|---|---|---|---|
| | Lit. data | From DTA | | |
| $(FeO)_2TeO_3$ | — | 1203 | 13.9 | 11.6 |
| $Fe_2(TeO_3)_3$ | 963 | 963 | 21.6 | 22.4 |
| $Fe_2Te_4O_{11}$ | 986 | 958 | 27.0 | 28.2 |
| $Cr_2(TeO_3)_2$ | 1133 | 1113 | 11.6 | 10.0 |
| $Cr_2Te_4O_{11}$ | — | 983 | 5.3 | 5.4 |

standard substances of high purity: $K_2SO_4$, KCl, NaCl and SnS, with phase transformations at 590, 770, 801 and 880°C respectively.

Calibration according to the enthalpy of fusion was carried out with NaCl, which has a heat of fusion of 7.22 kcal $mol^{-1}$ [8]. The areas on the DTA curves were calculated by a weight method. The entropies of the tellurites were calculated by a conventional method (Table 3).

Our literature search did not discover reports of any similar data: thus, we believe that this is the first report of its kind concerned with the thermal behaviour of selenium- and tellurium-containing materials.

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