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Novel features in solid phase transition behavior of TlI

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Abstract

Novel features in solid phase transition behavior in TlI are reported. These features include transition temperature $T_t = 181 \pm 2°C$ and transition enthalpy $\Delta H_t = 1180 \pm 50$ J/mol in contrast with the accepted 172°C and 875 J/mol, respectively. Differential scanning calorimetry (DSC) profiles exhibit endothermic peak broadness and doublets in contrast to the earlier reported single sharp endotherm. These results are interpreted in terms of possible polytypism arrangement in β-TlI and/or β-TlI particle size below the critical value required for transition singularity. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Solid TlI transition; Phase transition features

1. Introduction

The solid state is a most interesting and fascinating state of matter. Its importance bears on fundamental knowledge with regard to our best insights into the nature of forces that bind together atoms, ions, and molecules. Its practical/technological usefulness is evident in the multiplicity of beneficial solid state applications, such as lasers, masers, phosphors, sensors, etc.

The existence of polymorphic compounds presents us with simple case studies to probe atom–atom or ion–ion interactions at the most elementary level with the promise of leading to a better understanding of the nature of the solid state. A polymorphic compound indicates that the minimum internal energy or cohesive/binding energy of the crystal U_0 does not differ greatly from one structure to another. The enthalpy ΔH_t accompanying the structural transition represents the difference between the cohesive energies of the two structure states, i.e. $U_0(2) - U_0(1) = \Delta H_t$. Recently, we reported phase transition studies on TlI incorporating cations [1–3] and anions [4]. Yellow room temperature β-TlI, a double-layered orthorhombic structure related to NaCl [5], transforms to red α-TlI, with a Pm3m CsCl cubic structure, at 172°C with transition enthalpy $\Delta H_t = 875$ J mol^{-1}. In these studies we used TlI supplied by Aldrich Chem. Co. (Milwaukee, WI), Lot no. 02514HY CZ designated AL I with stated purity 99.999%. This 25 g TlI source was exhausted and to continue our studies we purchased two more 25 g samples, one from Aldrich Chem. Co., Lot no. 05129JG MQ designated AL II with stated purity 99.999% and the other from Alfa AESAR (Ward Hill, MA), Stock no. 11825 and Lot no. L02G20 designated AE I with stated purity 99.999%. The phase transition behavior along with temperature and enthalpy values of these latter TlI samples were distinctly at variance with the earlier

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results. A third TlI sample obtained from the University of Western Ontario supplied by Alfa AESAR, Lot no. G06C01 designated AE II with stated purity 99.999% also gave different transition temperature and enthalpy results from the earlier Aldrich sample but consistent with the latter TlI sample results.

This communication contains the recent results on the differential scanning calorimetry (DSC) study on the three recently acquired TlI samples along with interpretation to reconcile the disparity between these and the earlier reported data. The interpretations are based on transition behavior on particle size and/or possible structural polytypism.

2. Experimental

The three samples of TlI used in these measurements were from two sources: one from Aldrich Chem. Co. (Milwaukee, WI) designated AL II and the other from Alfa AESAR (Ward Hill, MA) designated AE I and AE II both with stated purity 99.999%.

Thermal analysis was done with the differential scanning calorimetry (DSC) accessory to the DuPont Instruments Computer/Thermal Analyzer unit for process monitoring, data acquisition and data analysis. The samples encapsulated in aluminum, copper, and gold pans were bathed in flowing N_2 (ultrapure) atmosphere gave the same traces. Only traces with accompanying quantitative data using aluminum and gold pans are reported here. The calorimeter was calibrated with In metal for temperature and enthalpy of fusion before the transition enthalpies of TlI were determined. The calibration was checked periodically.

The X-ray diffraction patterns obtained at room temperature and above 185°C using the X-ray diffraction facilities with Cu $K_{\alpha 1}$ radiation at the University of Western Ontario confirmed the β and α structures, respectively according to the X-ray powder data file.

The DSC traces were taken for a number of untreated stock samples and for samples subjected to different pretreatment conditions. The reported traces are for (i) untreated stock samples, (ii) recycled samples after different time intervals and starting temperatures, (iii) compressed room temperature ground and uncrushed disc portions and (iv) compressed uncrushed disc portion annealed at 180–190°C in oven.

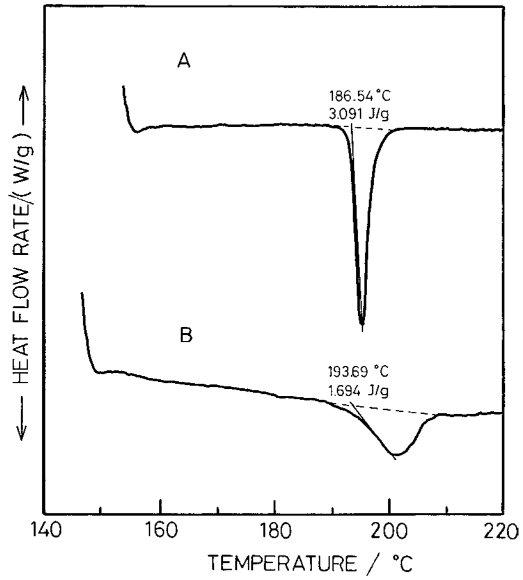

Fig. 1. DSC traces of Aldrich TlI, AL II: (A) untreated stock sample; (B) same sample as (A) cooled to room temperature taken 24 h later.

3. Results and discussion

DSC traces in Figs. 1 and 2 are for Aldrich, AL II received in 1996. Fig. 1A and Fig. 2A are for untreated stock samples. The same sample as 1A cooled to 120°C and taken 40 min later exhibited no thermal effect; Fig. 1B is for sample cooled to room temperature and taken 24 h later which shows partial ca. 50% recovery from hysteresis following no thermal effect after 40 min.

Fig. 2B is for the same sample as Fig. 2A trace, different from Fig. 1 sample, 20 h later cooled to room temperature. No thermal effect appeared after cooling 35 min later. The distinguishing features of Fig. 2A are the weak endotherm at ca. 170°C, in agreement with earlier results [1–3] and the strong endotherm doublet between 185°C and 210°C. Subsequent traces of stock untreated samples showed variations ranging between a single endotherm of Fig. 1A to narrow and sharp endotherm doublets shown in Fig. 3A–C. The variations in the DSC traces of Figs. 1–3 do not originate with instrumental artifacts as ascertained by consistently reproducible traces with reference standards. These variations are therefore attributed to non-uni-

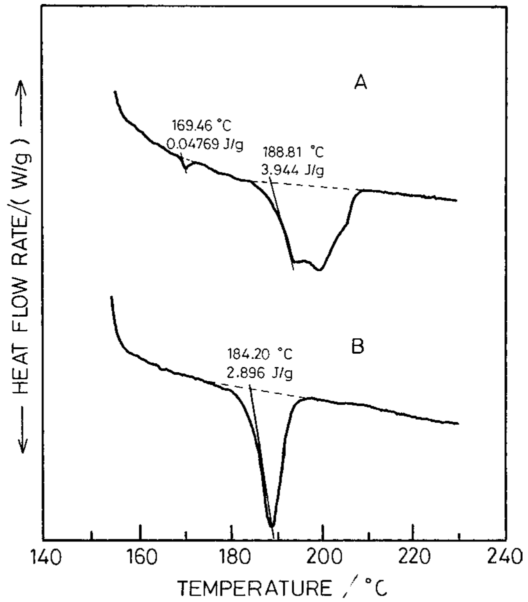

Fig. 2. DSC traces of another sample of Aldrich TlI, Al II: (A) untreated stock sample; (B) same sample as (A) cooled to room temperature taken 20 h later.

formity in the nature of the DSC 6–10 mg samples taken from stock TlI.

In an effort to reconcile the inconsistency of the AL II DSC traces stock TlI samples were compressed and annealed to obtain reproducible results. The stock was compressed to 1.4×10^4 kg pressure on disc 0.2 mm thick and 1.0 cm diameter at room temperature for 75 min. The DSC trace for a ground portion of the compressed disc gave a single endotherm similar to Fig. 1A and Fig. 2B with $T_t = 180^\circ C$ and $\Delta H_t = 2.637$ J/g. Subsequent heatings of this sample 4 h later showed unrecovered hysteresis. The room temperature sample 24 h later showed partial recovery, ca. 40%, from hysteresis similar to Fig. 1B. This compressed disc was annealed in oven at 220°C for 4 h and 30 min. The uncrushed portion of this annealed compressed disc showed consistently reproducible DSC traces and no evidence of hysteresis after repeated heatings every 30–40 min with $T_t = 181 \pm 2^\circ C$ and $\Delta H_t = 1180 \pm 50$ J/mol in both aluminum and gold pans. These cited T_t and ΔH_t values and their limits are from 14 DSC traces. The internal consistency in ΔH_t values was better for Al pans than for Au pans, within 2.5% and 4.5%, respectively. The difference is attributed to new Al pans relative to re-used Au pans lacking reproducible 100% geometry.

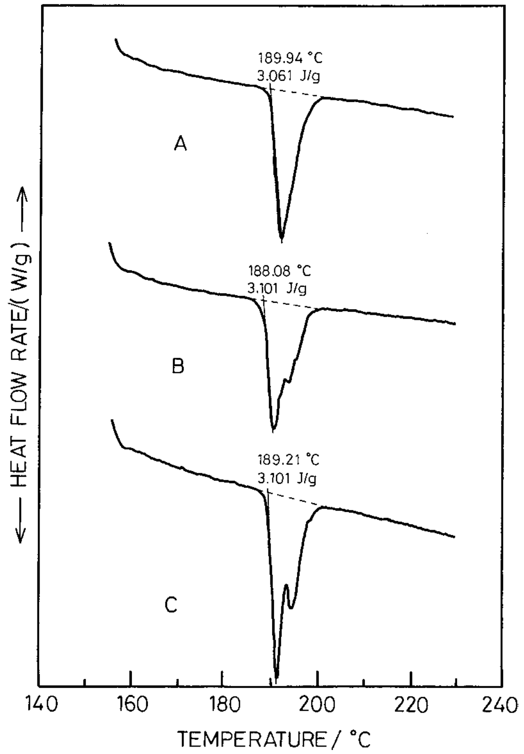

Fig. 3. DSC traces of another sample of Aldrich TlI, AL II: (A) untreated stock sample; (B) same sample as (A) cooled to room temperature taken 22 h later; (C) same sample as (B) cooled to room temperature taken 26 h later.

The DSC traces for the two compressed and annealed AESAR lots of TlI, AE I and AE II, not shown, reproduce the same features with T_t and ΔH_t values within 5% as those obtained for the pretreated Aldrich AL II lot of TlI. Some typical traces for the two untreated stock samples are presented in Figs. 4 and 5 for comparison with Fig. 1A and Fig. 2A for untreated AL II. The only distinguishing feature of AESAR samples was the sporadic appearance of hysteresis under the same experimental conditions for recycled heatings.

From the 42 DSC traces on the lots of TlI, AL II, AE I and AE II we attribute the variability of phase transition, $\beta \rightarrow \alpha$ profiles, T_t and ΔH_t values to the lack of structural consistency and/or lack of uniformity in particle size of the DSC samples, 6–10 mg, taken from the supplied stock. The 1991 Aldrich stock

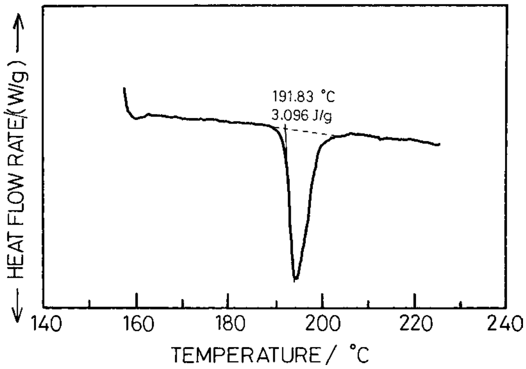

Fig. 4. DSC trace of untreated stock sample of AESAR TlI, AE I.

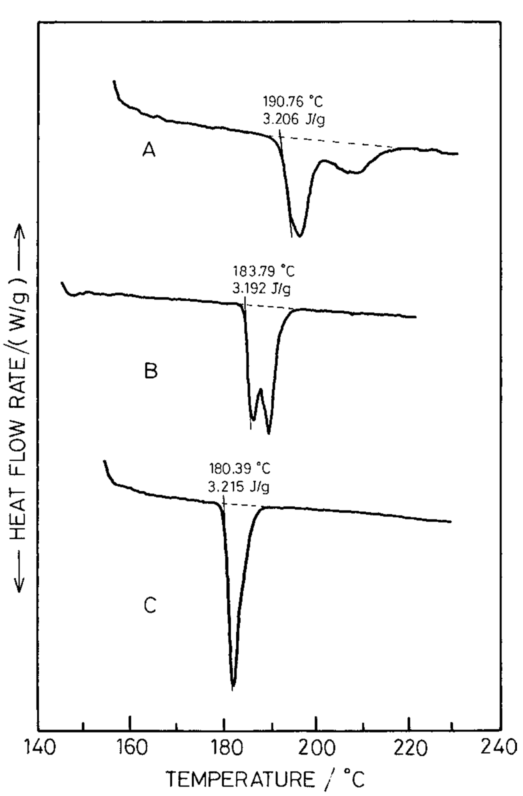

Fig. 5. DSC traces of AESAR TlI, AE I: (A) untreated stock sample; (B) same sample as (A) cooled to room temperature taken 15 days later; (C) same sample as (A) after annealing in oven at 186°C for 19 h taken 24 h later.

AL I was in lumps that had to be ground with mortar and pestle for DSC samples which gave reproducible $T_t = 172 \pm 2$°C and $\Delta H_t = 875 \pm 25$ J/mol. In contrast AL II, AE I and AE II were very fine powders that adhered to the pestle and exhibited slippery graphite-like properties on grinding attempts (colloidal dimensions?). The DSC behavior of ground samples showed no difference from non-ground stock samples. The results of this study demand an interpretation on two main features of solid phase transition, viz. (i) the variable thermal profiles of DSC traces with variable T_t and ΔH_t for samples taken from the same stock and (ii) the reproducible single endotherm with reproducible higher $T_t = 181$°C and $\Delta H_t = 1180$ J/mol for annealed compressed samples relative to the earlier reported reproducible $T_t = 172$°C and $\Delta H_t = 875$ J/mol. Furthermore, a preliminary report on crushed samples of the fused product of AL II TlI-rich compositions contained DSC traces with reproducible $T_t = 172$°C [4]. How does one reconcile these differences, beyond the experimental uncertainties, for TlI samples each with stated purity 99.999%?

The essential parameters or "dimensions" in a solid phase transition are described as (i) structural and (ii) thermodynamic. Although (iii) kinetics is not considered an essential parameter, it can be of significance in an auxiliary role, e.g. hysteresis in sluggish or quenchable transitions and also in delayed transitions effected by particle size.

The fact that mixed α- and β-structures of TlI, viz. CsCl cubic and orthorhombic, respectively, can exist, Fig. 1B and Fig. 2A suggest possible polytypism arrangement in β-TlI. Polytypism, common to metal iodides, is considered to be one-dimensional polymorphism wherein polytypes differ in the unit cell in one of the three dimensions [6]. Some interpolytypic transitions can occur within 10–20 K. The possible polytypism arrangement visualized in β-TlI is given in Fig. 6. Fig. 6A shows the accepted β-TlI structure where the projecting portion resembling the distorted NaCl unit appears regularly on the same face. However, the same inverted structure with the NaCl unit appearing on the opposite face can form a one-dimensional polytypic arrangement with the regular unit, viz. alternate right-hand left-hand projections. Polytypism linked to the kinetics parameter can account for the higher T_t value, 181°C versus 172°C, and the higher ΔH_t value, 1180 J/mol versus 875 J/mol and the observed varied thermal DSC profiles, Fig. 2A, Fig. 3B and C.

The dependence of DTA thermal effects on particle size of the solid through grinding has been reported earlier (see [7], and references therein). It is generally

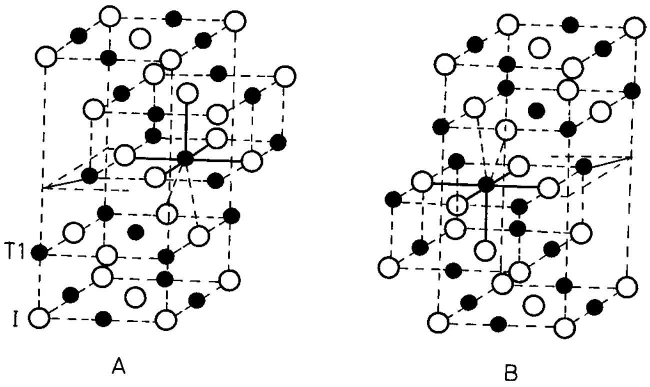

Fig. 6. Suggested polytypism arrangement in β-TlI alternating A and B units with projecting portion resembling NaCl unit facing each other, i.e. right-hand left-hand adjoining units.

accepted that the kinetics parameter plays a more dominant role when the particle size of the solid is below a critical value. Surface free energy or "surface energy" property is associated with particle size of the solid [8]. The formation of a new phase has its origin in "embryos" and the process of nucleation, nuclei growth, occurs only if the net free energy of nuclei formation ΔG given by

$$\Delta G = \tfrac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma, \tag{1}$$

is negative, where r is the radius of embryo, ΔG_v the bulk free energy decrease/unit volume and γ the surface energy/unit surface area. Either one or both possible limiting conditions can contribute to endotherm broadness or doublets: (i) if the individual particle size r is smaller than the required critical-sized embryo r_c, i.e. $r < r_c$, nuclei growth does not occur and (ii) the distance separating particles λ exceeds the vibrational frequency ν of the atoms such that these cannot jump across the interface or gap, i.e. $\lambda > \nu p$, where p is the probability for the required condition of criticality for the phase transition to occur. Both limiting conditions can be overcome by an increase in temperature enhancing the particle size by accretion/sintering and the resulting nucleation rate, R,

$$R = N \exp\left(\frac{-\Delta G_c}{kT}\right) \cdot n^* \nu p \exp\left(\frac{-E_a}{kT}\right), \tag{2}$$

where N is the sites/unit volume of the initial or parent phase, ΔG_c the free energy for critical-sized embryos, n^* the number of atoms surrounding the embryo of critical size with vibrational frequency ν and p the probability that an atom attaches to the embryo and E_a the activation energy for growth of critical-sized embryos into critical nucleus size. The prolonged hysteresis in the reverse $\alpha \rightarrow \beta$ transition and endotherm doublets or broadness suggest different nucleation rates in a given sample. Eq. (2) is the basis for subsequent heating DSC traces of the same sample showing endotherm narrowing and lowering of the transition temperatures T_t. The reproducibility of DSC trace profiles with constant ΔH_t and T_t for the compressed and annealed uncrushed disc samples indicate a common initial state for the solid TlI.

The DSC traces of fused 10 mol% guest ion in TlI-TlX compositions [4] indicate that guest ion presence eliminates any possible polytypism or the delayed kinetics effect originating with particle size.

In summary, the solid phase transition behavior in TlI reported herein is interpreted in terms of possible polytypism arrangement and/or sub-critical particle size.

Acknowledgements

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