Differential Scanning Calorimetric Analysis of Phase Transition in LCD Materials

D.S.Kushwaha¹, Jyotsna Sinha²

¹Institute of Engineering & Technology, Lucknow-22602, India
²R C Institute of Technology, GGSIP University Delhi, India

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 deferrential power Π, different from the normal Π variation only due to the heat capacity trace or baseline and the maximum Π 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 Π, different from the normal Π variation only due to the heat capacity trace or baseline and the maximum Π 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 different between the heat capacities before and after the transition.

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≤t₁, i.e. before beginning of the melting, the differential power Π(t) is only due to heat capacity of the solid material

\[
\Delta P(t) = m.C_{ps} \cdot \frac{T_p'}{R_o} - t_1 \quad (1)
\]

Where

\[
T_p' = \text{is the melting rate of the specimens},
\]

\[
t_2 - t_1 = \text{is the melting time of the specimen},
\]

\[
\gamma = \text{is the thermal resistivity of the specimen},
\]

\[
P = \text{is the specific mass time of the specimen}.
\]

2. Between t₁ & t₂ melting occurs at a constant temperature, and

\[
\Delta P(t) \text{ is given by :}
\]

\[
\Delta P(t) = T_p' / R_o \cdot (t-t_1) + m.C_{ps} \cdot T_p' \quad (2)
\]

Where,

\[
m = \text{is the mass of the sample},
\]

\[
C_{ps} = \text{the specific heat of the solid material}.
\]

3. At the end of melting, the sample is still at the melting temperature where as the programmed temperature is much higher so that sample has to reach the programmed temperature which implies the following variation of Π

\[
P(t) = \Delta P(t) = m.C_{pl} \cdot \frac{T_p'}{R_o} \cdot [m \cdot (C_{ps} - C_{pl}) - T_p']^+ \quad (3)
\]

Where \(C_{pl}\) is the specific heat of the liquid sample. By mathematical view equation (4) shows that Π(t) curves reach t h e base line for an infinite time. It will be considered that the sample reaches t h e programmed temperature at t e m p t₁ , wh ich is tak e n when it is impossible t o m easure t h e di fference between the baseline and the Π(t) curves.
4. For \( t > = t_3 \)

\[
\Delta P(t) = mC_p \Delta T_p \quad \text{(5)}
\]

The transition enthalpy molecules \( m \Delta h \) is given by

\[
m \Delta h = \int [mC_p, T_p' + \Delta T_p/R_o(t - t_3)] \, dt
\]

\[
= mC_p \Delta T_p (t_2 - t_1) + T_p' / 2R_o (t_2 - t_1)^2 \quad \text{(6)}
\]

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

\[
h = T_p' / R_o (t_2 - t_1) \quad \text{(7)}
\]

\[\text{Figure 1: Theoretical DSC melting curve of a pure material}\]

\[\Delta P \text{ is the power difference between the sample holder and the reference holder.}\]

\[\text{The heating rate } T_p' \text{ is constant}\]

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

\[
H = mC_p \Delta T_p + (m^2C_p^2T_p + 2m \Delta h T_p')^{1/2} \quad \text{(8)}
\]

Now \( N \) may be defined as the height \( h' \) where \( h' \) is the height of the peak for a mass \( 2m \) or a heating rate \( 2T_p' \).

So,

\[
N = \left[ \frac{1 + \left( \frac{h'}{mC_pT_p'} \right)^2 \Delta T_p}{1 + \left( \frac{2 \Delta h'}{mC_pT_p'} \right)^2} \right] \quad \text{(9)}
\]

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

\[1 < N < \sqrt{2} \quad \text{(10)}\]

The above expression of limits is only a mathematical consequence of equation (9) and here physical significance has to be examined. The upper limit is valid and can be understood in a simple way when \( T_p' \) or \( m \) tends to zero, it means that \( \Delta h \) is important and the heat capacity 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 to run twice a sample the following equation gives \( N \) in the case of two masses \( m_1 \) and \( m_2 \) leading respectively to two peak height \( h_1 \) and \( h_2 \).

\[N = \exp \left[ 0.69 \ln \left( \frac{h_2}{h_1} \right) \ln \left( \frac{m_2}{m_1} \right) \right] \quad \text{(11)}\]

3. Second Order Phase Transition

As a DSC Curve is the recording of the differential power

\[\Delta P \text{ versus time } \left( \frac{dt}{dP} \right) \text{. It is possible to write}\]

\[\Delta P = d\Delta w/dt = d\Delta w/dT_p \times dT_p/dt \quad \text{(12)}\]

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

\[\left( d\Delta w/dT_p = mC_p \times dT_p/dt = T_p' \right) \quad \text{(13)}\]

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

So, \( \Delta P = mC_p \times T_p' \quad \text{(14)}\)

Where \( m \) or \( T_p' \) are multiplied by two \( \Delta P \) 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,

\[h = m \times T_p' \left| C_{P1} - C_{P2} \right|\]

Where \( C_{P1} \) and \( C_{P2} \) are the specific heats before and after the transition. 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 pressure 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-

\[dW/dT = m \Delta h(T_f - T_m) / dt (T_f - T_m)^2 \quad \text{(15)}\]

Where,

\[T_f \quad \text{is the melting temperature of the pure material}\]
The height of the peak is given as under:

\[ h = \Delta P(T_m) = mC_p(T_m) \cdot T'_p \cdot \frac{dw}{dT} \cdot T'_p \]  

\[ \text{At the melting temperature } T_m \]  

\[ \frac{dw}{dT} = m \Delta h/(T_f - T_m) \]  

\[ \text{The height of the peak is given as under:} \]

\[ h = \Delta P(T_m) - mC_p(T_m) \cdot T'_p \cdot \frac{dw}{dT} \cdot T'_p \]  

\[ H = m \Delta h \cdot T'_p / (T_f - T_m) \]

Where \( m \) or \( T'_p \) multiplied by two, \( h \) is multiplied by two and so \( N = 2 \). It is the same result as for the second order transition where only heat capacities are in involved. This statement can prove the theoretical model of Gorter for second order transition [12]. In this model a Second Order Phase Transition is described as the end on non-isothermal first order transition [13, 14]. This is exactly what 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 thermodynamics, a Second Order Phase Transition is described as the end on non-isothermal first order transition [15]. This is exactly what happens in the case of melting of an impure material as described by the van’t Hoff equation. The values of \( N \) can give at least two results. It gives qualitative measurement of the relative importance of the first order phase transition and an anomalous behavior i.e. the transition is not a simple on the but other 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.

Reference


Author Profile

Dr. D S Kushwaha received his master’s degree in Physics from CSJM University Kanpur and for his PhD in LCD at IIT Kanpur. He also earned his M Tech degree in Information Technology from Allahabad Agricultural Institute Allahabad (India) and PhD (IT & Systems Engg) from Lor enz University S.A. and Doctor of Computer Science (D CSc) in Information Technology from Cornell State University S.A. He worked as a Professor of Computer Science & Information System at Ministry of Higher Education, Kingdom of Saudi Arabia (K.S.A). Presently he is working as a System Manager at a Institute of Eng ineering & Technology, Lucknow (India). He has also written many books on Computer Science & Information Technology and Liquid Crystal Devices (LCD) and published number of Research Papers in National and International Journals.

Ms Jyotsna Sinha received her Master’s Degree in Computer Science in 2002. She is currently pursuing her Research work in Liquid Crystal Display Technology and as of a spending as Director at RC Institute Of Technology, New Delhi (India).