

## Crystalloluminescence and temporary mechanoluminescence of $As_2O_3$ crystals

B P CHANDRA, P R TUTAKNE, A C BIYANI and B MAJUMDAR  
Department of Physics, Government Science College, Raipur 492 002, India

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**Abstract.** Crystalloluminescence and temporary mechanoluminescence of  $As_2O_3$  crystals are investigated. The crystalloluminescence spectra are similar to the photoluminescence and mechanoluminescence (of fresh crystals, in  $CO_2$  atmosphere) spectra. The mechanoluminescence spectra of freshly grown crystals taken in air consist of the superposition of the photoluminescence and nitrogen emissions. The mechanoluminescence spectra of old crystals of  $As_2O_3$  consist of only the nitrogen emission. The total number of crystalloluminescence flashes is linearly related to the total mass of the crystals grown. The mechanoluminescence intensity increases with the mass of the crystals. The mechanoluminescence intensity decreases with the age of the crystals and the rate of decrease increases with increasing temperature of the crystals. Different possibilities of crystalloluminescence and mechanoluminescence excitations in  $As_2O_3$  crystals are explored and it is concluded that crystalloluminescence and mechanoluminescence are of different origins.

**Keywords.** Crystalloluminescence; mechanoluminescence; photoluminescence; crystal-fracture;  $As_2O_3$  crystals.

### 1. Introduction

Crystalloluminescence (CRL), the emission of light during crystallization of certain substances from solution and mechanoluminescence (ML), the emission of light during mechanical deformation of certain solids are known for a long time (Harvey 1957). It has been reported from time to time that the CRL and ML should be correlated in their excitation mechanism (Trautz 1905; Gernez 1905; Weiser 1918; Belyaev *et al* 1963; Takeda *et al* 1973). We noticed that only a few of the mechanoluminescent crystals exhibit CRL during growth. This has attracted the attention to check the differences and similarities between the CRL and ML. The present paper reports the CRL and temporary ML of  $As_2O_3$  crystals and discusses the different origins of the CRL and ML excitations.

### 2. Experimental

Fifty grammes of  $As_2O_3$  were dissolved in 130 cc of hydrochloric acid of specific gravity 1.18 and this solution was then added slowly to 170 cc of hot water. For CRL studies, this solution was divided equally in eight beakers and the number of CRL flashes was counted visually in a dark room. The time taken in each case was determined using a stop watch. After the appearance of the particular number of CRL

flashes in the given beaker, the remaining solution was immediately poured into another container. Small crystals grown in this process stick to the walls of the beaker. The beakers having the crystals were allowed to dry for 24 hr and then the total mass of the crystals grown in each beaker was determined. When the liquid is poured out after counting the CRL flashes, it is possible that some crystals may be washed out. But the  $\text{As}_2\text{O}_3$  crystals stick to the walls of the beaker, and careful pouring would avoid errors considerably in the determination of the total mass of the crystals grown. The photomultiplier tube may also be used for counting the CRL flashes. Since the CRL emission is affected significantly by a slight change in the crystallization condition, and furthermore, since the CRL flashes of  $\text{As}_2\text{O}_3$  are intense, we preferred to count visually and simultaneously the CRL emission in all the beakers filled with  $\text{As}_2\text{O}_3$  solution. The CRL emission from  $\text{As}_2\text{O}_3$  solution in each beaker was counted visually by an independent person.

For the determination of the CRL spectra, the solution of  $\text{As}_2\text{O}_3$  in hydrochloric acid was filled in a glass vial and was then placed inside a sample holder in front of the slit of a Bausch and Lomb  $\frac{1}{2}$ m grating monochromator. The temperature of the sample-holder was nearly  $5^\circ\text{C}$ . The holder of vial had a slit which allowed the light to reach the slit of the monochromator. The CRL and ML spectra were taken by using the technique described in an earlier investigation (Hardy and Zink 1976). Integration time of several minutes were required to obtain the CRL spectra. The photoluminescence (PL) spectra were recorded by using a Spex spectrofluorometer. The crystals obtained from the solution used during the CRL studies were used for the determination of the ML and PL spectra. The ML intensity was measured using the method described previously (Chandra and Elyas 1977). For the determination of the ML intensity at different temperatures, the crystals were warmed by a heater coil wound round a ceramic cylinder placed on the crystal holder of the arrangement reported in the earlier investigation (Chandra and Elyas 1977). The heater coil was connected to a variac. The temperature of the crystals was measured by a copper-constantan thermocouple. The simultaneous measurements of the ML intensity *versus* compression, and the force *versus* compression curves of the crystals were carried out using a method described by Chandra and Zink (1980).

### 3. Results

Figure 1 shows the CRL, ML (of fresh crystals, in  $\text{CO}_2$  atmosphere) and PL spectra of  $\text{As}_2\text{O}_3$  crystals. It is seen that the CRL spectra are almost similar to the PL and ML (in  $\text{CO}_2$  atmosphere) spectra. The ML spectra (figure 2) of freshly grown  $\text{As}_2\text{O}_3$  crystals taken in air consist of the superposition of PL emission and the nitrogen emission. Figure 2 shows the ML spectra of one week old crystals of  $\text{As}_2\text{O}_3$  taken in air. It is seen that the ML spectra of the old crystals taken in air consist of only the nitrogen emission. No considerable differences were found in the intensity and spectra of PL between freshly grown and old crystals of  $\text{As}_2\text{O}_3$ .

The CRL emission takes place as individual flashes during the growth of the crystals. The duration of a single flash was found to be less than a microsecond. Figure 3 shows that the total number of the CRL flashes increases with the growth-time and tends to attain a saturation value after a particular value of the time. The growth-time was measured from the first appearance of the CRL flash. Figure 4 shows that the

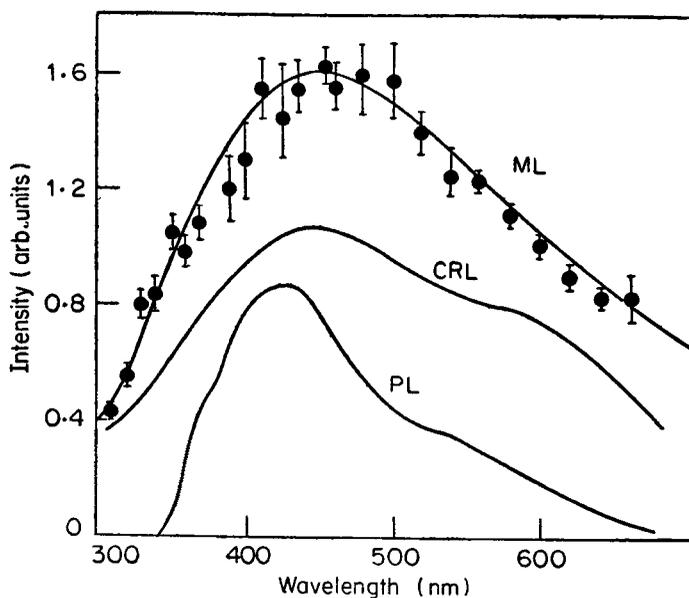


Figure 1. Crystalloluminescence, mechanoluminescence (of fresh crystals in  $CO_2$  atmosphere) and photoluminescence spectra of  $As_2O_3$  crystals.

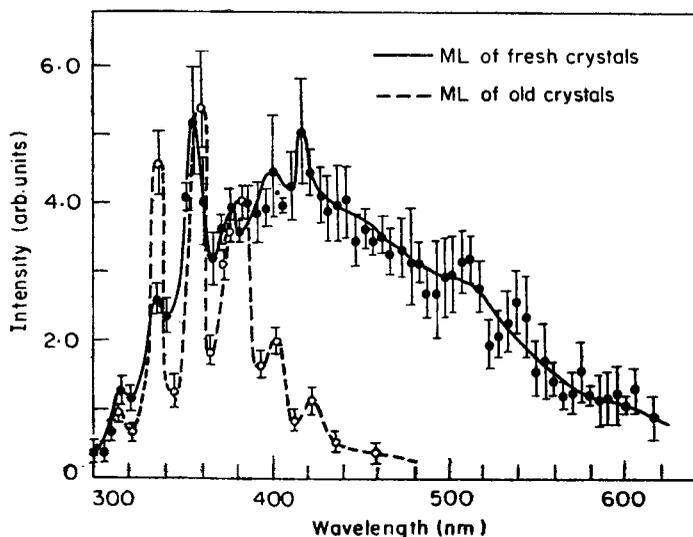


Figure 2. Mechanoluminescence spectra of freshly grown  $As_2O_3$  crystals taken in air and the mechanoluminescence spectra of one week old crystals of  $As_2O_3$  taken in air.

total number of CRL flashes is linearly related to the total mass of the crystals grown. Figure 5 shows the dependence of the ML intensity on the mass of the crystals. It is seen that after a particular mass, the ML intensity increases linearly with the mass

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of the crystals. Figure 6 shows the dependence of ML intensity on the age and temperature of the crystals. The ML intensity decreases faster with increasing temperature of the crystals.

The force *versus* compression and the ML *versus* compression curve of a  $3 \times 3 \times 2$  mm  $\text{As}_2\text{O}_3$  crystals are shown in figure 7. It is seen that the ML does not appear in the elastic and plastic regions of the crystals. The ML appears in the fracture region, that is, only during the steps occurring in the force *versus* compression curve of the crystal.

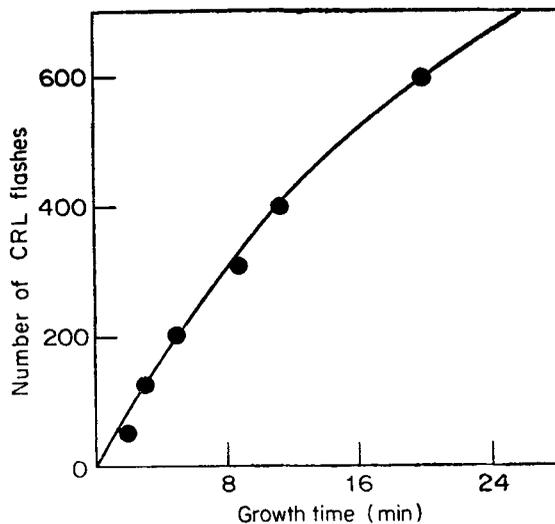


Figure 3. Growth-time dependence of the total number of CRL flashes and total mass of the crystals grown.

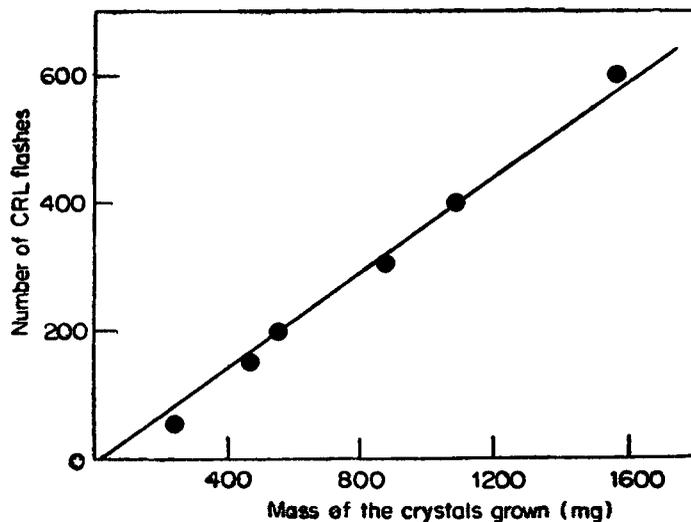


Figure 4. Dependence of the total number of CRL flashes on the total mass of the crystals grown.

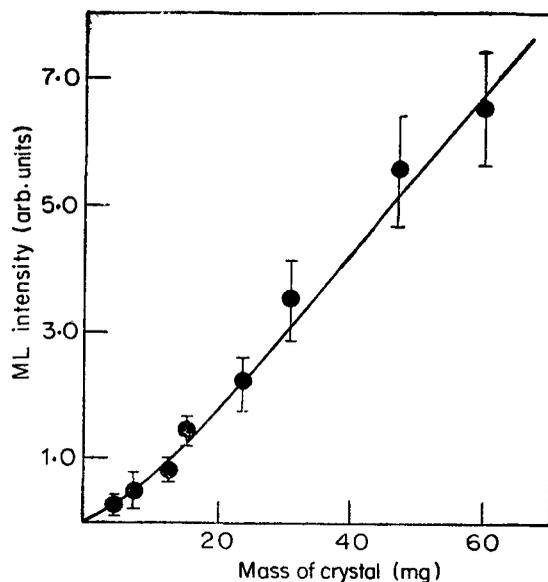


Figure 5. Dependence of the ML intensity on the mass of  $As_2O_3$  crystals.

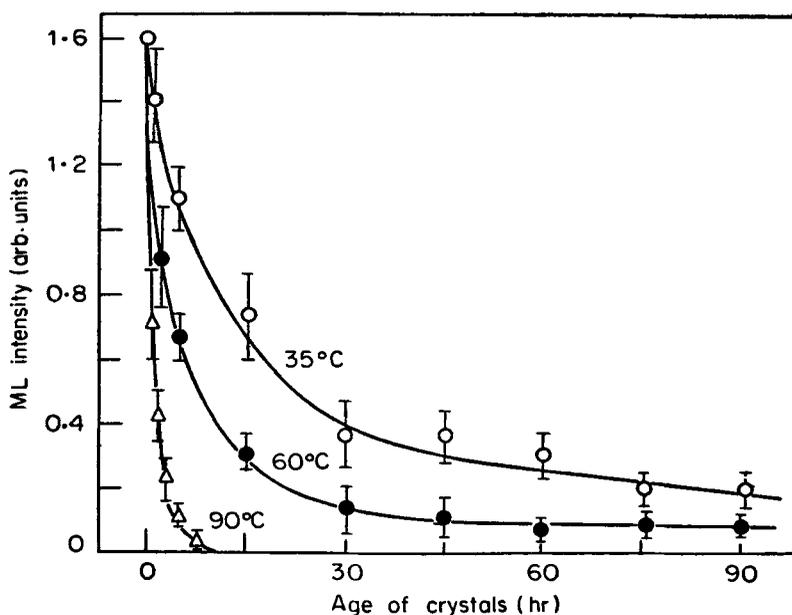


Figure 6. Dependence of the ML intensity on the age and temperature of  $As_2O_3$  crystals.

#### 4. Discussion

The main object of the present investigation is to understand the mechanisms of the CRL and ML excitations in  $As_2O_3$  crystals. On the basis of the observed results, the possible mechanisms are suggested below.

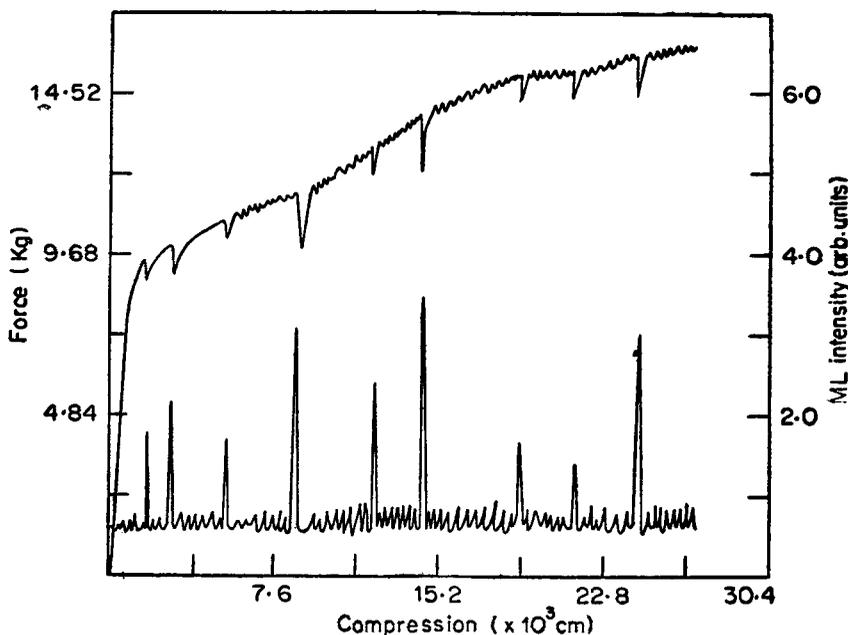


Figure 7. Mechanoluminescence *versus* compression and force *versus* compression curves of a  $3 \times 3 \times 2$  mm  $\text{As}_2\text{O}_3$  crystal (compression rate  $1.69 \times 10^{-3}$  mm/sec.).

#### 4.1 Crystalloluminescence

The linear relation between the number of CRL flashes and the mass of the crystals grown indicates that the CRL is directly related to the growth of the crystals. The CRL may thus be a probe for studying the growth kinetics of the crystals.

Four reasons for the CRL excitations may be expected : (i) recombination of ions, (ii) from the amorphous to crystalline transition, (iii) from phase change during crystallization, and (iv) from the dielectric breakdown by the electric field produced due to the microfracture during crystal growth (that is, similar to the ML excitation). Since CRL pulses are more intense as compared to the ML pulses, it is surprising how the microfracture during the growth of the crystals may cause more emission of light than the macrofracture produced during the deformation of the crystals. The intensity of CRL emission is maximum for a particular concentration of HCl, that is, for the specific gravity of acid between 1.115 and 1.125 at 25° C (Weiser 1918). Such dependence of CRL intensity on the concentration of HCl may not be understood from the microfracture mechanism of the CRL. Moreover, most of the mechanoluminescent crystals do not exhibit CRL, hence, the microfracture mechanism of the CRL excitation is not expected. The ML excitation is primarily due to the electric field produced between the newly created surfaces during fracture of crystals (Chandra 1981; Walton 1977).  $\text{As}_2\text{O}_3$  crystals are found in two phases, one claudetite belonging to  $P2_1/n$  space group (Becker *et al* 1951) and the other, arsenolite belonging to  $Fd3m$  space group (Lihl 1932). However, other crystalloluminescent crystals are not known to be polymorphic. Thus, it is difficult to assign the CRL excitation due to

the change of crystal structure. If the amorphous to crystalline transformation is responsible for the CRL excitation, then many crystals should exhibit CRL, which is not the case. Only limited crystals exhibit CRL. Further, this mechanism is also not able to explain the effect of crystallization conditions on the CRL emission. It seems that the CRL emission is of chemical origin. If the PL of the crystals is from the matrix ions or molecules, the CRL emission may be due to the recombination of ions during the growth of crystals. If the PL emission is from the defects, then the CRL emission may be due to the recombination of the defects with the other ions of the matrix. Since the details of the PL emission in  $As_2O_3$  crystals are not known, it is difficult to assign the states responsible for the CRL and ML emissions.

#### 4.2 Mechanoluminescence

The appearance of ML only during crystal fracture and the similarity of ML spectra to the superposition of the photoluminescence and nitrogen emissions, suggest that the electrical charging near the tip of the mobile cracks is responsible for the ML excitation. In centrosymmetric crystals like  $As_2O_3$ , the ML excitation cannot be attributed to the piezo-electrification of the newly created surfaces, since the excitation of ML is well known only in non-centrosymmetric crystals (Chandra 1981). The ML excitation in arsenolite crystals may be due to some other process of charging the newly created surfaces.

The arsenolite form is produced when crystals are grown from the gaseous phase which contains  $As_4O_6$  molecules or from solutions. The arsenolite structure always grows with some claudetite-like bonds (defective bonds). When grown from solution of HCl; the freshly prepared arsenic trioxide may contain less than 1% of these defective bonds in the cubic molecular crystal lattice (Garten and Head 1971). Only under special growth conditions, as for example, in alkaline solutions at 350°K, the pure monoclinic form is produced (Becker and Schonewald 1962). It may be expected that the phase transformation during the crystal fracture may cause light emission. However, it is difficult to understand how the transformation of claudetite structure to arsenolite structure may give energy sufficient to populate the excited state of the molecules. Secondly, there are many examples of phase transformation of crystals, particularly ferroelectric crystals; but light emission has not been observed during phase transformations. Thus, it is difficult to believe that phase transformation from claudetite to arsenolite may give rise to light emission. Moreover, this process cannot explain the nitrogen emission ML of  $As_2O_3$  crystals.

ML of  $As_2O_3$  crystals may arise from another type of electrical charging. Cleavage along certain directions of crystals can create charged surfaces. Cleavage along the charged directions requires more energy than cleavage along an uncharged direction. Thus, a crack normally propagates along an uncharged direction. Defects in the crystals create misoriented regions at least at microscopic levels (Van Bueren 1960). If a crack propagating along an uncharged direction reaches the misoriented region where a charged direction lies along the direction of the propagating crack, and if the crack has sufficient energy to pass through the misoriented regions, then the local charging of the region may occur. On the other hand, if the crack does not have enough energy to pass through the charged direction of the misoriented region, then a torque due to anisotropy of the cohesive energy may quickly bend the crack along an uncharged direction of the misoriented region. Thus, the appearance or

non-appearance of ML in  $As_2O_3$  crystals may be attributed to the respective ability or inability of the crack to pass through the charged directions of misoriented regions. It has been reported previously that ML activity is related to the number of claudetite phases in arsenolite crystals (Kaffanke and Lacmann 1970). This fact shows that the presence of claudetite phase is responsible for the creation of the charged surfaces. Since the charged direction of the claudetite phase may align along the uncharged direction of arsenolite phase, the possibility of charging the newly created surfaces due to the presence of claudetite structure may be possible. Arsenolite provides an example where the defective bonds are polarised and oriented towards the (111) plane (Garten and Head 1971). From the temporary behaviour of ML, that is, the decrease of ML intensity with the age of the crystals, it seems that either the transformation of claudetite phase to arsenolite phase takes place, or, the hardness of the defective region increases with the age of the crystals and consequently, the probability of passage of cracks through the charged direction of the misoriented region decreases.

It was believed earlier that the ML emission which is similar in spectra to the PL emission is due to the PL excitation by the gas discharge ML (Longchambon 1925; Walton 1977). The  $CO_2$  atmosphere completely suppresses the ML emission from molecular nitrogen; however there is still an intense ML emission resembling in spectra with the PL emission. This result suggests that the ML resembling the PL emission has an independent origin. It seems that the electric field produced near the tip of the mobile cracks excites both the molecules of the crystals and nitrogen. The ML emission resembling the PL emission may be due to the recombination of opposite charge carriers produced as a result of the intense electric field near the tip of the mobile cracks.

The configuration near the defective region of the crystals may change with the age of the crystals and thereby the charge density near the tip of the mobile cracks may decrease. As such the electric field near the tip of the mobile cracks in old crystals may decrease and may excite only the nitrogen molecules, but, may not excite the molecules of the crystals. Since the PL intensity does not change considerably and the intensity of gas discharge portion of ML also decreases with the age of the crystals, it seems that the charge density of the newly created surfaces decreases with increasing age of the crystals.

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