The phase diagram of the CeI$_3$–Ce system

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Abstract

The phase diagram of the system CeI$_3$–Ce has been determined by differential thermal analysis. The experimental data could only be explained by the assumption of three intermediate phases, which have compositions close to CeI$_{2.2}$, CeI$_2$ and CeI and all melt incongruently. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Cerium triiodide is one of the compounds that has been tested as target material for the nuclear transmutation of the fission product I-129 [1–3]. During the transmutation process, iodine is transmuted into xenon by neutron capture and as a result the iodine/cerium ratio decreases as a function of irradiation time. Because this may affect the melting behaviour of the targets during irradiation, knowledge of the CeI$_3$–Ce phase diagram is required. Therefore we have investigated the CeI$_3$–Ce phase diagram by differential scanning calorimetry over the whole composition range, as described in the present paper.

2. Experimental

CeI$_3$ was purchased from CERAC and purified by high-temperature sublimation before use. A special small-scale sublimator made of quartz was constructed and a removable molybdenum crucible served as sample container. The sample was heated at 1223 K in high vacuum and pure CeI$_3$ was deposited on a cold finger construction [4]. X-ray diffraction (XRD) analysis proved the sample (contained a sealed polythene) to be pure. Ce metal (ingot) was purchased from HIGHWAYS (99.9%). For the experiments small pieces were cut from the bar, after which the oxide layer was removed by polishing the metal surface in a glove box flushed with purified argon (O$_2$ and H$_2$O ≤2 ppm).

The samples were prepared by mixing Ce and CeI$_3$ in mole ratios between 0 and 1. They were encapsulated in molybdenum containers which were in turn enclosed in slightly larger, air-tight stainless steel containers. All handlings were done in an argon-flushed glove-box.

Differential thermal analysis (DTA) measurements were made in a modified Mettler TA 13-2000 apparatus. The mixtures were heated several times in a row to a temperature above the melting point until the results of the DTA runs were reproducible, indicating that equilibrium was achieved. The experimental

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Table 1
The experimental results (peak maxima) for the CeI_3–Ce system

Sample no.	Ce (mol%)	T_1 (K)	T_2 (K)	T_3 (K)	T_4 (K)
1	0		1027		
2	7.218		1026		
3	14.418	995	1013		
4	23.698	989	1014		
5	30.089	1013	1044		
6	34.475	1009	1072		
7	37.522	998	1074	1084	1129
8	50.014		1071	1081	1125
9	59.240	973	1074	1085	1114
10	66.667	993	1076	1083	1108
11	78.740	997	1073	1083	1099
12	85.016	997	1074	1086	
13	94.880	997	1069		
14	100	999	1075		

results are given in Table 1. In this table the peak maxima are given since onset temperatures were extremely difficult to be measured accurately as a result of the complex and overlapping peaks in the diagrams which would introduce large uncertainties.

The temperature scale of the apparatus was calibrated using the melting points of indium, tin, cadmium, lead and silver using the same double container construction used for the mixtures. The corrections applied were 1 K or less. The measurements were performed with a heating rate of 10 K min^{-1}. As a check of the procedure, the phase transformations in uranium metal (NBS standard) were also determined. The $\alpha \rightarrow \beta$ transition was found at (944±1) K and the $\beta \rightarrow \gamma$ at (1050±1) K, which is in excellent agreement with the recommended values [5].

After the DTA runs some containers were opened in a glove box and X-ray analysis of the mixtures (contained in sealed polythene) were performed. The XRD

apparatus was operated in air and as a result oxidation before or during the measurement could probably not be avoided.

3. Results and discussion

3.1. CeI_3 and Ce

The melting point of CeI_3 was found as a sharp and reproducible peak in the DTA curves. The onset temperature was (1012±1) K and the peak maximum was (1027±1) K. The latter value is in reasonable agreement with that derived by Dworkin and Bredig [6,7], (1033±2) K, from drop calorimetric measurements, and that by Corbett et al. [8], 1033–1034 K, obtained by thermal analysis.

In the DTA runs of cerium metal two phase changes were observed: the $\gamma \rightarrow \delta$ transition and the melting point of cerium. The onset temperatures were (995±2) K and (1068±2) K, respectively, the peak maxima (999±2) K and (1075±2) K. The latter values are in good agreement with the results of previous determinations reported in the literature, as summarised in Table 2.

3.2. The phase diagram

The phase diagram that has been derived from the experimental data is shown in Fig. 1. At the CeI_3-rich side of the diagram, an eutectic is observed between CeI_3 and an intermediate phase at about 18 mol% Ce and 992 K. The intermediate phase occurs at about 36 mol% Ce (I/Ce≈2) and melts incongruently at 1074 K. These results are in reasonable agreement with the findings of Corbett et al. [8,13] who reported the existence of the di-iodide $CeI_{2.00}$ which melts at

Table 2
The transition temperatures of cerium

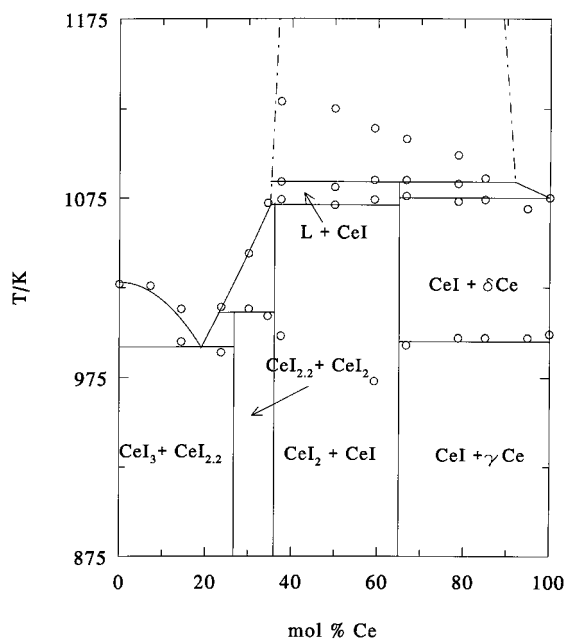| Author	Year	$T_{\gamma \rightarrow \delta}$ (K)	$T_{\sigma \rightarrow 1}$ (K)	Comments
Herman et al. [9]	1955	1007		
		999		
Spedding et al. [10]	1961	1003	1077	
Chiotti et al. [11]	1964	998	1070	
Gschneidner [12]	1965	999±5	1071±3	
This paper	1996	995±2	1068±2	Onset value
		999±2	1075±2	Peak maximum

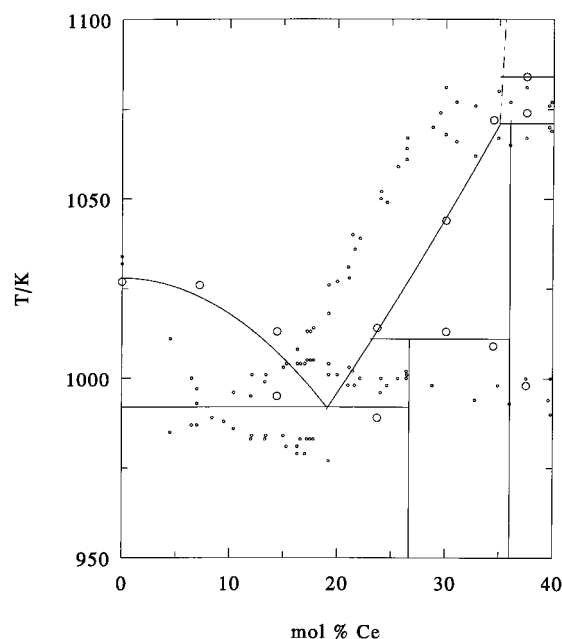Fig. 1. The phase diagram of the CeI$_3$–Ce system.

Fig. 2. The CeI$_3$-rich part of the phase diagram of the CeI$_3$–Ce system; large symbols, this study; small symbols, Corbett et al. [7].

1081 K. These authors also reported the existence of another intermediate compound CeI$_{2.4}$. Our data also suggest a compound with a composition between CeI$_3$ and "CeI$_2$", but at a somewhat different position, about 27 mol% Ce. This compound ("CeI$_{2.2}$") melts incongruently at ca. 1011 K. This value is close to that reported by Corbett et al. [8] for CeI$_{2.4}$, 1004 K.

In Fig. 2 our results for the CeI$_3$-rich part of the phase diagram are compared to those of Corbett et al. [8]. It can be seen that there is a systematic shift of about 30 K in the liquidus between 20 and 40 mol% Ce. As a result the eutectic composition found in the present work (~18 mol% Ce) differs considerably from that found by Corbett et al. 8.8 mol% Ce, though the temperatures (992 K in this work versus 988 K in that by Corbett et al.) are in good agreement. A possible explanation for this discrepancy is the influence of oxygen. Oxidation can affect the phase relations since the system will change from the binary CeI$_3$–Ce to the ternary CeI$_3$–Ce$_2$O$_3$–Ce. Assuming that cerium oxide behaves inert, the results suggest either oxidation of cerium metal in the study of Corbett et al., or of CeI$_3$ in our experiments. As explained in Section 2 we have taken many precau-

tions to limit the contamination with oxygen to a minimum:

1. vacuum sublimation has been used to obtain pure CeI$_3$;
2. the cerium metal was handled and polished in a glove box flushed with high purity argon;
3. the DTA experiments were performed in sealed molybdenum containers;
4. preparation of the mixtures and loading of the containers were also performed in a glove box flushed with high purity argon.

Similar precautions were taken by Corbett et al., with the exception of the vacuum sublimation of the iodide.

At the Ce-rich side of the diagram, the following effects are noted:

• A rapid disappearance of the characteristic peak of the $\gamma \rightarrow \delta$ transition in the pure metal which is no longer present below about 65 mol% Ce (I/Ce≈1).
• The intensity of the peak at 1075 K does not change over the composition range 100–40 mol% Ce. Evidently, this peak cannot be attributed to the melting

of pure Ce alone and a second effect takes place at this temperature obscuring its disappearance.

- Between about 35 and 90 mol% Ce a very strong peak at 1083 K is found, which partially overlaps with the peak at 1075 K. Its intensity is maximal between 60 and 79 mol% Ce.
- A small discontinuity in the baseline of the DTA diagrams between 37 and 79 mol% Ce after the last peak (T_4 in Table 1).

To our opinion, the first three observations can only be explained if a third intermediate phase exists, i.e. the peak at 1083 K is due to the incongruent melting point of, for example, a "CeI" phase. The peak at 1083 more or less coincides with that of the melting of the metal. The existence of an intermediate phase seems also to be confirmed by the X-ray diffraction analysis of the mixtures after the DTA runs. The X-ray analysis of sample 11 showed the presence of one phase and that of sample 9 of two phases that could not be identified as Ce or CeI_3, nor as CeOI or a cerium oxide that might be formed due to oxidation.

The "CeI" phase was not reported by Corbett et al. [8] who assigned the peak at 1081 K, corresponding to 1083 K in our results, to the melting of CeI_2. Mironov et al. [14], on the contrary, argued that this temperature is the synthetic temperature, corresponding to the decomposition of CeI_2 in two liquids. They also argued that a eutectic between Ce and CeI_2 occurs at 99.54% Ce, with a eutectic temperature of 1063 K. This was assigned by Corbett et al. as the melting point of pure cerium. These explanations are, however, not in agreement with our observations which show that the maximum intensity of the peak at 1083 K occurs at about 60–70 mol% Ce and that the intensity of the peak at 1073 K, which we assigned to the melting of CeI_2, has a maximum at about 30 mol% Ce.

For the observation of the small discontinuity in the baseline of the DTA diagrams we do not have a clear explanation.

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