Crystalloluminescence produced during the polymorphic phase transition of growing crystallites

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Abstract. The present paper reports the crystalloluminescence (CRL) produced during the polymorphic phase transition of growing crystallites and models the dynamics of the process. The CRL emission may take place during the polymorphic phase transition of crystals due to several processes such as production of micro-fracture of crystallites during the phase transition, thermal population in the over-strained sites and electronic excitation by the energy released during the phase transition. Considering the basic concepts of crystallization from the supersaturation solution, expressions are derived which are able to explain satisfactorily the temporal, thermal, spectral, concentration and other characteristics of the CRL. It is shown that the induction period for crystal nucleation, and the lifetime of supersaturation, may be determined from the CRL measurements.

1. Introduction

Crystalloluminescence (CRL) is a type of luminescence induced during the crystallization of substances. CRL is related to the crystal nucleation, crystal growth and excited state processes. CRL is not an inherent property of all substances. Only a limited number of organic and inorganic materials is known to be crystalloluminescent (Barsanti and Maccarrone 1991). The CRL emission may occur due to several processes such as (i) amorphous to crystalline transformation, (ii) polymorphic phase transition, (iii) micro-fracture of crystallites and (iv) chemical reaction during crystallization (Harvey 1957, Garten and Head 1963, 1966, 1970, Tsuda *et al* 1939, Walton 1977, Chandra *et al* 1982, Chandra and Zink 1980, Chandra 1982, Takeda *et al* 1973, Gibbon *et al* 1988, Barsanti and Maccarrone 1991).

The fundamental mechanisms responsible for the CRL produced during the polymorphic phase transition of growing crystallites may be understood as follows. Firstly, if micro-cracks are produced during the phase transition of crystals and if the crystal is mechanoluminescent, then the luminescence pulse may be produced during the phase transition of the crystals. Secondly, during the phase transition there may be a large change in the cell dimension and readjustments in the atomic coordination and bond distance. In this process of readjustment, the inter-atomic or inter-molecular distance may be considerably higher for some atoms or molecules, whereby the thermal population of the excited state may take place. This effect is the inverse of the thermal radiationless quenching of the excited states. Thirdly, if the energy released during the phase transition can directly excite the emitting centre, then also luminescence pulses may be produced during the phase transition of the crystals. There are several reports related to the occurrence of luminescence during

the phase transition of crystals (Takamori *et al* 1974, Johnston and Daniels 1961, Berry and Meson 1959, Trout *et al* 1972, 1975).

   In the present paper, an attempt has been made to explore theoretically the CRL produced during the polymorphic phase transition of growing crystallites.

2. Theory

Suppose a super-saturated state is produced by dissolving a salt of given mass into a solution of given volume. Then the supersaturated state will reach the saturated state by giving rise to crystallization. In this way the supersaturation state has a particular lifetime τ_s, which may be defined as the time in which the supersaturation decreases from its initial value S_0 to S_0/e, where e is the base of the Napier logarithm. It is worth to state that after the induction period the supersaturation of solution decreases exponentially with the crystallization time (Khamskii 1969). Thus, the time dependence of supersaturation may be expressed as

$$S = S_0 \exp\left[-\frac{(t - t_c)}{\tau_s}\right] \tag{1}$$

where t_c is the induction period of crystal nucleation or the incubation time of CRL.

   If we assume that the rate of generation g of embryo nuclei is proportional to the rate of decrease in supersaturation dS/dt and volume V of the solution, then we may write

$$g = -\gamma \frac{dS}{dt} V \tag{2}$$

where γ is the proportionality constant between the rate of generation of embryo nuclei and the rate of decrease of supersaturation for unit volume of the solution.

   From equation (1), we find that

$$-\frac{dS}{dt} = \frac{S}{\tau_s} = \alpha S \tag{3}$$

where $\alpha = 1/\tau_s$.

   From equations (1)–(3), we find

$$g = g_0 \exp[-\alpha(t - t_c)] \tag{4}$$

where $g_0 = \gamma V \alpha S_0$.

   It is known that the embryo nuclei may transform into solid precipitate after a particular time τ_e (Turnbull 1953, Felbinger and Neels 1966, Joshi and Antony 1979), known as the lifetime of embryo nuclei. If n is the number of embryo nuclei at any time t, and β_1 and β_2 are the rate constants of the transformation of embryo nuclei into crystalline nuclei and into amorphous nuclei, respectively, then we may write the following rate equation:

$$\frac{dn}{dt} = g - \beta_1 n - \beta_2 n$$

or

$$\frac{dn}{dt} = g_0 \exp[-\alpha(t - t_c)] - \beta n \tag{5}$$

where $\beta = (\beta_1 + \beta_2) = 1/\tau_e$, and τ_e is the lifetime of embryo nuclei.

   For $n = 0$, at $t = t_c$, the integration of equation (5) gives

$$n = \frac{g_0}{(\beta - \alpha)} \{\exp[-\alpha(t - t_c)] - \exp[-\beta(t - t_c)]\}. \tag{6}$$

Both the crystalline and amorphous nuclei are formed after the transformation of embryo nuclei. The rate of transformation of crystalline nuclei will be equal to the rate of formation of crystallites. Therefore, the rate of formation of the crystallites dN/dt may be given by

$$\frac{dN}{dt} = \beta_1 n + \beta_2 n = \beta n. \tag{7}$$

By substituting the value of n from equation (6) into equation (7) we obtain

$$\frac{dN}{dt} = \frac{\beta g_0}{(\beta - \alpha)}\{\exp[-\alpha(t - t_c)] - \exp[-\beta(t - t_c)]\}. \tag{8}$$

The integration of the above equation from the limit t_c to t gives

$$N = -\frac{\beta g_0}{(\beta - \alpha)\alpha}\{1 - \exp[-\alpha(t - t_c)]\} - \frac{\beta g_0}{(\beta - \alpha)\beta}\{1 - \exp[-\beta(t - t_c)]\}. \tag{9}$$

For $\beta \gg \alpha$, the above equation may be written as

$$N = \frac{g_0}{\alpha}\{1 - \exp[-\alpha(t - t)c)]\}. \tag{10}$$

By substituting the value of g_0, we obtain

$$N = N_0\{1 - \exp[-\alpha(t - t_c)]\} \tag{11}$$

where

$$N_0 = \gamma V S_0. \tag{12}$$

Equation (12) shows the dependence of the number of crystallites on the crystallization time. If P_t is the probability of the occurrence of polymorphic phase transition in a crystallite, then the total probability for the occurrence of phase transition in N crystallites will be $P_t N$. If each phase transition is followed by the emission of the CRL pulse, then the number of CRL pulses (N_p) may be given by

$$N_p = P_t N = N_{p_0}\{1 - \exp[-\alpha(t - t_c)]\} \tag{13}$$

where $N_{P_0} = P_t \gamma V S_0$.

Equation (13) shows that when a solution of a particular volume V having a given supersaturation S_0 is used for the CRL measurement, then the CRL emission should start after a particular time t_c, known as the incubation time of CRL. Initially the total number of CRL flashes emitted should increase linearly with $(t - t_c)$ and then it should deviate from the linear increase and finally it should attain a saturation value for longer duration of the crystallization time. The total number of CRL flashes should increase with the initial supersaturation S_0, and also with the volume of the solution V. As γ, S_0 and t_c may depend on the temperature, the total number of CRL flashes emitted and kinetics of the CRL should also depend on the temperature of the solution.

3. A comparison between the theoretical and experimental results

Arsenic trioxide (As_2O_3) can exist in two polymorphic modifications. One form is monoclinic, space group $P2_1/m$ (Becker and Pliethkand Stranski 1951), known a claudetite (Fruch 1951), and the other form is cubic, space group $Fd3m$ (Lihl 1932), known as arsenolite (Kaffanke and Lachman 1970a, b). It is the arsenolite form which is produced when crystal growth occurs from the gaseous phase or, usually, when crystallization takes place from solutions. However, the arsenolite structure is seldom perfect, as it contains claudetite-like bonds ('defective bonds'). When grown from solutions of hydrochloric acid,
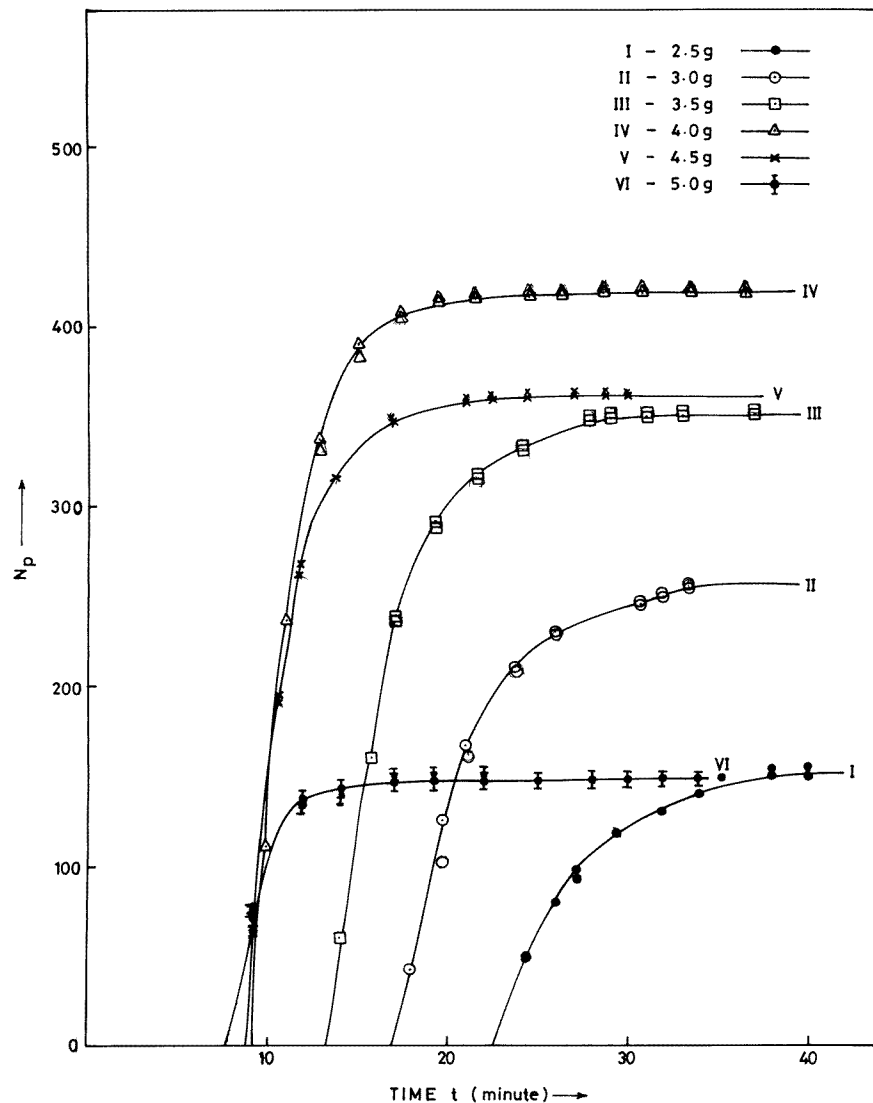
Figure 1. The dependence of the total number of CRL flashes (N_p) emitted on the crystallization time (t) for As_2O_3 (curves I–VI correspond to 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0 As_2O_3 in the solution.

the freshly prepared arsenic trioxide may contain less than 1% of the defective bonds in the cubic molecular (As_4O_6) crystal lattice (Garten and Head 1970). Only under rather specialized growth conditions (for example, in alkaline solutions at 350 K) is the pure monoclinic form produced (Becker and Schonewold 1962). It has been reported that during the crystallization process both cubic and monoclinic crystals were formed, and that the change from the monoclinic crystals form is accompanied by luminescence (Guinchant 1905, Walton 1977, Chandra *et al* 1985). Here, we will compare the experimental results on the CRL of As_2O_3 obtained by Chandra *et al* (1985) with the theoretical results obtained in the present investigation.
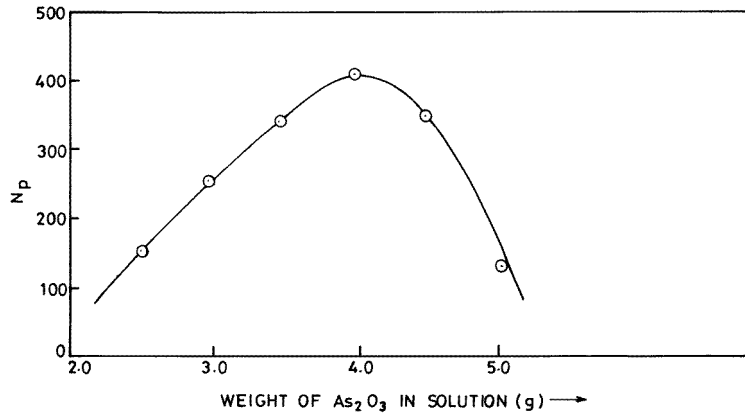
Figure 2. The dependence of the total number of CRL flashes (N_p) on the weight of As_2O_3 in the solution.
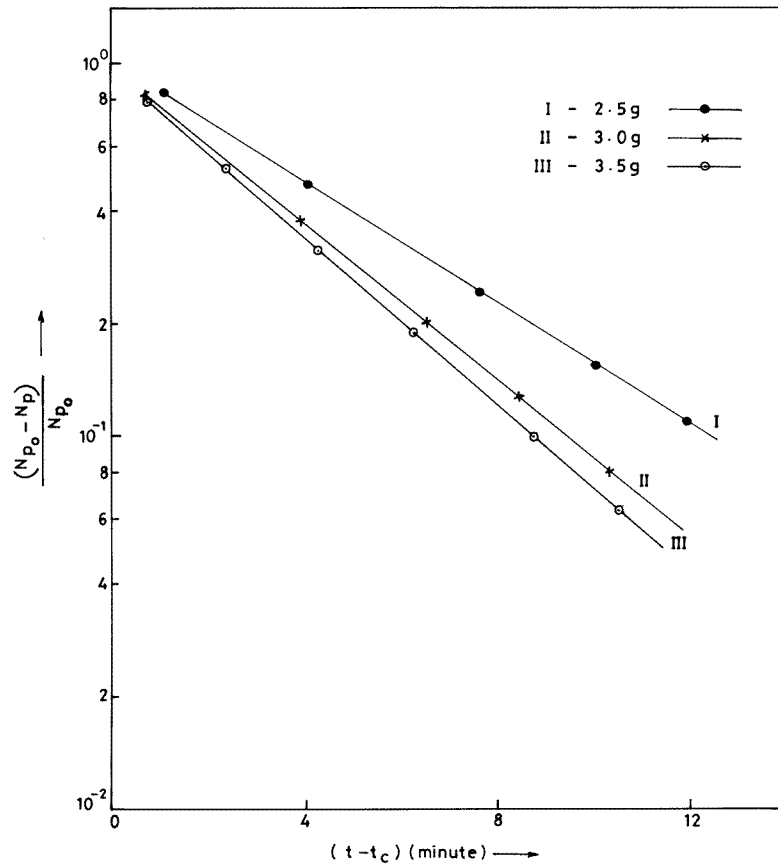

Figure 3. A plot of $\log\{(N_{p_0} - N_p)/N_{p_0}\}$ versus crystallization time ($t - t_c$) for As_2O_3, for different weights of As_2O_3 in the solution.
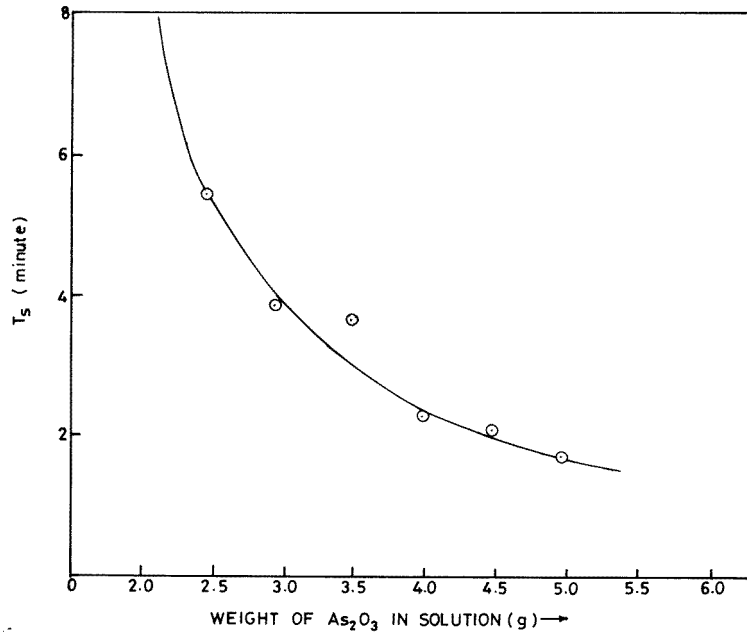
Figure 4. The dependence of the lifetime of the supersaturated state (τ_s) on the concentration, i.e. on the weight of As_2O_3 in the solution.

It is to be noted that in our previous study (Chandra *et al* 1985) the main emphasis was on the dependence of induction period on the concentration of the solution and thereby the determination of the critical size of crystal nucleus. However, in the present investigation, emphasis has been given to developing a theory for CRL and for its support use has been made of the previous experimental observations.

For CRL studies, a solution was prepared by dissolving a known amount of As_2O_3 in 13 cm^3 concentrated HCl (specific gravity 1.12) by heating until a clear solution was formed. This solution was then slowly added to 17 cm^3 hot distilled water. The CRL flashes start appearing after a particular, reproducible time. This time duration, between preparation of solution and appearance of the first CRL flash, known as the incubation time, was noted. The total number of CRL flashes being produced were noted at regular intervals of time, until the total number of flashes produced with time became constant. The CRL flashes were counted using an IC-based digital flash counter which has the following five major parts: (i) photomultiplier circuit, (ii) current to voltage converter, (iii) voltage comparator, (iv) transistor amplifier, and (v) digital counter (Chandra *et al* 1987).

Figure 1 shows the dependence of the total number (N_p) of CRL flashes produced on the crystallization time (t). It is seen that for a given concentration of the solution, the CRL emission starts after a particular value of the incubarion time, then the value of N_p increases and finally it attains a constant value for longer duration of the crystallization time. These facts indicate that there is no appearance of new CRL flashes after a particular value of crystallization time (t). The total number of CRL flashes emitted depends on the concentration of solution. The rate of increase of N_p with the crystallization time, and the incubation time (t_c) for CRL emission also changes with the concentration of solution. It is to be noted that a CRL, flash is of nearly 10 μs duration. In fact, the reading of
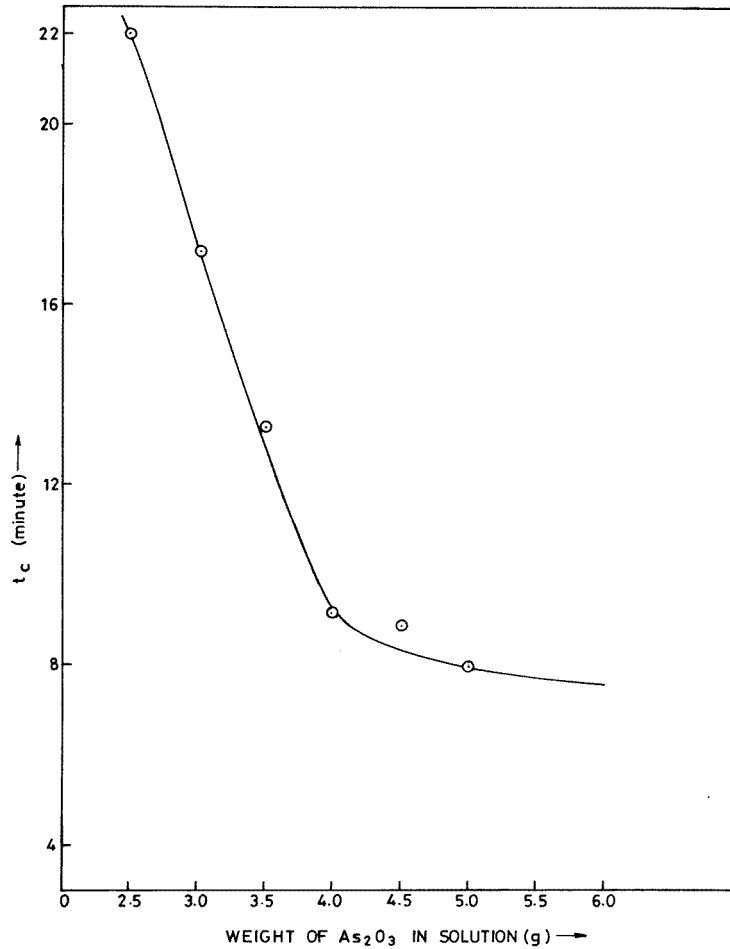
Figure 5. The dependence of the incubation time (t_c) of CRL on the concentration of solution, i.e. on the weight of As_2O_3 in the solution.

the flash counter starts increasing gradually with the number of CRL flashes emitted. As the observations were taken for the time taken for the emission of 50 flashes, counts below $N_p \sim 50$ do not appear in figure 1. It is evident from figure 1 that there is a good agreement between the experimental and theoretical results.

Figure 2 shows that the value of N_p initially increases with the concentration of the solution, attains a maximum value and then decreases with further increase in the concentration of solution. There is no appearance of CRL flashes for very low or for very high concentration of the solution.

Figure 3 shows that the plot of $\log((N_{p_0} - N_p)/N_{p_0})$ versus crystallization time ($t - t_c$) is a straight line with a negative slope. This fact indicates that the correlation between N_p and t follows the equation (13). It is seen that the slope of the $\log((N_{p_0} - N_p)/N_{p_0})$ versus ($t - t_c$) plot changes with the concentration of the solution. Thus, equation (13) shows that the value of τ_s changes with the concentration of the solution. Figure 4 shows that the value of τ_s decreases with increasing concentration of the solution.

The incubation times (t_c) for the appearance of CRL flashes were determined for different concentrations of the solution. It is seen from figure 5 that the value of incubation time (t_c) decreases with increasing concentration of the solution.

Initially, the total number of flashes emitted increases with the concentration of the solution because more crystallites are formed. For very high concentration of the solution, the total number of CRL flashes emitted decreases because a comparatively large number of crystallites are formed in a shorter time duration. Thus, the average size of crystallites may be small whereby the probability of phase transition may decrease. As a matter of fact, the CRL emission may be optimum for a particular concentration of the solution.

Chandra *et al* (1982) have recorded the CRL spectra of As_2O_3 and compared them with the corresponding mechanoluminescence (ML) and photoluminescence (PL) spectra. It has been found that the CRL spectra approximate the ML and PL spectra.

Finally, it may be said that there is a good agreement between the theoretical and experimental results.

4. Conclusions

The CRL emission may take place during the polymorphic phase transition of crystals due to several process such as production of micro-fracture of crystallites during the phase transition, thermal population in the over-strained sites and electronic excitation by the energy released during the phase transition. Considering the basic concepts of crystallization from the supersaturated solution, expressions are derived which are able to explain satisfactorily the temporal, thermal, spectral, concentration and other characteristics of CRL. Furthermore, the induction period for crystal nucleation and the lifetime of supersaturation may be determined from the CRL measurements.

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