Thermochimica Acta, 80 (1984) 181–183
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

A DSC STUDY OF THE PHASE DIAGRAM OF THE SYSTEM TeO_2–Cs_2TeO_3

E.H.P. CORDFUNKE and V.M. SMIT-GROEN
Netherlands Energy Research Foundation ECN, Petten (The Netherlands)

(Received 11 April 1984)

INTRODUCTION

Very little is known about the cesium tellurites; only the compound Cs_2TeO_3 has been mentioned in the literature, although its properties have not been investigated. In this paper a systematic investigation of the phases present in the TeO_2–Cs_2TeO_3 system, and a determination of its phase diagram are presented.

EXPERIMENTAL

As starting materials for the preparation of the cesium tellurites were used Cs_2CO_3 (Merck, reinst, 99.5%), heated in air at 300 °C, and TeO_2 (BDH, 99.95% purity) also heated in air at 300 °C. A chemical and X-ray analysis proved them to be pure. All samples were stored in an argon-filled glove box, in which all other handlings (sampling, weighing) were performed. DSC measurements were carried out in a Mettler TA 2000 apparatus using platinum crucibles. X-ray analyses were performed with a Nonius Guinier camera, using Cu $K\alpha_1$-radiation.

RESULTS

The phases in the TeO_2–Cs_2TeO_3 system

Mixtures of Cs_2CO_3 and TeO_2 in molar ratios varying from 0.1 to 6.0 were intimately mixed in the glove box, placed in gold boats, and heated in argon in a silica tube at 450–500 °C for at least 15 h. After heating, the samples were carefully ground in a mortar, and heated again. The progress of the reaction was followed by X-ray analysis. After 3–4 times, the samples no longer changed. The detection limit in mixtures of phases by X-ray analysis is $< 1\%$.

In the above mentioned mixtures only three distinct phases could be

0040-6031/84/$03.00

TABLE 1

Interplanar spacings of the strongest reflections on the X-ray patterns of the cesium tellurites [a]

$Cs_2Te_4O_9$					
d (Å)	3.229	3.122	3.057	2.066	2.038
$100\ I/I_0$	>100	100	100	60	50
$Cs_2Te_2O_5$					
d (Å)	3.355	3.021	1.799	2.135	2.688
$100\ I/I_0$	100	80	80	60	50
Cs_2TeO_3					
d (Å)	3.391	3.288	2.362	1.939	1.959
$100\ I/I_0$	100	100	70	60	50

[a] The d-values have been corrected with SiO_2 as an internal standard. A complete list can be obtained from the Joint Committee on Powder Diffraction Standards (JCPDS).

detected, at molar ratios Cs/Te = 0.5, 1.0, and 2.0, indicating the existence of the phases $Cs_2Te_4O_9$, $Cs_2Te_2O_5$, and Cs_2TeO_3, respectively. All phases were white coloured and very hygroscopic.

We have succeeded in preparing single crystals of the three tellurite phases, and a crystal structure determination is underway [1]. The five strongest reflections on the X-ray patterns of these phases are listed in Table 1.

The phase diagram

Mixtures of various compositions of the pure cesium tellurite phases were heated in the DSC apparatus in purified argon; heating rates of 2, 5 and 10 °C min^{-1} were applied. The pure substances showed a sharp, reproducible melting point (Table 2), whereas the mixtures had two peaks, as expected, which could be separated in most cases by varying the heating rate. The phase diagram is shown in Fig. 1 from which it is evident that $Cs_2Te_4O_9$ and Cs_2TeO_3 melt congruently, whereas $Cs_2Te_2O_5$ has an incongruent melting point. The last compound has a non-reversible phase transition at ~ 288 °C, but after melting the low-temperature form crystallizes again.

TABLE 2

Melting points of the phases in the TeO_2–Cs_2TeO_3 diagram

Compound	Melting point (°C)
TeO_2	730.7 ± 0.3
$Cs_2Te_4O_9$	549.5 ± 0.5
$Cs_2Te_2O_5$	439.4 (incongr.)
Cs_2TeO_3	810.5 ± 0.3

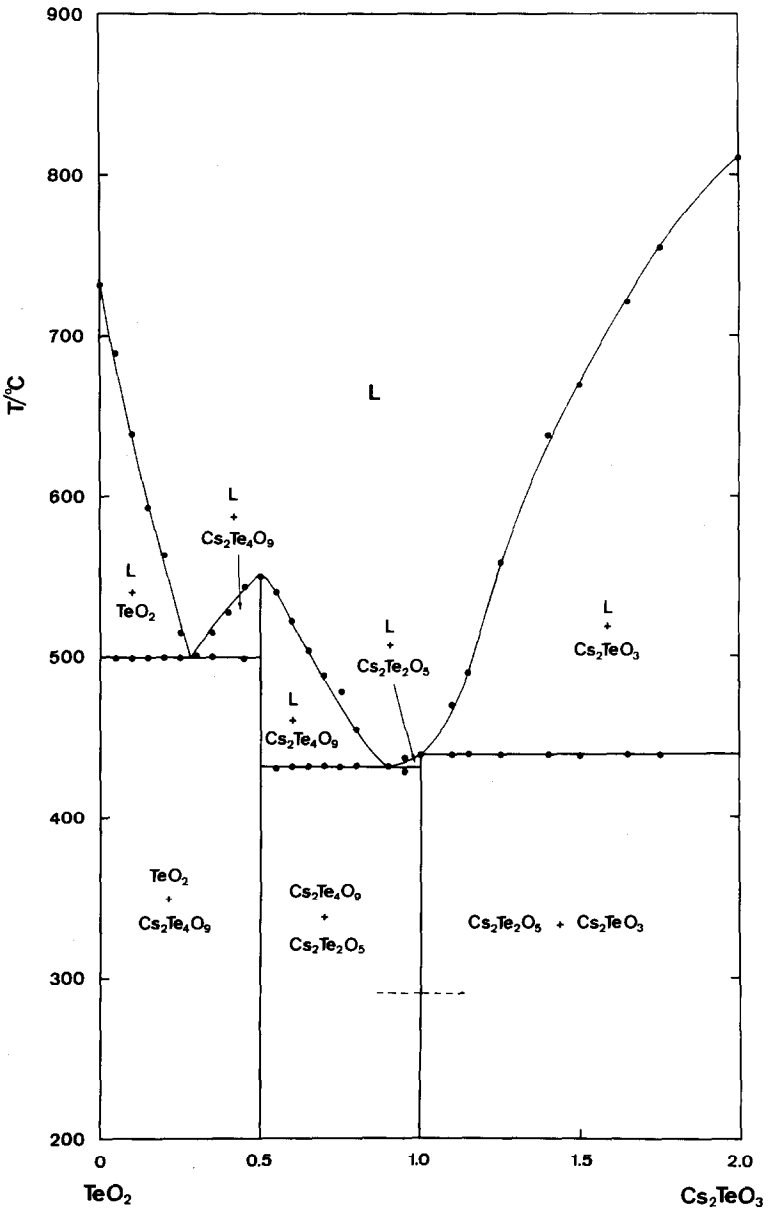

Fig. 1. The phase diagram of the system TeO_2–Cs_2TeO_3.

ACKNOWLEDGEMENT

The authors are grateful to Mr. P. van Vlaanderen for his assistance in the X-ray work.

REFERENCE

1 B.O. Loopstra, in preparation.