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ON THE CESIUM-RICH PART OF THE Cs-Te PHASE DIAGRAM

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On the cesium-rich part of the Cs–Te phase diagram

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Abstract: The cesium-tellurium system in the region between 33 and 55 at.% Te has been investigated with X-ray diffraction and DSC. The existence of the compounds Cs_5Te_3 and CsTe is demonstrated. The latter compound exhibits a structural transition at elevated temperature, as does the compound Cs_2Te. The earlier reported compounds Cs_3Te_2 and Cs_5Te_4 do not exist.

Keywords: cesium, tellurium, phase diagram, DSC, X-ray diffraction

1 Introduction

The cesium-tellurium system is of particular interest, since both cesium and tellurium are important fission products which, once released during a nuclear reactor accident, may contribute largely to health- and environmental effects[1]. Estimation of the release behaviour of cesium and tellurium requires knowledge of the phase diagram and the thermochemical properties of the compounds in this system. According to equilibrium calculations of Cordfunke and Konings[2], and Imoto and Tanabe[3] the predominant tellurium containing species in an operating fuel rod is Cs_2Te. Decomposition of Cs_2Te due to increasing temperature, or reactions with other fission products and reactor materials, can lead to formation of compounds in the Cs–Te system which contain more tellurium.

Cesium, tellurium and their compounds cause corrosion of cladding and construction materials in the primary system of a nuclear reactor. These phenomena have been investigated by Richards[4]. Here again, knowledge of the compounds in the Cs/Te system and their properties is required.

A critical review of all available data of the Cs–Te phase diagram has recently been published by Sangster and Pelton[5]. Their assessment of the phase diagram is mainly based on the work of Chuntonov et al.[6], Adamson and Leighty[7], and Prins and Corfdunke[8]. The assessed phase diagram of Sangster and Pelton is shown

in figure 1. This phase diagram clearly demonstrates that in the region between Cs_2Te and Cs_2Te_3 additional information is needed on the stable compounds and their transition temperatures. Concerning this region of the phase diagram, Schewe-Miller and Böttcher[9] reported the existence of a compound Cs_5Te_3, and in addition reported that the sample with the composition Cs_3Te_2 appeared to be a mixture of Cs_5Te_3 and free tellurium. Hobbs and Pulham[10] reported the existence of the compound CsTe which they called 'Cs_2Te_2' referring to the K-Te system.
This paper describes a series of X-ray diffraction and DSC experiments, conducted to solve the Cs-rich part of Cs-Te phase diagram.

2 Experimental

Sample preparation

In the region between Cs_2Te and Cs_2Te_3 samples were prepared by the reaction of a weighed amount of tellurium(Cerac, 99,95%), contained in a pyrex ampoule, with a weighed amount of cesium (Highways, 99,95%) in a narrow capsule. The latter capsule was placed upright inside the first ampoule, which was evacuated, sealed, and slowly heated in a resistance furnace to 773 K and kept at constant temperature for 16 hrs. The ampoules were slowly cooled to room temperature and opened in a glove box containing purified argon. The reaction products were thoroughly powdered and heated again to 950 K in a sealed quartz ampoule for about 12 hrs. After this treatment the ampoule was slowly cooled to room temperature, opened and the reaction mixture was analyzed by X-ray powder diffraction, using a Guinier type camera. No attack of the container materials was observed after these heat treatments.

DSC experiments

DSC measurements were performed using a Mettler TA13 apparatus. About 100 mg of a sample was put into a small quartz ampoule, with a very thin (<1mm) polished bottom surface for improved heat transport. The ampoules, filled with argon, were evacuated to 2 cm Hg pressure and sealed. An empty quartz ampoule of equal dimensions was used for reference in the DSC measurements. Temperature calibrations were done with In, Zn, Sb, and Ag samples, all contained in identical sealed quartz ampoules. On heating the samples, transition temperatures were distinguished, either as a peak, or as a change in the slope of the base line. Each ampoule, containing a sample, was heated three times with slow cooling of the sample in between the measurements. The enthalpy of transition and the enthalpy of fusion of Cs_2Te were determined using a Bähr DTA-701 apparatus. Temperature and caloric calibrations were done using Zn, Sb and Ag, contained in sealed quartz ampoules of equal dimensions under argon atmosphere.

High-Temperature X-ray diffraction

High-temperature X-ray diffraction was performed using a Guinier-Lenné type camera. The samples were pressed into a small-mesh platinum wire-netting and contained in a small polyethylene bag to protect the sample from oxidation on placing it into the camera. The camera was then evacuated and filled with dry helium before measurement. The polyethylene bag was removed by heating the sample once to 473 K. The polyethylene melts and no interference of the polyethylene in the diffraction pattern was observed during the actual measurement. The temperature of the samples was slowly increased (0.5°C/min) during measurement of the diffraction pattern, resulting in a diffraction pattern as a function of temperature. Error limits of 20 K should be placed on transition temperatures determined with this technique.

3 Results

The compounds present after reaction, as analyzed by X-ray diffraction, and the transition points of these samples recorded in the Mettler DSC, are given in table 1, in the order of increasing tellurium content. A summary of the special points in this part of the Cs–Te phase diagram is given in table 2 and the phase diagram itself is given in Fig. 2.
In the region between Cs_2Te and Cs_2Te_3 the compounds Cs_5Te_3 and CsTe have been identified by their diffraction pattern. The diffraction pattern of Cs_5Te_3 corresponds exactly with the pattern reported by Schewe-Miller and Böttcher[9]. These authors reported that Cs_5Te_3 has a monoclinic unit cell with lattice parameters a=2.111 nm, b=0.6655 nm, c=1.507 nm and β=134.53°. A change in the diffraction pattern of Cs_5Te_3 is observed at about 515 K, indicating a structural change of this compound. This structural change is comparable with the structural change at ± 470 K in K_5Se_3, as is described by Schewe-Miller and Böttcher[9]. This is a structural change from the nonstandard monoclinic setting I2/m, a=15.054, b=15.053, c=6.653, γ=90.96° into a tetragonal structure with γ=90.00°. As no enthalpy effects are observed at ± 515 K in any of the samples containing Cs_5Te_3 it is suggested that this structural transition is not a first order transition. This was also suggested by Schewe-Miller and Böttcher who observed no discontinuous change in cell volume of the K_5Se_3 going from the monoclinic to the tetragonal form. Cs_5Te_3 melts incongruently at 934±5 K.

The previously reported compound Cs_3Te_2 appears to be a mixture of Cs_5Te_3 and CsTe; the compound Cs_3Te_2 does not exist. The diffraction pattern of CsTe corresponds to the reported pattern of this compound by Hobbs and Pulham[10], who prepared their sample by means of hydrogen reduction of $Cs_2Te_2O_5$. The sample of CsTe obtained in the present study, is slightly substoichiometric in tellurium. X-Ray diffraction patterns of this compound were made on single-coated film with a focusing Guinier de Wolff camera (FR552, Enraf-Nonius, Delft, The Netherlands) using $CuK\alpha_1$-radiation (λ=1.54060 Å) with α-SiO_2 as an internal standard. CsTe has an orthorhombic unit cell, spacegroup Pba2(32) or Pbam(55) with lattice parameters a=1.16396(9) nm, b=0.61309(6) nm and c=0.49669(6) nm. The Smith and Snijder[11] figure of merit for CsTe is: F_{29}=94 (0.0064,48) range 2θ=15-54°, (34 reflections were observed , from which 29 were selected for the refinement)

As no enthalpy effects are observed at 670 and 720 K in the samples containing Cs_2Te and Cs_5Te_3, these enthalpy effects need to be assigned to transitions related to the compound CsTe. This conclusion is supported by the fact that the enthalpy effects of the transitions at 673±5 K and 723±4 K increase with increasing CsTe content in samples consisting of a mixture of Cs_5Te_3 and CsTe. High-temperature X-ray diffraction

analysis of CsTe revealed that the diffraction pattern of the room temperature form of CsTe indeed disappears at about 670 K. At this temperature a new diffraction pattern develops, which disappears at about 720 K. On further heating again a new pattern is seen which remains till 920 K. The latter pattern also remains after cooling of the sample to room temperature, indicating an irreversible process, which can be caused either by oxidation of the sample or by reaction with the platinum wire-netting. The platinum wire-netting has after heating indeed turned black and brittle.
However, when the sample was transformed in its high-temperature form during heating in the camera at 710 K and kept at that temperature during 4 hours, and then cooled to room temperature, the diffraction pattern of the room temperature form of CsTe returned. This demonstrates that the structural transition is reversible and can be completely ascribed to CsTe. This structural transition is demonstrated in Fig. 3, which shows the X-ray diffraction pattern of CsTe as a function of temperature. The diffraction pattern of the high-temperature form of CsTe is very vague and contains only a few lines. The melting of β-CsTe is clearly seen.
The results of high-temperature X-ray diffraction on samples containing a mixture of Cs_5Te_3 and CsTe, and of CsTe and Cs_2Te_3 thus confirm the transition points, which are found by DSC measurements.

The enthalpy effect at 895 K in samples containing mixtures of Cs_2Te and Cs_5Te_3 is caused by a structural transition of Cs_2Te. This could be concluded from the increase in enthalpy effect of this transition as the sample contained more Cs_2Te and less Cs_5Te_3. The melting point of Cs_2Te is determined at 1104±2 K. The enthalpy of transition of Cs_2Te to β-Cs_2Te is determined to be 1.95±0.23 kJ/mol. The enthalpy of fusion amounts 7.1±1.0 kJ/mol.

4 Discussion

Prins and Cordfunke[8] did not find the compound CsTe in their study of this system. Using the same reaction temperature as these authors did, again, this compound was not found either. However, increasing the reaction temperature to 773 K did lead to formation of this compound. At 573 K the system probably does not attain chemical equilibrium. As Prins and Cordfunke had not found the diffraction pattern of pure CsTe, they assigned the diffraction pattern of the mixture of Cs_5Te_3 and CsTe to the compound Cs_3Te_2. Their diffraction pattern, which was not indexed, actually was a mixture of the patterns of Cs_5Te_3 and CsTe.
Based on X-ray analysis, Schewe-Miller and Böttcher[9] report the presence of free tellurium coexisting with Cs_5Te_3 in a mixture with 40 at.% Te. According to the phase diagram CsTe should have been the second compound present in this mixture. Since the diffraction patterns of tellurium and CsTe differ significantly, misinterpretation is hardly possible. The presence of free tellurium can only be explained when the system is not yet in chemical equilibrium.
The compound Cs_5Te_4 was proposed by Chuntonov et al.[6] in order to explain their experimental determined transition point at about 720 K. They assumed that it was an incongruent melting point of Cs_5Te_4. In this study it is shown that this transition point could be assigned to the melting of CsTe. No evidence was found in this study

for the existence of Cs_5Te_4.

The measured transition points in the Cs-Te phase diagram in the region between Cs_2Te and Cs_2Te_3 in this study are in good agreement with the reported transition points by Sangster and Pelton[5].

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Table 1: Results of the reaction of cesium with tellurium and transition temperatures of the reaction products recorded with DSC

Composition	Reaction products		Transition temperatures [K]		
at.% Te		eutectic	transition	incongr. melt.	liquidus
33.2	Cs_2Te		895		1104
34.4	$Cs_2Te + Cs_5Te_3$		895	937	1065
35.3	$Cs_2Te + Cs_5Te_3$		895	937	1034
36.3	$Cs_2Te + Cs_5Te_3$		895	936	1013
37.3	Cs_5Te_3			936	
37.4	$Cs_5Te_3 + CsTe$		678	717	926
40.0	$Cs_5Te_3 + CsTe$		671	721	915
44.4	$Cs_5Te_3 + CsTe$		670	724	837
47.3	$Cs_5Te_3 + CsTe$		670	728	-
48.0	$Cs_5Te_3 + CsTe$		669	724	-
48.5	CsTe	610	678		713
49.1	CsTe	618	682		713
49.8	$CsTe + Cs_2Te_3$	622	652		-
52.1	$CsTe + Cs_2Te_3$	620	668		-
55.0	$CsTe + Cs_2Te_3$	621			-

Table 2: Special points of the Cs–Te phase diagram between 30 – 55 at.% Te

Reaction	at.% Te	Temperature, K	Reaction Type
$Cs_2Te \rightleftharpoons \beta\text{-}Cs_2Te$	33.2	895 ± 2	structural transition
$\beta\text{-}Cs_2Te \rightleftharpoons L$	33.2	1104 ± 2	congruent melting
$Cs_5Te_3 \rightleftharpoons \beta\text{-}Cs_2Te + L$	33.2–37	934 ± 5	incongruent melting
$CsTe \rightleftharpoons \beta\text{-}CsTe$	49	673 ± 5	structural transition
$\beta\text{-}CsTe \rightleftharpoons Cs_5Te_3 + L$	37–49	723 ± 4	incongruent melting
$CsTe + Cs_2Te_3 \rightleftharpoons L$	55	618 ± 5	eutectic

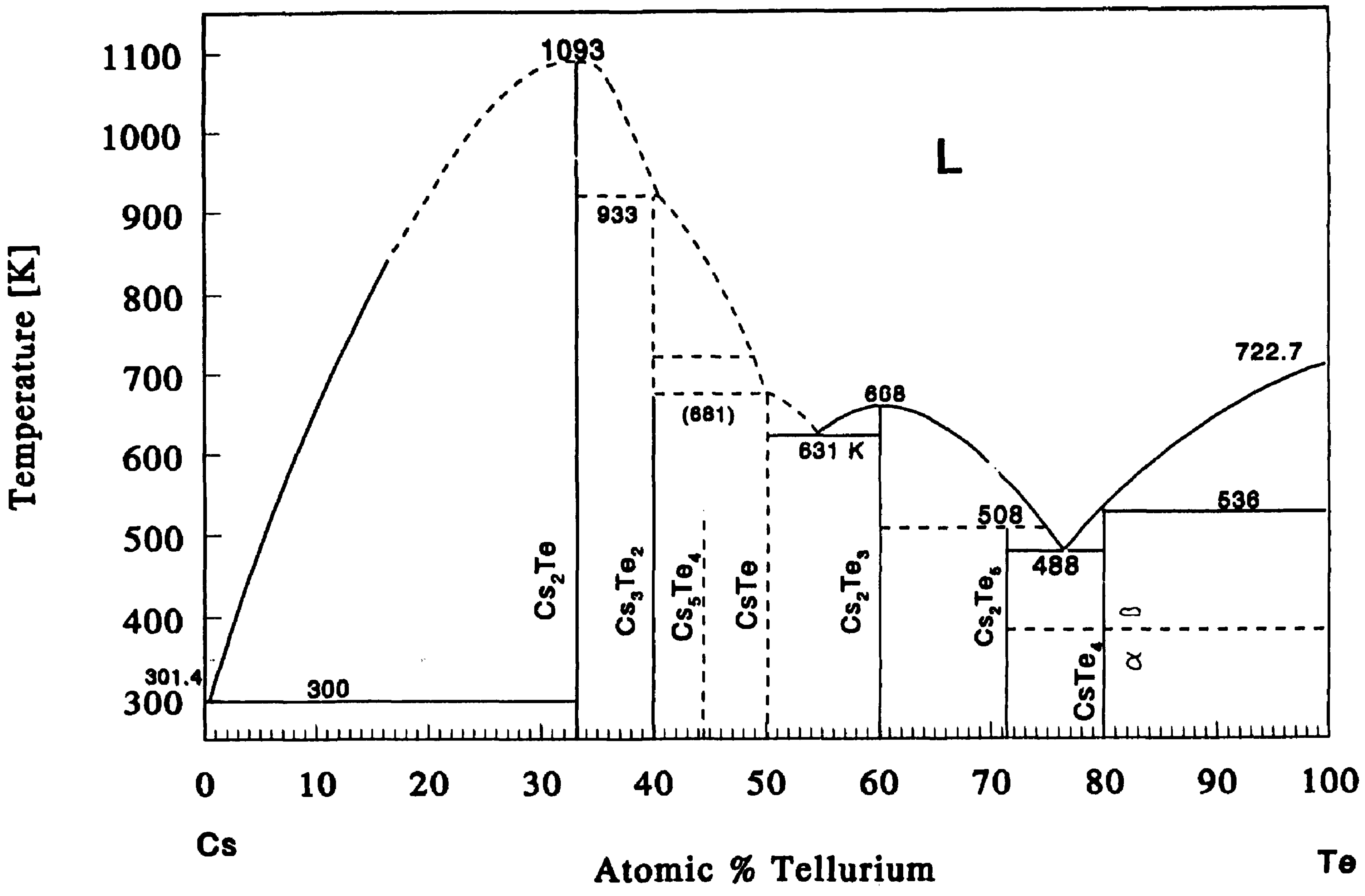
Figure captions:

Figure 1: The assesed phase diagram of the Cs–Te system according to[5]

Figure 2: The Cs–Te phase diagram between 30 and 56 at.

Figure 3: High-temperature X-ray diffraction pattern of CsTe illustrating the structural transition at 673 K and the melting at 723 K.

Figure 1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1000
900
800
700
600
500
400
300
Temperature [K]
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933
L
722.7
668
(681)
631 K
508
536
488
301.4
300
Cs_2Te
Cs_3Te_2
Cs_5Te_4
CsTe
Cs_2Te_3
Cs_2Te_5
$CsTe_4$
β
α
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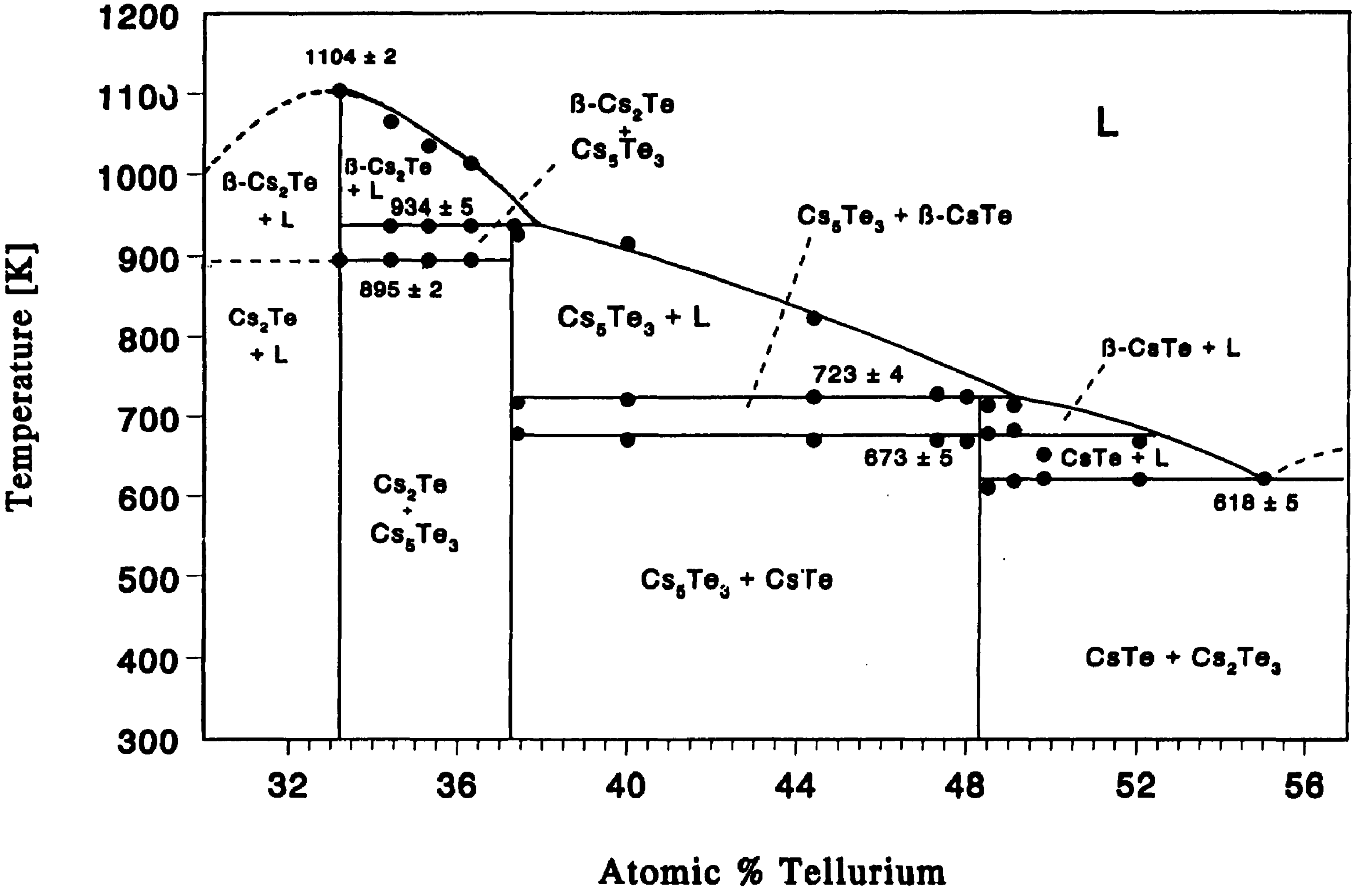
10
20
30
40
50
60
70
80
90
100
Cs
Atomic % Tellurium
Te

Figure 2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1100
1000
900
800
700
600
500
400
300
Temperature [K]
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36
40
44
48
52
56
Atomic % Tellurium
1104 ± 2
ß-Cs₂Te + Cs₅Te₃
L
ß-Cs₂Te + L
ß-Cs₂Te + L
934 ± 5
Cs₅Te₃ + ß-CsTe
895 ± 2
Cs₂Te + L
Cs₅Te₃ + L
ß-CsTe + L
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673 ± 5
CsTe + L
618 ± 5
Cs₂Te + Cs₅Te₃
Cs₅Te₃ + CsTe
CsTe + Cs₂Te₃

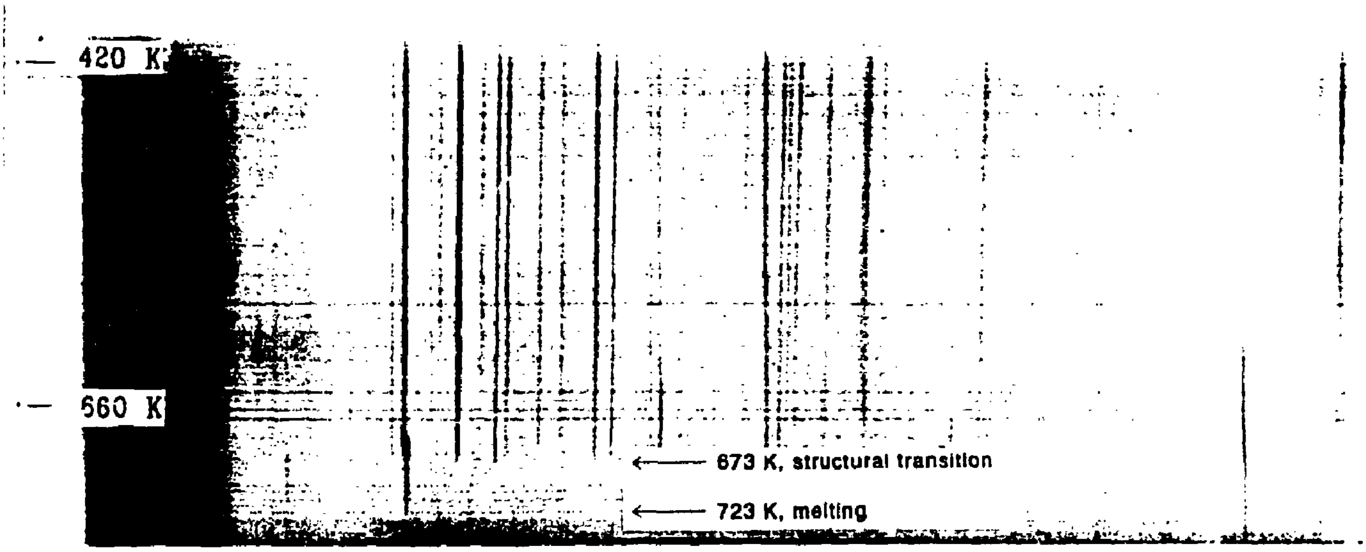

Figure 3: High-temperature X-ray diffraction pattern of CsTe, illustrating the structural transition at 673 K and the melting at 723 K.