

Differential Scanning Calorimetric Analysis of Phase Transition in LCD Materials

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Abstract: The phase transition has been described according to the current thermo-dynamical theories as a first order or second order, recorded on the Differential Scanning Calorimetry (DSC) traces as an anomalous change in the differential power ΔP , different from the normal ΔP variation only due to the heat capacity of the material where height h of the peak as the distance between the heat capacity trace or baseline and the maximum ΔP during the course of the phase transition is exposed. In case of a pure second order phase transition, this height is the different, between the heat capacities before and after the transition. In case of pure first order phase transition, this height is different, between the heat capacities before and after the transition.

Keywords: phase transition, transition peak, DSC scan, specific heat, transition energy

1. Introduction

In present work it is our aim to explain the phase transition with the help of different experimental techniques. The Differential Scanning Calorimetry (DSC) [1, 2] scan is also used for detection of phases and explaining phase transition. The phase transition which will be described here according to the current thermo-dynamical theories as a first order or second order one is recorded on the DSC traces as an anomalous change in the differential power ΔP , different from the normal ΔP variation only due to the heat capacity of the material. This variation sharp or smooth will be called "transition peaks" [4,5]. We define height h of the peak as the distance between the heat capacity trace or baseline and the maximum ΔP during the course of the phase transition. In the case of a pure second order phase transition this height is the different between the heat capacities before and after the transition. In case of pure first order phase transition, this height is difference between the heat capacities before and after the transition. In case of pure first order phase transition [3], it is simply the maximum height of the peak above the baseline. A number N is defined as $N = h'/h$ where h' being height of the transition peak when the mass or the heating rate are doubled. The theoretical values of N will be determined in the case of an isothermal first order phase transition, a second order phase transition and a non isothermal first order phase transition (case of impure material).

2. Isothermal First Order Phase Transition

Several models have been exploited to explain DSC scan melting peaks in pure materials these models are valid for any isothermal first order phase transition here we have used only simplest expression to explain the melting peak. The temperature of specimen during the transition remains constant. This approximation as far as the thermal resistance of the specimen can be considered negligible. The model proposed by O'Neil may be reduced to the following form:

$$\gamma T'_p (t_2 - t_1)^2 / R_o^2 A^2 p \Delta H \ll 1 \quad \text{-----}(1)$$

Where

- T'_p : is the melting rate of the specimens
- $(t_2 - t_1)$: is the melting time of the specimen
- γ : is the thermal resistivity specimen
- P : is the specific mass time of the specimen

If the sample temperature is assumed to be constant during melting the theoretical melting curves has the general shape as explained in the appended curve.

1. For $t \leq t_1$, i.e. before beginning of the melting, the differential power $\Delta P(t)$ is only due to heat capacity of the solid material

$$\text{So, } \Delta P(t) = m \cdot C_{ps} \cdot T'_p \quad \text{-----} (2)$$

Where,

- m : is the mass of the sample
- C_{ps} : the specific heat of the solid material

2. Between t_1 & t_2 melting occurs at a constant temperature, and

$\Delta P(t)$ is given by :

$$\Delta P(t) = T'_p / R_o (t - t_1) + m C_{ps} \cdot T'_p \quad \text{-----} (3)$$

3. At the end of melting, the sample is still at the melting temperature whereas the programmed temperature is much higher so that sample has to reach the programmed temperature which implies the following variation of $\Delta P(t)$

$P(t)$

$$\text{So, } \Delta P(t) = m c_{pL} T'_p + [m (c_{ps} - c_{pL}) \cdot T'_p + T'_p / R_o (t_2 - t_1)] \exp (t_2 - t) / m R_o \cdot c_{pL} \quad \text{-----}(4)$$

Where c_{pL} is the specific heat of the liquid sample. By mathematical view equation (4) shows that ΔP curves reach the base line for an infinite time. It will be considered that the sample reaches the programmed temperature at time t_3 , which is taken when it is impossible to measure the difference between the baseline and the ΔP curves.

4. For $t > t_3$

$$\Delta P(t) = mc_p L T'_p \text{ ----- (5)}$$

The transition enthalpy molecules $m\Delta h$ is given by t_2
 $m\Delta h = \int_{t_1}^{t_2} [m.C_{ps} \cdot T'_p + T'_p/R_o(t - t_1)] dt$

$$= m.C_{ps} \cdot T'_p(t_2-t_1) + T'_p/2R_o(t_2 - t_1)^2 \text{ -----(6)}$$

From figure below, the height h of the peak has the following expression i.e.

$$h = T'_p/R_o(t_2 - t_1) \text{ ----- (7)}$$

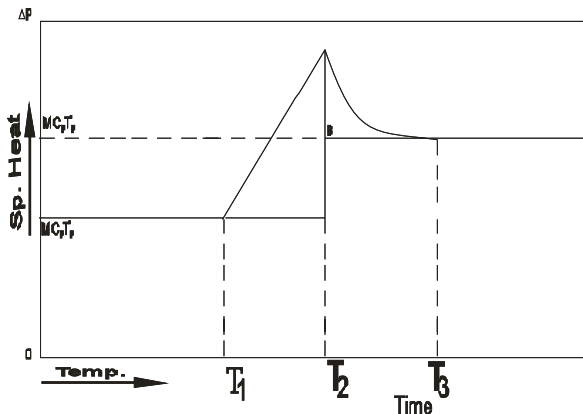


Figure 1: Theoretical DSC melting curve of a pure material ΔP is the power difference between the sample holder and the reference holder. The heating rate T'_p is constant

From equation (6) & (7) we get,

$$H = -mC_{ps} T'_p + (m^2.C_{ps}^2 T'_p + 2m \Delta h T'_p)^{1/2} \text{ -----(8)}$$

Now N may be define as h'/h where h' is the height of the peak for a mass $2m$ or a heating rate $2 T'_p$.

So,

$$N = \frac{2[-1+(1+(h'/m.C_{ps}^2 T'_p + R_o T'_p)^{1/2})]}{[-1+(1+(2\Delta h/m.C_{ps}^2 T'_p + R_o T'_p)^{1/2})]} \text{ ---- (9)}$$

Where m or T'_p tends to zero, N tends to $\sqrt{2}$ and when m or T'_p tends to infinity, N tends to 1

The function being without extremum

$$1 < N < \sqrt{2} \text{ ----- (10)}$$

The above explanation of limits is only a mathematical consequence of equation (9) & there physical significance has to be examined. The upper limit is valid & can be understood in a simple way when T'_p or m tends to zero, it means that Δh is important and the heat capacities negligible. Thus the transition peak is a triangle whose area B will be zero in fig no. 3

$$N = \sqrt{2}$$

On the contrary the lower limit cannot be reached since the basic assumption of this model is that the melting curve has the shape shown in fig no. 3 which implies that T'_p and m

are small. The exact limit for T'_p and m depends on the nature and geometry of the sample.

It will be much favorable to multiply T'_p by two rather than m . The first reason is experimental, since it is easier to run twice the same sample than to run two different samples. Secondly, this model assumes that the thermal resistance R_o is independent of mass. This is true only when the special case is taken to ensure that the specimen geometry particularly the contact with the pan and its position remains constant. When it is not possible run twice a sample the following equation gives N in the case of two masses m_1 & m_2 leading respectively to two peak height h_1 and h_2 .

$$N = \exp [0.69 \ln (h_2/h_1)/\ln(m_2/m_1)] \text{ -----(11)}$$

3. Second Order Phase Transition

As a DSC Curve is the recording of the differential power

ΔP versus time t [6]. It is possible to write
 $\Delta P = d\Delta w/dt = d\Delta w/dT_p \cdot dT_p/dt \text{ -----(12)}$

Where T_p is the programmed temperature. The equation No (12) is valid only in the absence of First Order Phase Transition.

$$(d\Delta w/dT_p = mc_p \text{ and } dT_p/dt = T'_p) \text{ ----- (13)}$$

Equation (12) is then the same as equation (2)

$$\text{So, } \Delta P = mc_p \cdot T'_p \text{ ----- (14)}$$

Where m or T'_p are multiplied by two ΔP is also multiplied by two.

A second order transition is recorded by DSC as a change of heat capacity, without involving a transition energy equation (14) is so valid for describing such a transition [7-8]. In this case,

$$h = m \cdot T'_p |C_{p2} - C_{p1}|$$

Where C_{p1} and C_{p2} are the specific heats before and after the transmission. As a Consequence, $N=2$.

4. Non-Isothermal first order transition (Impure-material)

In case of impure material the First Order Phase Transition is generally non isothermal. The presence of impurity lowers the melting point and broadens the melting point peak [9]. If the impurity is soluble at any quantity in material, one can describe the melting curve using Van't Hoff equation [10, 11]. This equation is commonly used in DSC technique for measuring the purity of sample.

It can be written as under-

$$dw/dT_s = m \Delta h(T_f - T_m)/ dt (T_f - T_s)^2 \text{ -----(15)}$$

Where,

T_f is the melting temperature of the pure material

T_m is the melting tempers of the impure material
 Δh the specific enthalpy of transition

T_s a t temperature where a c ertain am ount of m aterial has melted.

dw/dT_s is related to th e power ΔP involved i n t he transformation at temperature T_s .

$$\Delta P(T_s) = m \cdot C_p(T_s) \cdot T'_p + dw/dT_s \cdot T'_p \text{-----} (16)$$

At the melting temperature T_m

$$dw/dT_s = m \Delta h / (T_f - T_m) \text{-----} (17)$$

The height of the peak is given as under:

$$h = \Delta P(T_m) - m C_p(T_m) \cdot T'_p = dw/dT_s \cdot T'_p \text{-----} (18)$$

$$H = m \Delta h \cdot T'_p / (T_f - T_m) \text{-----} (19)$$

Where m or T'_p multiplied by two, h is multiplied by two and so $N = 2$. It is th e sam e result as for th e second order transition wh ere only heat capacities are in volved. This statement can prove th e theoretical m odel of Gorter for second order t ransition [12]. In th is model a Second Order Phase Transition is described as th e end on non-isothermal first order transition [13, 14]. This is ex actly wh at happens in the case of melting of an impure material as described by the van't Hoff equation.

Table 1: Summary of theoretical N Parameters for various Phase Transition

| Transition | N |
|--|--------------------|
| 1. Isothermal First Order Phase Transition impure material | $1 < N < \sqrt{2}$ |
| 2. First order Phase transition | 2 |
| 3. Second Order Phase transition | 2 |

5. Conclusion

The above mathematical derivation gives light to elaborate the theoretical model for second order phase transition of LCD materials. In th is model a Second Ord er Ph ase Transition is described as th e end on non-isothermal first order t ransition [15]. This is ex actly wh at happens in th e case of melting of an impure material as descri bed by the van't Hoff equation. The values of N can give at least two results. It gives qu alitative m easurement of th e relative importance of seco nd order com ponent i n th e first order phase tran sition and an anomalous behavior i.e. t he transition is not a sim ple one but ano ther phenomena is hidden as for instant two transition very close together and giving only one peak. [16, 17]. During the DSC scan, thermal curves exposes their endothermic and exothermic shapes and in the same sample the peaks of the curves may be different and may show different phases

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