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Polymorphism of As_2Te_3: structural studies and thermal behaviour of rhombohedral β-As_2Te_3

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Abstract

The polymorphic behaviour of As_2Te_3 was investigated by differential scanning calorimetry. The irreversible transition enthalpy of rhombohedral β-As_2Te_3 into monoclinic α-As_2Te_3 was measured ($\Delta_{\beta\to\alpha}H = -9.6 \pm 0.4$ J g^{-1}, $T_{\beta\to\alpha} = 513$ K). The β-As_2Te_3 is isostructural with Sb_2Te_3.

Using the Clapeyron equation, it can be shown that the rhombohedral form is probably identical with the previously detected high pressure form.

INTRODUCTION

It is known that arsenic telluride, As_2Te_3, shows at least two polymorphic forms. The first variety, α-As_2Te_3, is stable and crystallizes in the monoclinic system; a second form, named β, was first obtained under pressure by Kirkinskii and Yakushev [1] when studying the high pressure phase diagram of α-As_2Te_3; however, its crystalline features were not investigated. Another variety of As_2Te_3, also called β, was more recently obtained at atmospheric pressure by Han Wan Shu et al. [2] by moderate quenching of the molten compound. This modification was assigned to the rhombohedral system on the basis of the arguments developed by the authors. In fact, owing to its formation conditions, which are difficult to attain, it was never prepared in a single-crystal state, which would have made the structural determination more easy.

The same authors claimed to have shown by differential thermal analysis (DTA) that the irreversible conversion of the metastable phase, β, into the stable modification, α, at temperatures ranging from 400 to 500 K, was accompanied by other exothermal effects; accordingly, using temperature-

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scanned X-ray diffractometry with the very low scanning rate of 1.1×10^{-3} K s^{-1}, they should have detected the formation, at 363 K, of a previously unknown intermediate phase which yielded the stable modification at 423 K. Unfortunately, these studies were not reported in detail. This paper presents a differential scanning calorimetric investigation of the $\beta \rightarrow \alpha$ transition together with an X-ray diffraction analysis. Our main aim was to determine whether the high pressure β phase found by Kirkinskii and Yakushev and the atmospheric pressure metastable variety might be the same.

EXPERIMENTAL

The β-As_2Te_3 was obtained by moderately fast quenching of the molten compound at 773 K. This operation required careful manipulation because a higher or lower quenching rate would result in the formation of a glassy phase or of the stable α-As_2Te_3 phase, respectively. A high thermal conductivity of the sample has been shown to favour the homogeneous formation of β-As_2Te_3; therefore this was increased by quenching only a little of the bulk sample (0.5 g).

It was necessary to confirm the homogeneity of the sample by checking for the presence of different polymorphic varieties or of glassy phases. The checks were performed by radiocrystallography and, directly, by differential scanning calorimetry (DSC) during the recording of the thermodynamic results on the enthalpy of the $\beta \rightarrow \alpha$ transition.

The DSC system used was a Mettler FP 800 thermal analyser with an FP 85 heating cell, connected to an Epson HX 20 computer.

The samples were weighed using a microbalance sensitive to 0.01 mg. A heating rate of 10 K min^{-1} was used.

X-ray studies were performed by means of an Enraf–Nonius FR 552 Guinier camera (114.9 mm in diameter) using Cu $K\alpha_1$ radiation, $\lambda = 1.5405$ Å (50 kV, 20 mA, 0.5–1.5 h exposure time).

DSC RESULTS

The DSC scans gave two types of thermogram. The first, represented by curve A in Fig. 1, was characterized by a single exothermal effect of $\Delta_{\beta \rightarrow \alpha} H = -9.6$ J g^{-1} (-18.02 kJ mol^{-1}), which began at 500 K and continued up to 550 K. In the second, a first exothermal effect which began at about 430 K, was followed by a second which spread over the temperature range up to 550 K. A very slight departure from the base line can be noticed before the first exothermal effect (curve B). Curve A was confirmed as that representing the thermal nature of the $\beta \rightarrow \alpha$ transition, as the X-ray spectra of the samples at the end of the runs are those of α-As_2Te_3 [3–5]. The results of five runs are summarized in Table 1.

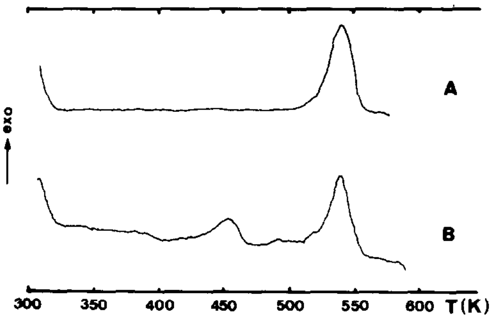

Fig. 1. DSC curves (experimental conditions are reported in the text) for the β-$As_2Te_3 \rightarrow \alpha$-$As_2Te_3$ transformation. Sample masses: curve A, 36.36 mg; curve B, 18.06 mg.

In curve B, the observed slight departure from the base line could be explained by the occurrence of a glass transition due to the presence of a small amount of glass formed during the quenching of the sample. This transition was in the temperature range 391–398 K, which agrees roughly with the 378–396 K range attributed by Platakis [6] to the glass transition of vitreous As_2Te_3. An exothermal peak starting at about 423 K was observed; this could be attributed to the recrystallization of the metastable liquid fraction into β-As_2Te_3, as shown by an X-ray diffraction spectrum of a sample obtained at about 473 K. In fact a similar spectrum for β-As_2Te_3 has been previously reported in the literature [2,7]. A second exothermal effect was observed from about 503 K up to about 563 K, and was attributed to the $\beta \rightarrow \alpha$ transition, as shown by the X-ray diffraction results of samples obtained at the end of the runs. Moreover, the mean value of the enthalpy change corresponding to the second peak was approximately equal to that of the $\beta \rightarrow \alpha$ transition shown in curve A.

TABLE 1

Enthalpy change values for the β-$As_2Te_3 \rightarrow \alpha$-$As_2Te_3$ transformation

Run no.	Sample mass [a] (mg)	Peak integration T range (K)	$\Delta_{\beta\rightarrow\alpha}H$ (J g^{-1})
1	23.12	478–563	−9.8
2	36.36	483–568	−9.3
3	18.06	473–563	−9.6
4	10.46	488–563	−10.1
5	15.44	488–568	−9.2
			mean −9.6 ± 0.4

[a] Results obtained by means of single block samples.

TABLE 2

Crystal data for monoclinic α-As_2Te_3 (space group $C2/m$, $Z = 4$)

	Carron [3]	Kanishcheva et al. [4]	Stergiou and Rentzeperis [5]
a (Å)	14.339	14.364	14.3573
b (Å)	4.006	4.025	4.0199
c (Å)	9.873	9.889	9.8990
β (deg)	95.0	95.14	95.107
V (Å^3)	565	569	569.1
d_{calc} (g cm^{-3})	6.26	6.21	6.217

TABLE 3

Crystal data and atomic parameters for rhombohedral β-As_2Te_3 and Sb_2Te_3

	β-As_2Te_3 (Han Wan Shu et al. [2])	Sb_2Te_3 (Anderson and Krause [7])
a (Å)	4.058	4.264
b (Å)	4.058	4.264
c (Å)	29.59	30.458
V (Å^3)	422	480
Z	3	3
d_{calc} (g cm^{-3})	6.29	6.50
$z(Te_2)$ [a]	0.2147	0.2128
z(As or Sb)	0.4036	0.3988

[a] Te_1 atoms lie in position $3a$ (0, 0, 0) and Te_2 and As or Sb atoms lie in position $6c$ (0, 0, z) of the space group $R\bar{3}m$ (hexagonal axes).

DISCUSSION AND CONCLUSIONS

From DSC experiments in the range 298–600 K, it has been proved that the β form of As_2Te_3 does not melt but transforms irreversibly into the α form. Structural studies have indicated that the β form described by Han Wan Shu et al. is the more dense one (see Tables 2 and 3) and that it is isostructural with Sb_2Te_3 [8] (Table 3). Assuming that the high pressure β variety investigated by Kirkinskii and Yakushev and that formed at atmospheric pressure are the same, the enthalpy change associated with the $\alpha \rightarrow \beta$ transformation under pressure should not be far from $+9.6$ J g^{-1}, provided that the variation of $\Delta_{\alpha \rightarrow \beta}H$ with increasing pressure is considered to be reasonably small.

However, the slope dp/dT of the interpolated straight line reported graphically by the authors is also negative: we have estimated it to be equal to -19.23 J cm^{-3} K^{-1}. Therefore according to the Clapeyron equation applied to the α-As_2Te_3–β-As_2Te_3 equilibrium, the volume change, $\Delta_{\alpha \rightarrow \beta}V$, is also negative and the high pressure β variety is more dense than the stable α form. We then estimated the $\Delta_{\alpha\to\beta}V$ value at room temperature (293 K), according to the temperature range of the X-ray experiments from which the density computings had been previously performed. We obtained

$$\Delta_{\alpha\to\beta}V = \frac{\Delta_{\alpha\to\beta}H}{T(\mathrm{d}p/\mathrm{d}T)} = \frac{9.6\ \mathrm{J\,g^{-1}}}{(293\ \mathrm{K})(-19.23\ \mathrm{J\,cm^{-3}\,K^{-1}})}$$

$$= -1.7\times10^{-3}\,\mathrm{cm^3\,g^{-1}}$$

Assuming that the compressibilities of α- and β-As_2Te_3 are about the same, this value agrees well with those derived from the α-As_2Te_3 volume results reported by Kanishcheva et al. [4] and more recently by Stergiou and Rentzeperis [5], i.e. $\Delta_{\alpha\to\beta}V = -2\times10^{-3}$ cm^3 g^{-1} and $\Delta_{\alpha\to\beta}V = -1.87\times 10^{-3}$ cm^3 g^{-1} respectively.

This good agreement (10–15% deviations on a volume difference may be considered as satisfactory) supports quantitatively the argument that the high pressure β variety and the form obtained by quenching may be the same, as, moreover, was suggested qualitatively by the crystallographic observation of the change from the wave-shaped chains in α-As_2Te_3 crystals into the more compact network of planar layers in crystalline β-As_2Te_3.

REFERENCES

1 V.A. Kirkinskii and V.G. Yakushev, Izv. Akad. Nauk SSSR, Neorg. Mater., 10 (1974) 1431–1435.

2 Han Wan Shu, S. Jaulmes and J. Flahaut, Mater. Res. Bull., 21 (1986) 1509–1514.

3 G.J. Carron, Acta Crystallogr., 16 (1963) 338–343.

4 A.S. Kanishcheva, Yu.N. Milhailov and A.P. Chernov, Izv. Akad. Nauk SSSR, Neorg. Mater., 18 (1982) 949–952.

5 A.C. Stergiou and P.J. Rentzeperis, Z. Kristallogr., 172 (1985) 139–145.

6 N.S. Platakis, J. Non-Cryst. Solids, 24 (1977) 365–376.

7 Han Wan Shu, S. Jaulmes and J. Flahaut, J. Solid State Chem., 74 (1988) 277–286

8 T.L. Anderson and H.B. Krause, Acta Crystallogr. Sect. B, 30 (1974) 1307–1310.