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Impurity effects on polymorphism in GeO_2 by DTA

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Polymorphism in GeO_2 is of considerable interest from the point of view of chemical bonding. It has been reported in the literature that the metastable (hexagonal, h) to stable (tetragonal, t) phase transformation below about 1200 K was not feasible in the absence of impurities. A systematic DTA study of the effects of Li^+, Na^+ and K^+ impurities on the thermodynamic sequence of phase transitions in GeO_2 (t) is presented in this paper. The t form of GeO_2, relatively free from alkali metal impurities, was obtained by autoclaving the h form in a silica tube at 623 K under a steam pressure of 10 to 15 MPa. However, the t form so obtained (by autoclaving in silica) was found to exhibit metastable melting nearly 30° below the normal melting point of the high temperature h modification. The latent heat of this metastable melting transition derived from the DTA data is reported here for the first time and it is found to be approximately equal to the sum of the latent heats of t to h transition and the normal melting transformation of the h form. The effect of alkali metal ions on the kinetics of melting transition of the h form is also discussed.

1. Introduction

Considerations of crystal chemistry predict polymorphism in GeO_2, whose ratio of radii is close to the critical value of 0.414, which is the boundary value between those for tetrahedral and octahedral coordination of anions around the central cation [1, 2]. As expected GeO_2 exists even at room temperature in at least three different modifications [2] namely the tetragonal (t), hexagonal (h) and the vitreous (l). The metastability of the higher heat content phases, namely the 'h' and the 'l', arises due to the covalent nature of the bonding. Though it has been recognized in the literature [3, 4] that the transformation of the metastable 'h' to stable 't' phase was not feasible in the absence of impurities, no systematic investigation has been made so far on the effect of impurities on the thermodynamic sequence of phase transitions in GeO_2. However, different techniques like high-temperature solution ($2PbO–B_2O_3$) calorimetry [2], fluorine bomb calorimetry [5], differential thermal analysis (DTA) [6], the Majumdar and Ray [7] method of the Clausius–Clapeyron equation, and solid electrolyte e.m.f. method [8–10] have been employed to determine the standard enthalpy changes between these polymorphs. The present paper mainly reports the synthesis of the stable t form GeO_2 by autoclaving in a silica test tube at 623 K under a steam pressure of 10 to 15 MPa. This new method of synthesis has yielded the t modification, which is relatively free from alkali metal impurities, and hence facilitates a systematic investigation of the effect of standard additions of Li^+, Na^+, K^+ or Mg^{2+} on the reversibility of the t to h and h to l transitions in GeO_2.

2. Experimental procedures

2.1. Materials

GeO_2 (h) of purity better than 99.98% was used as the starting material. Doping of GeO_2 was effected by a standard addition technique by adding appropriate quantities of dilute solutions of alkali or magnesium carbonates. The following

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TABLE I Spectrographic analysis of germanium dioxide*

Sample	Impurities (ppm)				
	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
As-received or autoclaved in silica	5 to 20	20 to 30	40	< 50	< 50
GeO_2 (t) from lithium germanate method	of the order of 200	25 to 50	40	< 50	< 50
GeO_2 (t) from autoclaving in pyrex	5 to 10	80	25	< 50	< 50
GeO_2 (h) + 100 ppm Li^+ by standard addition	70	60	–	< 50	< 50
GeO_2 (h) + 10 ppm Li^+ by standard addition	of the order of 10	50	–	< 50	< 50

*Semi-quantitative; silicon pick-up not estimated since SiO_2 is isostructural to GeO_2.

methods of synthesizing the t form from the as-received h form were attempted.

2.1.1. Isothermal method

A sample of GeO_2 (h) was heated in a platinum boat at a constant temperature of 653 ± 1 K in air.

2.1.2. Hydrothermal method [3]

The sample was encapsulated in a silica test tube with 0.1 wt% germanium metal powder under a water vapour pressure of 3 kPa (after outgassing to 10^{-3} Pa at 500 K) at room temperature. This capsule was then heated to 973 K for 65 h.

2.1.3. Autoclaving in silica (based on the P–T diagram [11] of GeO_2)

The h form was taken in a fused silica test tube and suspended over a calculated quantity of distilled water in an autoclave. It was subsequently heated to 623 K under a steam pressure of 10 to 15 MPa for 4 to 8 h and cooled.

2.1.4. Autoclaving in pyrex

Same as the method in Section 3.1.3. except that a pyrex test tube is used in place of fused silica.

2.1.5. Lithium germanate method

Lithium germanate was synthesized from the solid-state reaction between Li_2CO_3 and GeO_2 (in equimolar ratio) at 1173 K for 24 h. The h form was mixed with 0.1 wt% lithium germanate and heated to 1173 K for 24 h followed by 6 h at 1223 K. X-ray diffraction and spectrographic analyses were used for phase identification of the product and estimation of the impurities. A thermoanalyser Model Mettler TA1 was used for the DTA-TG studies. The DTA-TG holder consisted of a platinum–10 wt% rhonium/platinum (S type) differential thermocouple whose differential junctions could be located at the centres of the sample and reference materials in suitably designed platinum crucibles. The temperature calibration of the DTA assembly was checked using standard materials in alumina cups and was found to correspond to IPTS-68 [12] within ± 2 K up to the melting temperature of argon for scan rates of 2 to 15° per min. Further, for the transitions in GeO_2 no systematic trend in the dependence of transition temperature on the scan rates in the range 2 to 15° per min was observed. Therefore all the DTA runs reported here were taken to a scan rate of 10° per min. Alumina powder (less than 100 microns) was used as a reference material for DTA. A recorder sensitivity of 100 μV (full scale) was found to give a reasonably steady base line in a static air environment in the DTA runs.

3. Results

Spectrographic analyses of the as-received, autoclaved and doped samples of GeO_2 are given in Table I. A summary of the phase analyses of the products from different methods of synthesis is given in Table II. The transition temperatures from several DTA runs on samples prepared by methods listed in Table II are summarized in Table III; the DTA traces of these experimental runs are given in Figs. 1 to 4.

4. Discussion

The conventional methods, namely isothermal heating [4] and hydrothermal synthesis [3] (with 0.1 wt% germanium and water vapour saturated at

TABLE II Results of phase analyses of GeO_2 samples

Technique	Experimental conditions	Phase identified by X-ray diffraction	Reference
Isothermal heating	653 ± 1 K, 120 h	h	[4]
Hydrothermal syntheses	'h' ± 0.1 wt % Ge + 3 kPa H_2O vapour pressure at RT; encapsulated and heated to 1173 K/65 h	h	[3]
Autoclaving in pyrex	623 K, 10 to 15 MPa, 4 to 8 h	t	
Autoclaved in silica	623 K, 10 to 15 MPa, 4 to 8 h	t	
Lithium germanate method	'h' + 0.1 wt % Li_2, GeO_3 heated to 1173 K, 24 h and 1223 K, 6 h	t	[9]

RT) were not successful in converting the as-received h into t modification. When this "pure" sample (99.98 wt % GeO_2, $Li^+ < 10$, Na^+, $K^+ < 100$, see Table I) was treated by any of the following methods, the h form could be transformed into the t form:

1. Lithium germanate method (1000 ppm Li^+).
2. Doped with 100 ppm Li^+.
3. Autoclaved in silica or pyrex.

This shows that the pure h form could be transformed into the t form with the addition of Li^+ (> 10 ppm) or by autoclaving (Table II).

The DTA trace of the t form synthesized by the lithium germanate method is shown in Fig. 1a. The two endotherms on heating and the exotherms on cooling were found to be reversible in a number of thermal cyclings (more than 6) either in air or in high vacuum. Room temperature X-ray powder diffraction had established the products to be the t form, proving the reversibility of the h to t and melting phase transitions. The fact that this reversibility was due solely to lithium was confirmed in the DTA traces (Figs. 1b and c) of the pure h form doped with 100 and 10 ppm Li^+, respectively, by the standard addition method.

The two transition temperatures obtained as averages of several DTA runs are given in Table III. These values are 1314 ± 8 K (1041° C) and 1385 ± 8 K (1112° C) in good agreement with 1306 ± 10 K (1033° C) and 1389 ± 4 K (1116° C) reported in [4].

The t form prepared by autoclaving in the silica test tube exhibited metastable melting phenomena giving rise to an endotherm shown in Fig. 2. This transition occurred at 1354 ± 3 K (1081° C) compared to 1359 ± 5 K (1086° C) reported in [4], but on subsequent cooling and thermal cycling between 1100 and 1400 K there was no peak and a reason-

TABLE III Transition temperatures for GeO_2

Sample treatment	t → h T_1 (K)	h → l T_2 (K)	t → l T_3 (K)
Hexagonal (as-received)		1390 ± 3 K [13]*	
Tetragonal Li_2GeO_3 doped			
+ 100 ppm Li^+†	1314 ± 8 [12]	1385 ± 8 [12]	
+ 10 ppm Li^+†			
't' form form autoclaving in silica + 100 ppm Na^+†	1345 [1]	1384 [2]	
't' form from autoclaving in silica + 100 ppm K^+†	1349 [1]	1387 ± 6 [3]	
Autoclaved in pyrex	1334 ± 1 [2]	1389 ± 2 [2]	
Autoclaved in silica	–	–	1354 ± 3 [3]

*The number in parentheses indicates the number of runs.
†Doped by the standard addition method.

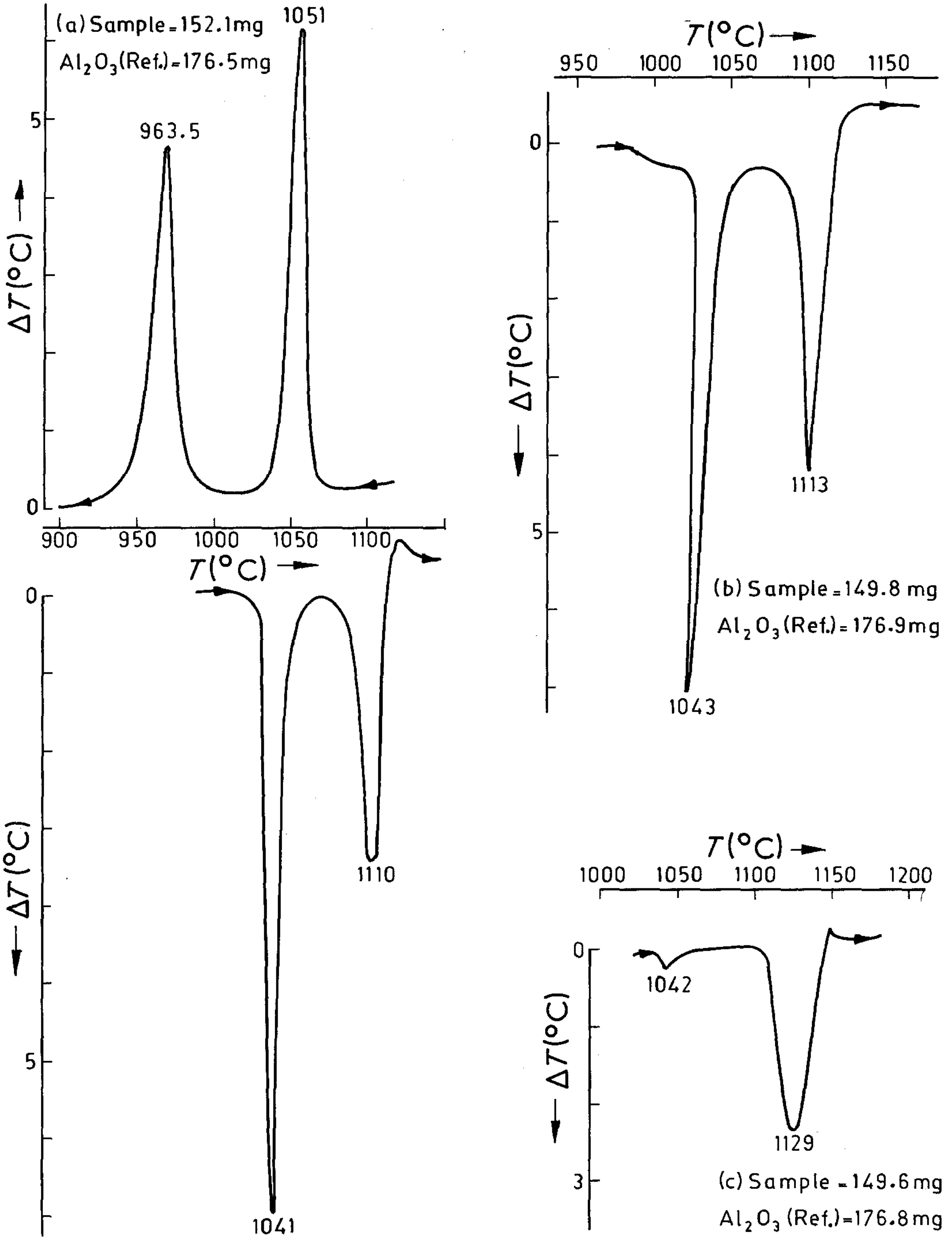

Figure 1 DTA trace using S-type differential thermocouple recorded with sensitivity of 100 μV (full scale) at a scan rate of 10° min^{-1} for GeO_2. (a) The t form synthesized using Li_2GeO_3 (1000 ppm Li^+) while heating and cooling, (b) the h form + 1000 ppm Li^+ (Li_2CO_3), and (c) the h form + 10 ppm Li^+.

ably steady base line could be observed on the DTA channel. Thus the metastable melting was an irreversible transition. The physical properties of the product obtained on cooling showed it to be the vitreous modification. On examination of the simultaneous TG trace obtained during the first heating, the expanded weight scale (full scale: 1 mg) registered a loss of weight. This weight loss corresponded to 0.16 wt% GeO_2. It is known that the h form could retain water of crystallization of

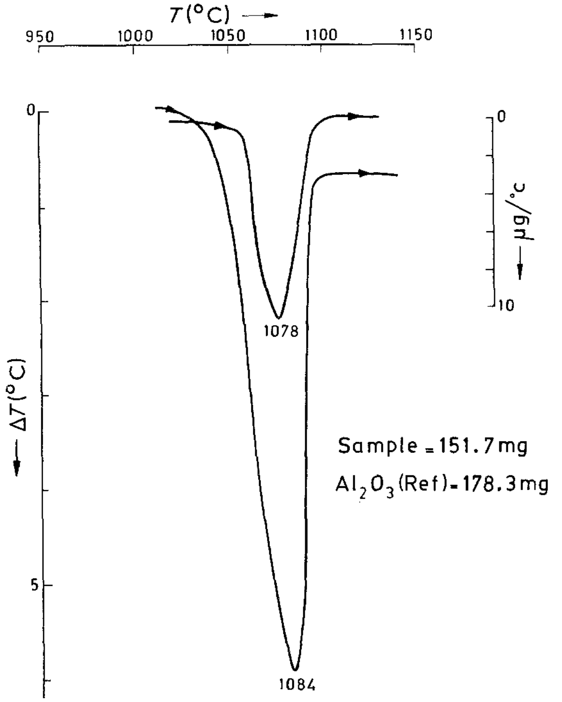

Figure 2 DTA and DTG traces using an S-type differential thermocouple for GeO_2 autoclaved in silica. The scan rate is 10° min^{-1}, and recorder sensitivity is 100 μV (full scale).

up to 3.3 mol% corresponding to the composition of pentagermanic acid $H_2Ge_5O_{11}$. However, 0.16 wt% is equivalent to 0.63 mol% of water in GeO_2. This step loss of water is represented in Fig. 2 as a DTG curve. In general, all the autoclaved samples (in pyrex or silica) exhibited a similar weight loss of the same magnitude around the first transition on the initial heating.

DTA traces of the pure h and t forms synthesized by autoclaving the h form in pyrex or in silica test tubes are shown in Fig. 3. The endothermic transitions in Figs. 3a and b were irreversible and the products were identified as the vitreous form. Further, autoclaving in pyrex had resulted in pick up of Na^+ (see Table I) which has significant bearing on the metastable melting peak of silica autoclaved GeO_2. Fig. 3c shows two peaks on the first heating of the sample autoclaved in pyrex. On cooling and on subsequent thermal cycles only one peak was observed and the product was identified as the h modification (by X-ray diffraction). To understand the behaviour of the samples autoclaved in pyrex, DTA of silica autoclaved samples doped with 100 ppm of Na^+ or 1000 ppm of K^+ was taken (Figs. 4b and c) and compared with that from pyrex (Fig. 4a). It can be seen clearly that the Na^+ or K^+ impurities present in at least 100 ppm concentration prevented the metastable melting transition of the t form resulting from autoclaving in silica, and gave rise to two peaks on heating and only one on cooling. The product was found to be the h form by phase analysis. Transition temperatures observed with Na^+ and K^+ doping are given in Table III.

The values of the enthalpies of the two phase transitions from different techniques are given in Tables IV and V, based on the summary by Navrotsky [2]. For the h to t transition the standard enthalpy change ΔH_1 from calorimetric [2, 5] and earlier DTA [6] measurements agree well with e.m.f. measurements [8]. Hence an average value of $21.3 \pm 3\,kJ\,mol^{-1}$ is assigned for this phase transition. Further, ΔH_1 is not a very sensitive function of temperature as seen from Table IV.

TABLE IV Enthalpy data on the tetragonal to hexagonal phase transition in GeO_2

Technique	ΔH (KJ mol^{-1}) at T (K)		
	298	965 ± 2	T_{eq} (ΔS (JK^{-1} mol^{-1}))
Fluorine bomb calorimetry [5]	25.4 ± 1.4	–	–
Solution ($2PbO + B_2O_3$) calorimetry [2]	21.8 ± 1.3*	21.6 ± 1.0	21.3* (16.7)
DTA [6]	–	–	21.1 ± 2.5
Clausius–Clapeyron [7]	–	–	23.0 ± 0.8
Solid electrolyte e.m.f. I [8]	–	–	21.5 ± 3 (18.3)
Solid electrolyte e.m.f. II [10]	–	–	24.6 ± 0.8 (18.1)

*Computed from heat capacity data and experimental values at 965 ± 2 K [2].

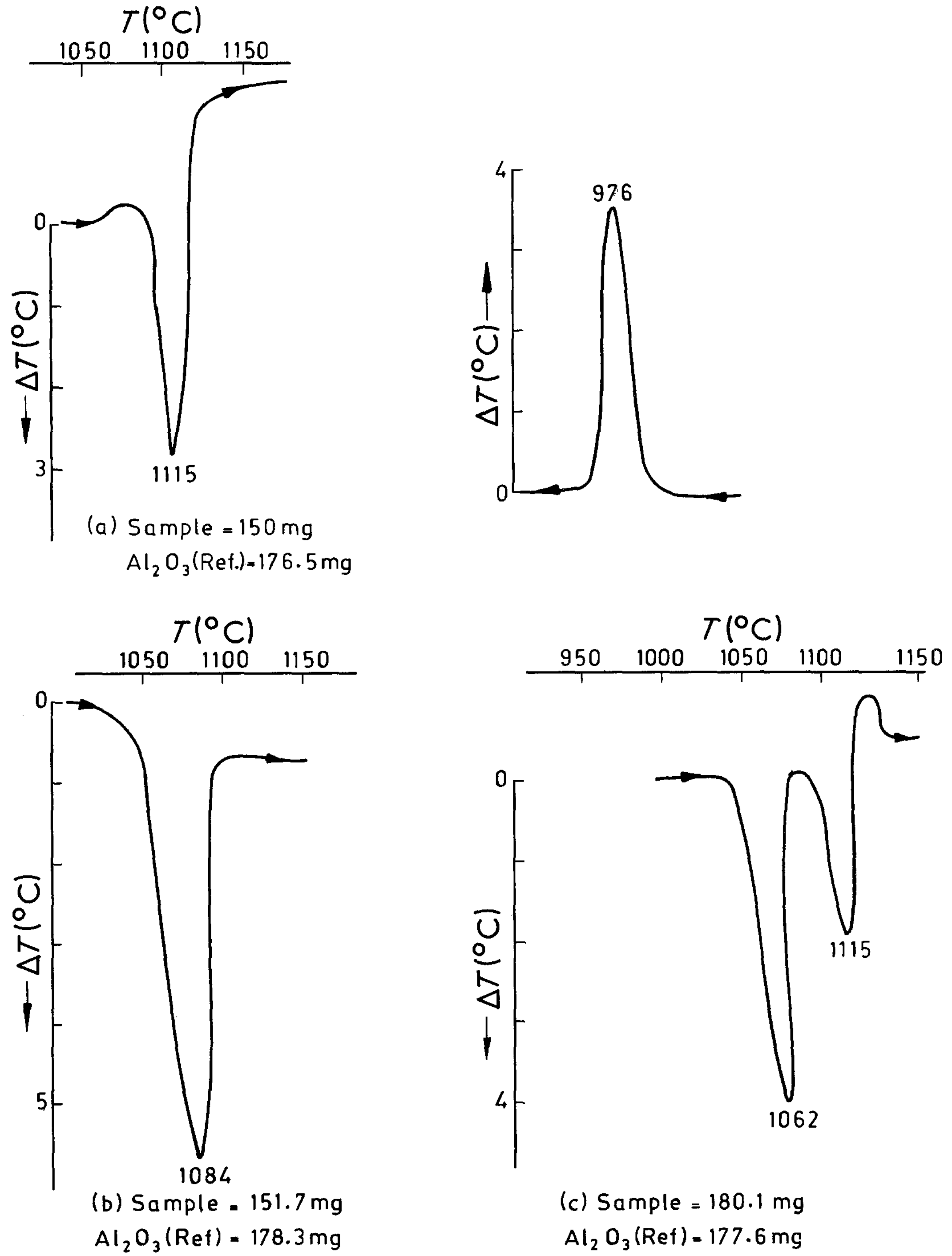

Figure 3 DTA trace using an S-type differential thermocouple recorded with a sensitivity of 100 μV (full scale) at a scan rate of 10° min^{-1} for GeO_2. (a) GeO_2 (h) as-received, (b) t form (autoclaved in silica), and (c) t form (autoclaved in pyrex) while heating and cooling.

For the melting transition, the corresponding change in standard enthalpy can be assigned an average value of $16.6 \pm 3\,\text{kJ}\,\text{mol}^{-1}$. This value is used to calibrate the area under the DTA peak in Fig. 2 (same as Fig. 3a), for a given set of experimental variables, such as scan rate, sensitivity, weight of the reference material etc. Using this calibration, the enthalpy change for the metastable

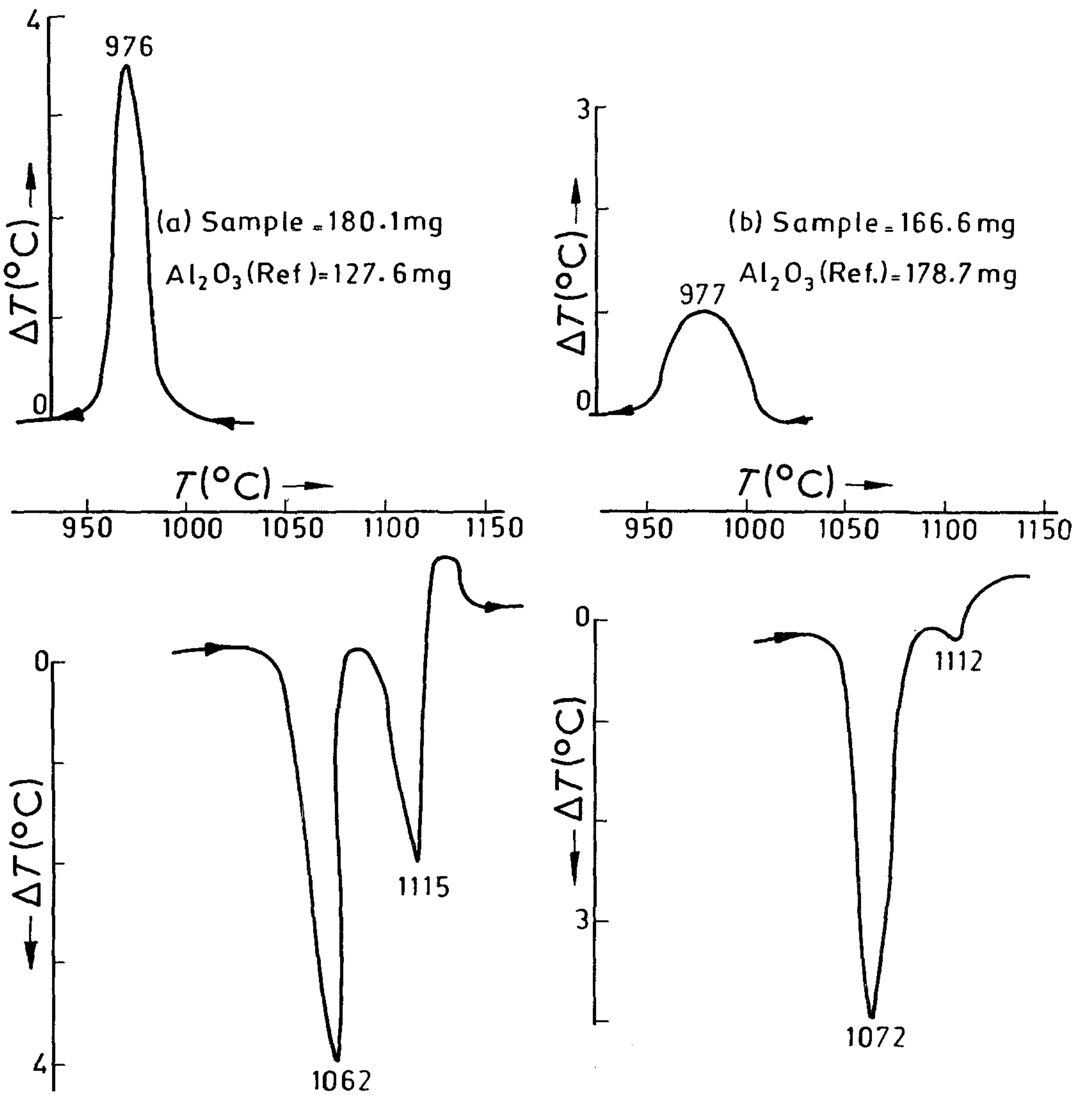

Figure 4 DTA traces (heating and cooling) using an S-type differential thermocouple recorded with a sensitivity of 100 μV (full scale) at a scan rate of 10° min^{-1} for GeO_2. (a) the t form (autoclaved in pyrex), (b) autoclaved in silica + 100 ppm Na^+ (Na_2CO_3), and (c) autoclaved in silica + 100 ppm K^+ (K_2CO_3).

TABLE V Enthalpy data on the hexagonal to vitreous phase transition in GeO_2

Technique	ΔH (KJ mol^{-1}) at T (K)		
	298	965 ± 2	T_{eq} (ΔS (JK^{-1} mol^{-1}))
Fluorine bomb calorimetry [5]	15.7 ± 0.6	–	–
Solution (2PbO + B_2O_3) calorimetry [2]	14.8 ± 2.9*	15.4 ± 2.5	16.1 ± 2.9* [1]
DTA [6]	–	–	17.1 ± 2.1
Low temperature heat capacity [14]	13.7 ± 0.29	9.29	–

*Computed from heat capacity data and experimental data at 965 ± 2 K [2].

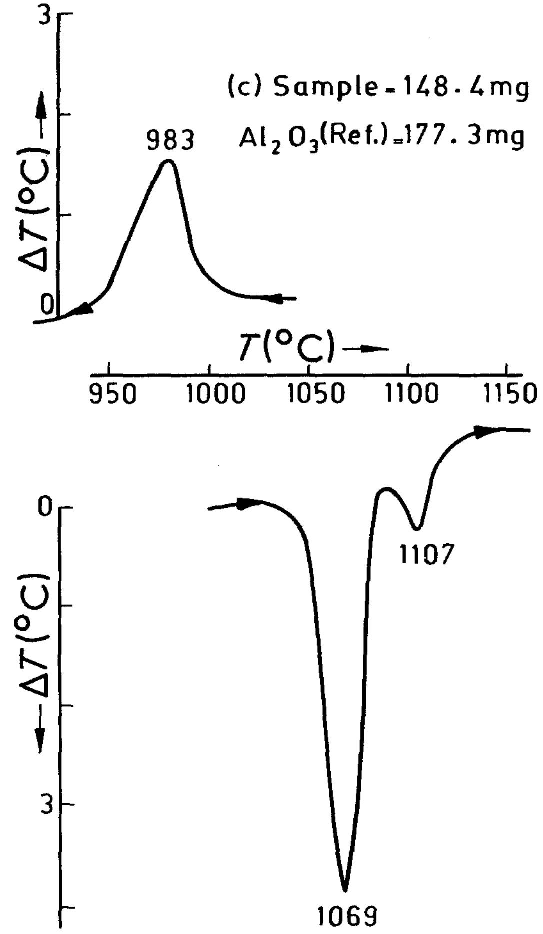

Figure 4 Continued.

TABLE VI Effects of Li^+, Na^+ or K^+ dopant on the kinetics of melting of GeO_2 (h)

Dopant	$\ln \Delta T = A - B/T$	
	A	$B \times 10^{-5}$
Li^+	204.956	2.794
Na^+	225.562	3.125
K^+	281.054	3.873

melting, ΔH_3, at the transition temperature T_3 is calculated to be $39.6 \pm 3\,\mathrm{kJ\,mol^{-1}}$. This is in agreement with the value of $37.9\,\mathrm{kJ\,mol^{-1}}$ for $(\Delta H_1 + \Delta H_2)$. Further, the contribution to this latent heat of transition by the chemical bonding energy of 0.6 mol % water (due to step loss of weight) at T_3 would be negligible ($\sim 5\%$ assuming the chemical bonding energy $\leqslant 10$ times ΔH_2). If this could be corrected for, then the agreement would be even better.

An attempt was made to study the effect of doping with 50 ppm Mg^{2+} on the metastable melting of silica-autoclaved sample. It was found to have no effect.

If one compares the DTA traces of, say the melting transition of the h form containing 100 ppm Li^+ (Fig. 1b) with those containing 100 ppm Na^+ (Fig. 4b) and 100 ppm K^+ (Fig. 4c) one can see that they became increasingly sluggish by changing the dopant from Li^+ to K^+. To quantify this effect on the rate of melting transition of the h form, the DTA endotherms in (Figs. 1b, 4b and 4c) were fitted into the following equation suggested by Piloyan [15].

$$\ln \Delta T = A - B/T$$

The Piloyan equation is shown to be valid for 5 to 6 interpolated temperature values between initiation and maximum temperatures of these DTA peaks; see Fig. 5. The straight line fits in Fig. 5 are listed in Table VI. According to Piloyan

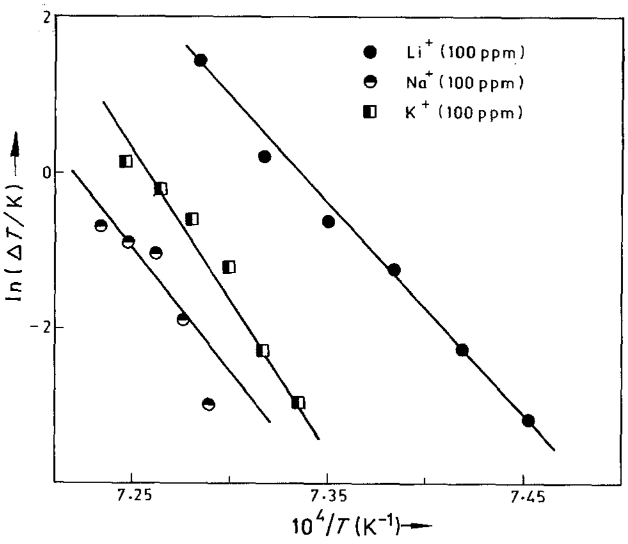

Figure 5 Application of Piloyan equation to the melting transition of GeO_2 (h) doped with (a) 100 ppm Li^+ (see Fig. 1b), (b) 100 ppm Na^+ (see Fig. 4b), and (c) 100 ppm K^+ (see Fig. 4c).

the slope B is related to the activation energy of the process. Thus, one can see from Table VI that the slope B (hence the activation energy) increases by about 20% each time the dopant is changed from Li^+ to Na^+ and from Na^+ to K^+.

It is concluded that a pure form of GeO_2 in the h modifications does not transform into the t form readily up to the transition temperature, without the addition of at least 10 ppm of Li^+ (or by autoclaving). This chemically pure h form exhibits irreversible melting at the normal melting point. Pure t form, obtained free of alkali metal impurities, exhibits irreversible and metastable melting at about 30° below the normal melting point of GeO_2; this form invariably retains about 0.6 mol% water of crystallization up to the transition temperature. Na^+ or K^+ at concentrations of about 100 ppm can produce a h form (from the t form) that exhibits reversible melting at the normal point. Even without autoclaving, Li^+ (in 100 ppm concentration) can convert the h form into the t phase that exhibits a normal and thermodynamic sequence of solid-state and melting transitions. With respect to energy GeO_2 is a peculiar system in which the solid-state transition is more energetic (21.3 kJ) than the melting transition (16.6 kJ). With respect to percentage this difference is nearly 30% of the latent heat of melting of the h form. If one compares the ionic radius of Li^+ (0.06 nm) with those of Na^+ (0.055 nm) and K^+ (0.133 nm) the charge densities of the latter are 40 and 34% of the former (Li^+) ions. Therefore it is possible and the Li^+ ions are able to make both phase changes reversible, whereas Na^+ and K^+ can render only the less energetic melting transition reversible. Even here the transition becomes more sluggish as the dopant is changed from Li^+ to Na^+ or K^+.

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