Tetrahedral manganese (II) complexes—intense and unique type of mechanoluminophores

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Abstract. Intense and unique type of mechanoluminescence (ML) is found in tetrahedral manganese (II) complexes. During the excitation of ML by the impact of a piston onto the crystal, the ML intensity initially increases with time, attains a maximum value and then decreases. After retardation of the piston, the decay rate of ML is faster during crystal deformation; however, its value decreases after cessation of the deformation and becomes equal to the decay rate of phosphorescence. The ML disappears below the melting point. Since the crystals of tetrahedral manganese (II) complexes are centrosymmetric, the local non-centrosymmetric sites near the defects are attributed to be responsible for the mechanoluminescence excitation.

1. Introduction

When certain solids are subjected to stress beyond particular levels, light emission follows their deformation. This physical process of light emission is known as mechanoluminescence (ML) or triboluminescence. Studies on ML have so far been concentrated on four major fields: (i) new ML materials (ii) mechanism of ML (iii) spectroscopy of ML and (iv) construction of new devices for the ML measurements (Zink 1978; Chandra 1985; Walton 1977). Recently, the ML of metals and glasses has attracted the attention of many workers (Borisova *et al* 1976; Molotskii 1978; Krauya *et al* 1981; Zink *et al* 1982; Chapman and Walton 1983).

   We have measured ML in nearly 500 inorganic and 600 organic crystals and have found that the crystals of tetrahedral Mn(II) complex, that is, ditriphenylphosphine oxide manganese bromide exhibit ML whose intensity is highest among all the crystals. The ML of these crystals is so intense that it can be seen in daylight by simply pressing the crystals between two glass plates. Some unique behaviours have been found in tetrahedral Mn(II) complexes viz (i) the ML of tetrahedral Mn(II) complexes disappear much below their melting point whereas the ML of other molecular crystals ceases near their melting point, (ii) the curve between ML intensity and time of phosphorescent tetrahedral Mn(II) complexes has two peaks whereas the time dependence of the ML of

the crystals whose ML spectra resemble nitrogen emission, or fluorescence emission, possesses only one peak, and (iii) the appearance of intense ML in non-piezoelectric crystals of the tetrahedral Mn(II) complexes (Wiesner *et al* 1967; Morosin and Graber 1967; Brassy and Robert 1976) contradicts the expectation that only piezoelectric crystals may exhibit bright ML (Chandra 1981). Because of these unique behaviours, we have investigated the ML of tetrahedral Mn(II) complexes. The present paper reports the time dependence, strain rate dependence and temperature dependence of the ML of $Mn(\phi_3PO)_2Br_2$, $(Et_4N)_2MnBr_4$, $(Me\phi_3P)MnCl_4$ and $(\phi_3PO)_2MnCl_2$ tetrahedral Mn(II) complexes and explores the mechanism of the deformation-induced population of the excited states (ϕ stands for Ph_3).

2. Experimental

The tetrahedral Mn(II) complexes $(\phi_3PO)_2MnBr_2$, $(Et_4N)_2MnBr_4$, $(Me\phi_3P)MnCl_4$ and $(\phi_3PO)_2MnCl_2$ were prepared following the method of Goodgame and Cotton (1961). These crystal complexes were grown by slow evaporation of their solution in
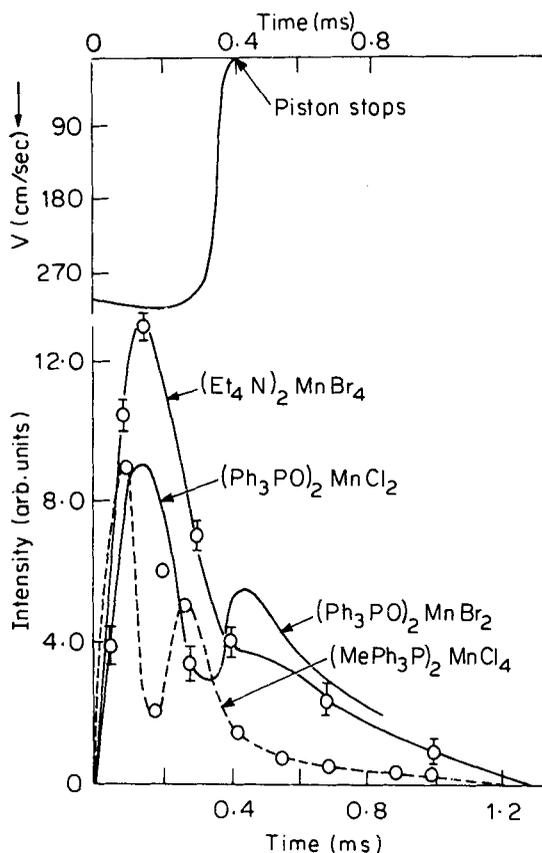

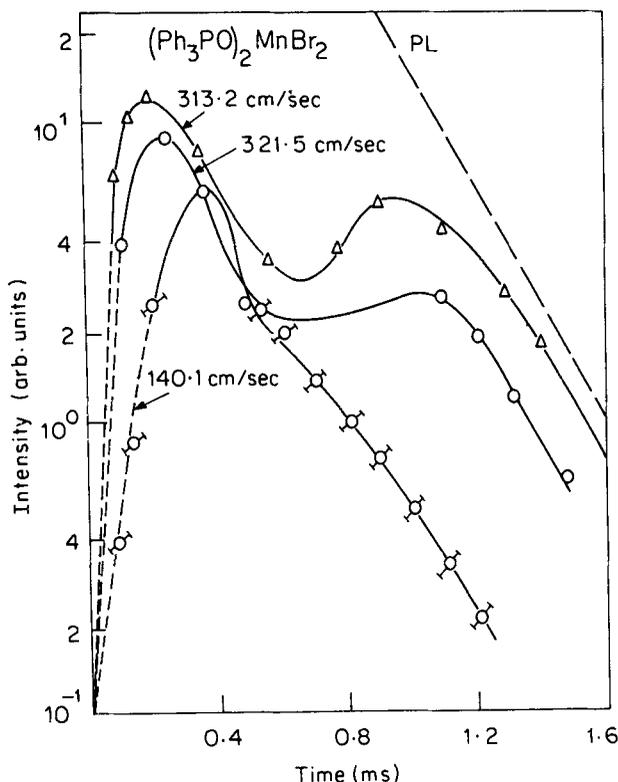**Figure 1.** Time dependence of the mechanoluminescence intensity I_{ML} (bottom) and the velocity v (top) of the piston.

Figure 2. Plot of the logarithm of the ML intensity in $Mn(Ph_3PO)_2Br_2$ vs time for different impact velocities.

ethanol or methanol. The time dependence of ML is determined using an instrument (Chandra and Zink 1980) based on an air-driven piston. The piston velocity was measured by a velocity transducer (Hewlett Packard model LV Syn 6 LV). The crystal was placed on a lucite or quartz plate inside a vertically adjustable sample holder below the piston. The luminescence is monitored from below the transparent plate by using a photomultiplier tube (IP 28, response time 7 μsec) connected to a dual beam storage oscilloscope (Tektronix 564). The piston is released to start the experiment and then moves under the force of compressed gas. The piston velocity could be increased upto 500 cm/sec by increasing the pressure of the gas. To trigger the oscilloscope, the crystal was covered with aluminium foil connected to one of the battery terminals. The other terminal was connected to the piston. The rise and decay of the luminescence and the piston velocity are simultaneously recorded. ML at different temperatures were measured following the method described earlier (Chandra and Deshmukh 1982). The crystal size was $2.5 \times 2.5 \times 2.5$ mm.

The ML spectra were recorded using a grating monochromator (Bausch & Lomb, $\frac{1}{2}$ m) and photomultiplier tubes (EMI 9558 Q) following the method described earlier. The photoluminescence (PL) spectra were determined by a Spex spectrofluorometer. The PL decay was determined using a pulsed xenon lamp and a storage oscilloscope.

3. Results

Figure 1 shows the time dependence and piston velocity used for ML excitation and the time dependence of the ML intensity of $(Ph_3PO)_2 MnBr_2$, $(Et_4N) MnBr_4$, $(MePh_3P) MnCl_4$ and $(Ph_3PO)_2MnCl_2$ crystals. ML appears during the impact of the piston on to the crystal. The ML intensity increases with time, attains a maximum value and then descreases with time. The ML in $(Ph_3PO)_2MnCl_2$ crystals disappears as soon as the piston stops. The ML in $(Ph_3PO)_2MnBr_2$, $(Et_4N)MnBr_4$ and $(MePh_3P) MnCl_4$ crystals appears even after the stopping of the piston. Figure 1 shows that the kinetics of ML in these three crystals changes just before the stopping of the piston. It should be noted that the crystals of $(Ph_3PO)_2 MnCl_2$ are non-photoluminescent; however, the crystals of $(Ph_3PO)_2 MnBr_2$, $(Et_4N) MnBr_4$ and $(MePh_3P)MnCl_4$ are phosphorescent. Actually the crystal deformation is produced by the piston movement. Thus, the time at which piston stops, may be taken as the time after which no crystal deformation takes place.

Figure 2 shows the time dependence of ML of $(Ph_3PO)_2MnBr_2$ crystals for different impact velocities. It is seen that the peak corresponding to the ML intensity vs time increases and shifts towards shorter time values with increasing values of the impact velocity of the piston. The solid line represents the decay after the change in kinetics or roughly after the piston has stopped. The slope of the dotted curve increases with increasing value of the impact velocity. However, the slope of the solid line is independent of the value of the impact velocity and is nearly equal to the slope of the PL decay.

It is found that the peak I_m of the ML intensity vs time increases linearly with impact velocity. The total intensity of ML, i.e. the area below ML intensity vs time curve, increases and attains a saturation value for higher values of the impact velocity.

The effect of temperature on the time dependence of ML intensity is shown in figure 3 for an impact velocity of 313·2 cm/sec. The peak I_m of the ML intensity vs time and the total intensity I_T of ML, that is, the area below the ML intensity vs time curve, decreases with increasing temperature. The time t_m, corresponding to the peak of the ML intensity vs time curve decreases slightly with increasing temperature of the crystals.

It is seen from figure 4 that ML disappears at 200 and 160°C in $(Ph_3PO)_2MnBr_2$ and $(Et_4N)MnBr_4$ crystals respectively. Similarly ML disappears at 110 and 100°C in $(MePh_3PO)MnCl_4$ and $(Ph_3PO)_2MnCl_2$ crystals respectively. The temperature at which ML disappears is much lower compared to the melting point of the crystals. The melting points of $(Ph_3PO)_2 MnBr_2$, $(Et_4N)_2MnBr_4$, $(MePh_3P)MnCl_4$, and $(Ph_3PO)MnCl_2$ crystals are 242, 300, 214 and 244°C respectively. The ML decay time τ is determined from the slope of $\log I$ vs t curve. It is found that τ decreases with increasing temperature of the crystals. Figure 5 shows that the plot of $\log \tau$ vs $1000/T$ is a straight line with a positive slope. This plot suggests the relation

$$\tau = \tau_0 \exp(E_a/kT), \tag{1}$$

where τ_0 is a constant, k the Boltzmann constant and E_a the activation energy. The value of E_a is found to be 0·115, 0·099, 0·093 and 0·095 for $(PH_3PO)_2MnBr_2$, $(Et_4N)_2MnBr_4$, $(MePh_3P) MnCl_4$ and $(Ph_3PO)_2MnCl_4$ crystals respectively.

Figure 6 shows that the ML spectra of $(Ph_3PO)_2 MnBr_2$, $(ET_4N)_2MnBr_4$ and $(Ph_3PO)_2MnCl_2$ crystals are similar to their PL spectra. The ML spectra of
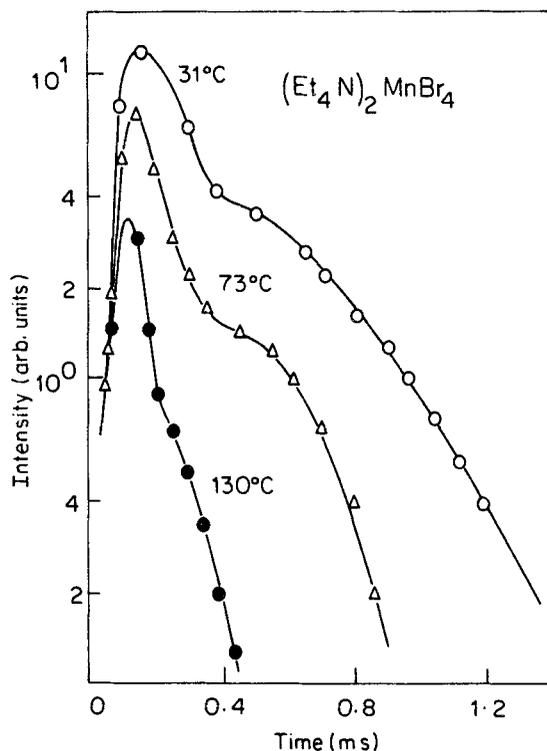
Figure 3. Plot of $\log I$ vs t for different temperatures of $(Et_4N)_2 MnBr_4$ crystals.
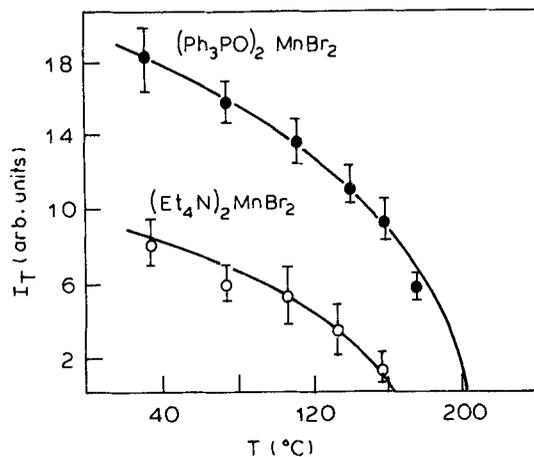

Figure 4. Dependence of the total ML intensity I_T on the temperature of the crystals.

$(MePh_3P) MnCl_4$ crystals have peak at 525 nm. Some portion of ML in the tetrahedral Mn complexes is also due to the nitrogen emission which is not shown in the figure. The nitrogen emission is nearly 100, 140, 56 and 15 times less than the ML emission resembling the PL emission, for $(Ph_3PO)_2 MnBr_2$, $(Et_4N)_2 MnBr_4$,
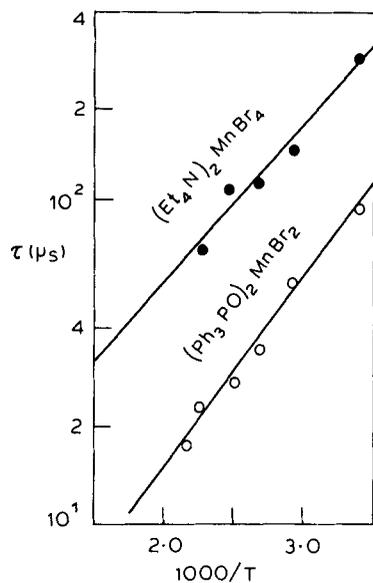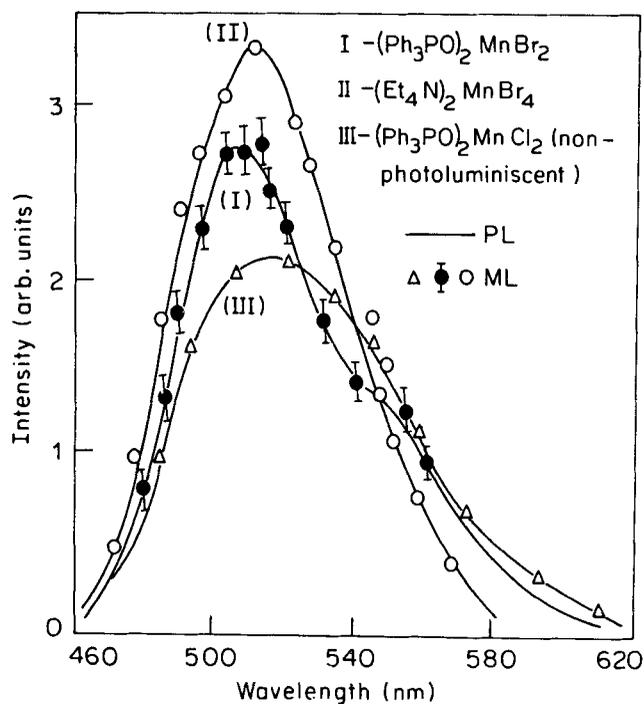
Figure 5. Plot of $\log \tau$ vs $1000/T$.

Figure 6. ML and PL spectra of the tetrahedral Mn(II) complexes.

$(MePh_3P)MnCl_4$ and $(Ph_3PO)_2MnCl_2MnCl_2$ crystals respectively. The PL emission in tetrahedral Mn(II) complexes is assigned to the $^4T_1 \rightarrow {}^6A_1$ transition (Vala *et al* 1972; Lawson 1967). The ML emission similar in spectra to the PL emission may also be assigned to the $^4T_1 \rightarrow {}^6A_1$ transition. When the ML spectra were taken in the CO_2 atmosphere, no nitrogen emissions were found suggesting an independent origin of solid state ML.

4. Discussion

The ML of tetrahedral Mn(II) complexes will be discussed in three parts: (i) effect of deformation on ML, (ii) mechanism of ML and (iii) effect of temperature on ML.

4.1 *Effect of mechanical deformation on ML*

The resemblance of the spectra of solid state ML with photoluminescence suggests two possibilities for the mechanical-induced excitation of luminescence centres: the thermal population of the excited state at high pressure and, the electrical excitation of the luminescence centres. As the pressure coefficient of the energy corresponding to the peak of the PL emission is less, ML excitation may not occur as a result of the thermal population during the mechanical deformation of the crystals (Hardy and Zink 1976). ML excitation should be due to the electric field produced during the mechanical deformation of the crystals.

Figure 1 indicates that after the piston retardation, initially the ML intensity decreases faster and then changes just before stopping of the piston used for deformation. Since, ML spectra of tetrahedral Mn complexes consist of solid state luminescence and nitrogen emission, the two kinetics may be speculated to be due to the two types of emission. The following results eliminate this possibility suggesting that the two kinetics are the intrinsic characteristics of the crystals: (i) the ratio of the nitrogen emission is much less as compared to the ML emission, resembling PL emission, (ii) the time dependence of ML taken in CO_2 atmosphere where nitrogen emission is absent also contains the two kinetics, and (iii) when the time dependence of ML is studied for a particular wavelength region (where nitrogen emission is absent) by placing a monochromator or a filter between the sample and the photomultiplier tube, then the ML emission also contains the two kinetics.

The second possibility of the change in ML kinetics during the stopping of the piston may be that the moving piston may get rebounded after attaining zero velocity and if there is ML emission during pressure release, then the superposition of the ML produced during the impact and that produced during the pressure release may change the ML kinetics. Our experiment suggests that ML intensity produced during the pressure release is much less compared to the ML intensity produced during pressure application. Thus, the increase in ML intensity observed during the stopping of the piston may not be due to the superposition of the ML both during the impact and release of the pressure. Further, this cannot explain the absence of ML emission after the deformation of the crystals whose ML spectra resemble their fluorescence or nitrogen emission ML. It is to be noticed that only the ML of phosphorescent crystals exhibits two kinetics. The third possibility may be the delayed recombination of

electrons with the recombination centres. After excitation of electrons during mechanical deformation, some of them may recombine radiatively giving rise to ML; however, some of them may get dropped into the traps. Latter, the electrons which have dropped into the traps may return to the excited state and may recombine with the luminescence centres. Thus, the decay time of ML may be similar to the decay time of PL. This process may hold good in inorganic phosphors where the traps are responsible for the emission.

The fourth speculation of change in the ML kinetics during the stopping of the piston may be the smaller value of the impact generated electric field during the stopping of the piston. An electric field similar in shape to the impact wave may be produced during the impact of a piston on to the crystal. Although the electric field produced during deformation may excite luminescence centres, it may also perturb the ground and excited states of the system and consequently the decay rate may decrease. Thus, ML may decay with compression rate of the crystals during deformation and may decay with the decay rate of PL after deformation. This process may give rise to changes both in ML intensity and ML decay after the stopping of the piston. This process seems to be responsible for the deformation-induced after-glow of the crystals. The decrease in PL intensity and decay time is well known and has been studied by many workers (Yokoyama *et al* 1976; Bullot and Cordier 1978; Popovic and Menzel 1979). It is seen from figures 1 and 2 that for a short time interval in the region between the retardation and stopping of the piston, the ML intensity has a hump or becomes constant with respect to time. This may occur when the rate of decrease in the ML excitation due to the rate of decrease in the compression is compensated by the rate of increase in the probability of radiative transition with the decreasing electric field.

4.2 *Mechanism of ML*

The crystals of tetrahedral Mn(II) complexes are centrosymmetric; hence, ML excitation in these crystals may not be directly induced by piezoelectrification. No charge development was found when the crystals were mechanically deformed. This fact further confirms the centrosymmetric nature of the crystals of tetrahedral Mn(II) complexes. From the studies of ML in saccharin crystals, it is known that impure saccharin crystals are intense mechanoluminescent and lose ML when they are purified. This suggests that the chemical impurities in crystals may produce local sites which are non-centrosymmetric (although the crystal as a whole is centrosymmetric). The passage of cracks through these sites during mechanical deformation of the crystals, may give rise to an electric field which may cause the dielectric breakdown of the crystals and the subsequent recombination of charge carriers may give rise to luminescence.

4.3 *Effect of temperature on the ML*

It has been described that ML intensity of $(Ph_3PO)_2 MnBr_2$, $(Et_4N)_2MnBr_4$, $(MePh_3P)MnCl_4$ and $(Ph_3PO)_2MnCl_2$ crystals disappears at 200, 160, 110 and 100°C respectively, which are much less than their melting points. If the non-centrosymmetric nature of the local sites are taken to be responsible for ML excitation in these crystals, then the critical temperature, T_c, at which ML disappears should be related to the

temperature at which the local sites loose their centrosymmetric nature. With increasing temperature more and more of the non-centrosymmetric local sites become centrosymmetric and that is why the ML intensity decreases with increasing temperature and disappears at a particular crystal temperature.

It has been reported that the decrease in ML intensity follows the relation $I_T = I_T(1 - T/T_c)^n$, where n lies between 0·45 and 0·60 for non-piezoelectric crystals and between 0·90 and 1·10 for the piezoelectric crystal. This suggests that the decrease in charge density may cause the decrease in ML intensity with increasing temperature of the crystals; however, both the decrease in the charge density and area of newly created surfaces may be responsible for the decrease in ML intensity with increasing temperature of the piezoelectric crystals. Also, the decrease of decay time with temperature is well known in luminescence.

Acknowledgements

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