CHAPTER V

THEORETICAL APPROACH TO THE PROLONGED MECHANOLUMINESCENCE IN CLAYS AND OTHER MINERALS
5.1 INTRODUCTION

The ML accompanying fracture is almost always greater than that accompanying elastic and plastic deformation. The fracture cannot be accomplished without a great deal of deformation. What makes fracture most different from deformation is the formation of large energetic new surfaces where light emission usually overwhelms the residual deformation luminescence. The new surfaces sputter off electrons, ions, neutral molecules and fragments of molecules, many of which are involved in the production of ML.

Fracto mechanoluminescence (FML) has a great deal of potential to understand the following facts and devices: (i) Earthquake and mine failure (Brady and Rowell 1986), (ii) earthquake lights (Derr 1973 and Freund 2003) and moonquake lights (Zito 1989), (iii) dynamics and mechanics of fracture (Chandra and Zink 1980, Chandra et.al. 2008), (iv) design of damage sensors (Sage et.al. 1999, 2000), (v) design of fracture sensors (Chandra and Zink 1980, Chandra et.al. 2008, Takada et.al. 1997, Sage et.al. 1999), (vi) fuse-system for army warhead (Glass and Dante 1977, Dante 1983), and (vii) design of safety management monitoring system (Xu 2010). Such potentials of fracto ML require deep understanding of the correlation between fracto ML and fracture. It is expected that the models of deformation and fracture to explain ML may help to explain and predict earthquakes. In this connection laboratory studies on minerals (Brady and Rowell 1986, Dickinson et.al. 1991, Cress et.al. 1987) and theories that focus on piezoelectric voltage (Den 1973, Baird and Kennan 1985, Warwick et.al. 1982), dislocation motion (Slifkin 1993), electric field oscillation (Khatiashvili 1988), coronal discharge (Lockner et.al. 1983) or dielectric breakdown (Brady and Rowell 1986, Cress et.al.1987) have already improved our understanding.
For a long time fracture was used as the technique for inducing ML in crystals. On the other hand, Chandra et.al. (1977) reported that the ML may be used in studying the fracture of crystals. In 1980, Chandra and Zink reported that when a crystal is deformed slowly using an Instron testing machine, then the ML pulses appears concurrently with the steps occurring in the stress-strain curve of the crystal in which the ML intensity of the pulse depends on the magnitude of the steps in the stress-strain curve. Chandra and Zink (1980) also deformed the crystal impulsively using the impact of a moving piston and it was found that, after the impact of piston onto the crystal, initially the ML intensity increases with time, attains a peak value and then it decreases with time. In this case, the ML intensity is directly related to the rate of creation of new surfaces and the total ML intensity is directly related to the total area of newly created surfaces of the crystals. The time corresponding to the peak of ML intensity is found to decrease with the impact velocity of the piston and it is found to increase with the thickness of the crystals. The peak ML intensity is found to increase with increasing impact velocity and also with the increasing cross-section of the crystals. It is found that the total ML intensity initially increases with the impact velocity of the piston and then it attains a saturation value for higher values of the impact velocities. The total ML intensity is found to increase with volume or mass of the crystals. Chandra and Zink (1980) reported that the time duration of the ML pulse produced by the movement of a single crack is of the order of tens of a microsecond. Chandra and his co-workers also reported the impulsive excitation of ML in other crystals such as coloured alkali halide crystals, II-VI semiconductors, Mn complexes, etc. (Chandra 1983, Chandra et.al. a, b, 1986, 1987, Tiwari et.al. 1994).

Maeda (1983) has studied the high time-resolved observation of ML of crystalline sucrose. A cleavage test along the plane (001) and a
uniaxial compression test in which the load axis was perpendicular to the plane (001) were made. ML was observed simultaneously at the time cleavage began. The time lag between them is less than $10^{-7}$ sec. Intensity variation of the ML activity correlates with the load variation, though the correlation is not quantitative. In the uniaxial compression test, there are two cases. In one case, a crack generation accompanies ML and acoustic emission. In the other case, a crack generation accompanies only an acoustic emission. This difference in the two cases is explained by the difference in crack mode (tensile or shear).

Maeda (1986) has reported the activities of ML sample failure of granite. The intensity of ML was determined by photo-counting at a time resolution of 100 microseconds. The pattern of ML activities of each sample is classified into a sequence of the precursory activity, the burst of ML at failure, and the following decaying after-glow and it is found to be extremely similar to the pattern of the foreshock-main-shock-aftershock sequences for natural earthquakes. The after-glow continues rather long time compared to the process-time of sample failure. The after-glow was shown to be sustained by consecutive generation of cracks in fragments without being subjected to any external force. Most of the samples showed tangible precursory activities of ML, which were observed up to twenty milliseconds prior to failure of samples. The initiation of these events closely relates to changes in the stress change rate. The intensity of ML is affected by humidity contained in a sample.

Sage et al. (Sage et.al.a, b, 1999, 2000) have designed real-time damage sensor using intense mechanouminescent materials, in which fibre optic transmission of ML could be used to detect damage in regions of aircraft that are difficult to inspect visually. In this case, the damage can be monitored by measuring the fracto ML intensity and the location of damage can be determined using colour-coading with different
Mechanoluminescent materials (Sage et al. 1999), fibres with different cladding or fine tubes filled with fluorescent solution. They have demonstrated that for resins and glass fibre reinforced plastic (GFRP) composites, mechanoluminescent sensors act as truly global damage sensors, whereas for glass carbon reinforced plastic (CFRP) composites, the damage sensing is localized to areas close to the embedded photoluminescent fibre. They have reported that, when a load impacts onto the mechanoluminescent material, then initially the ML intensity increases with time, attains a peak value and later on it decreases with time.

Chakravarty and Phillipson (Chakravarty and Phillipson 2004) have investigated the ML and the potential of fracture surfaces. Spectral evidence suggests that the ML of the majority of materials is due to electrical discharge. Gas discharge is also invoked to explain the ML of certain materials in which there is no spectral evidence for it. A technique for determining if the ML of a material is due to discharge, independent of spectral information, is described. Electrostatic probes are used to monitor the potential of the fracture surfaces of a crystal during cleavage. The signal from a photomultiplier reveals if the ML is due to discharge between the fracture surfaces. The use of this technique is illustrated through studies of sucrose, sodium chloride, and a highly ML (and highly photoluminescent) terbium complex. Oppositely charged fracture surfaces are found in sucrose; however, the sense of the electrification is opposite to that predicted by the existing theory of piezoelectric charging. It was confirmed that the ML of both sucrose and sodium chloride is associated with electrical discharge. In contrast, the ML of the terbium complex commenced prior to electrical discharge. This demonstrates that the ML of this material is not due to the fluorescent re-emission of the
ultraviolet component of the discharge spectrum, as had been suggested previously.

Mamadov et al. (2009) have reported the time-resolved ML of optical materials. The ML of optical materials (quartz, silicate and organic classes), in which the ML accompanying impact and friction consists of numerous flashes of about ten microsecond duration, having an identical shape-linear during ignition (for 1-4μs) and exponential damping (with a mean time of 7-25 μs). The ignition is explained by the formation and growth of cracks on the shores of which electronically excited free radicals are located, while the damping is shown to be the relaxation of the electron excitation after the cessation of friction.

The ML of alkaline earth oxides has been studied using three point bend (Langford et al. 1987). It is found that the crystals of MgO start showing ML during plastic deformation, but the ML intensity at fracture is very high. The ML in these crystals also appears in the post-fracture region. The fracto-ML produced during the cleavage of III-V semiconductors have been studied by many workers, in which the infrared emission has been observed (Nakayama 1994, Li et al. a, b, 1993, Takamori et al. 1974). Bergeron et al. (2006, 2008, and 2011) have studied the ML induced by hypervelocity impact of a projectile onto a backside of plate whose front side was coated with ZnS: Mn phosphors. In this case, the ML intensity has been found to increase with increasing impact velocity.

In the past, rapid photographic methods and CCD cameras have been used effectively to map the ML emission both from deformation and fracture. High-speed photography has clearly shown the localization of the plastic deformation preceding the fracture of quartz to certain slip planes and the evolution of the slip with time (Brannon et al. 1983, Brooks 1965). Donaldson and Dickinson (Donaldson and Dickinson
have shown that the images of the failure, i.e. fracture, of adhesive bonds by peeling tape made with the ML emission were correlated with the force (stress) and the development of wrinkles to show that at a critical curvature and strain the adhesive undergoes brittle failure, followed by a period of low strain. Light emission was concentrated around fibers during failure of a composite indicating delamination (Krauya et.al. 1981). Sweeting (1990) created image of fracturing candy by placing the candy toroids on the film with Plexiglas separators and striking with a hard rubber hammer. Images of the ML produced by a needle on a turntable of mechanoluminescent alumina show clearly that three regions experience high stress-at the contact site and both before and after it (Miura and Nakayama 2001). Filter showed that the sites before and after the needles probably emitted lightning, but that under the needle emitted blackbody radiation that developed more slowly. The ML emission pattern captured by a CCD camera faithfully mapped the fractures in a lanthanide-doped epoxy, indicating that failure can be detected without interference from deformation luminescence (Sage et.al.1999). It is expected that the improving sensitivity and ability to resolve in both time and space will greatly add the study of the deformation and fracture of materials (Brannon et.al. 1985, Chandra 1985).

The theory of fracto ML proposed previously (Chandra et.al. 2012) explains satisfactorily the dependence of peak ML intensity $I_m$ and total ML intensity $I_T$ on the impact velocity and size of crystals; however it predicts longer time $t_m$ corresponding to the peak of ML intensity versus time curve and suggests only the quadratic increase of ML intensity with time. In the present paper, a general theory of fracto ML is explored, which is able to explain satisfactorily the rise of ML intensity with time, and the dependence of $t_m$, $I_m$ and $I_T$ on the impact velocity, size of
crystals and temperature of crystals. Furthermore, the theory is also able to explain satisfactorily the fracto ML of phosphorescent crystals, in which in addition to fracture region, the ML also appears in the post-fracture region of the crystals.

During the study of luminescence in clay minerals and its possible role in the early stages of periodic evolution, it was found that not only does the fracturing or grinding of certain clays bring about a burst of light during the time the mechanical stress is applied, but after the stress is removed a surprisingly high photon flux continues, although at a diminishing rate, for several days (Coyne et.al. 1981). The first burst of light can be observed by the unaided eye in a dark room; the latter process can be easily detected by a photomultiplier tube. So far as known to us, no theoretical studies of long-term photon emission in rock minerals have been carried out in which the photon emission were excited by mechanical stress without subsequent heating. The present chapter reports the theoretical studies made on the long decay fracto mechanoluminescence of clays and clay materials and makes the comparison between the theoretical and experimental results, whereby a good agreement was found.

5.2 MECHANISM OF THE FRACTO ML OF CLAYS AND OTHER MATERIALS

Till now, the present level of our understanding of the nature of the material after fracture is even more limited. Although stress is relieved at the time of failure of the material, the motion of dislocations does not reverse (Falk and Langer 2000). In fact, dislocation motion may occur in quite different directions without the unidirectional driver, because the material is especially transformed in the vicinity of the propagating crack.
As such a new collection of defects and dislocations may be created and annihilated upon fracture (Farkas 2000). The microscopic SEM and STM examination of the simple salts presumably indicates that imperfections cause the cracks to propagate along many planes with many stops, starts and redirections to leave extremely rough surfaces. There are braking of bonds, at least in networks and polymers. Chemical reactions occur, especially when air is present. The relaxation of new surface and the new dislocations take place by further motion of dislocations including pop out on the surface, electron and ion (molecule) motion across the surface and through the surrounding gas, and vibrational or thermal equilibration. In fact, in vacuum the fresh surface can take hours to relax to equilibrium.

The long-lasting emission of electrons, ions and neutrals after fracture provides a monitor for the surface relaxation, and it also gives the information about the migration of defects and the relaxation of the entire body of the material from the damage caused during plastic deformation and fracture. Mathison et.al.(1989) have observed long-lasting emission of electrons from the damaged areas of the fracture surface of LiF when cleaved by a three-point bend, but there were no electron emission from areas where there was a clean cleavage. Dickinson et.al.(1984) have reported that, in vacuum even the simple lightning-emitting materials like sucrose exhibit intense emission at the moment of fracture followed by long-lived faint emission from dislocations sweeping electrons to the surface. Dickinson et.al.(1991) have reported that the emission of electrons and photons is accompanied by the emission of ions and neutrals, when more dislocations pop to the surface after fracture and the surface is bombarded with high-energy electrons. Cress et.al.(1987) and Donaldson et.al.(1988) have reported that the energy carried by these dislocations is sufficient to break bonds, ionize fragments and eject ions and molecular fragments into the plasma above the new surface and
chunks of material into the surroundings. Generally, the long-lived emission that is intense in vacuum is at least partially quenched by air, especially by the oxygen. (Dickinson et.al.1984, Donaldson and Dickinson 1989). The multiple decay times in the ML intensity verses time curve characterize the different kinds of defects producing the ML light, and they are the norm for nearly all the materials studied under vacuum (Donaldson et.al. 1986 and Zhenyi et.al. 1988).

The ML induced by the fracture and grinding of clays and other materials can be understood with respect to the following points:

(i) The grinding or fracture of clays and other materials into the powder form produces a large number of dislocations.

(ii) The dislocations produced during grinding and fracture of crystals may relax and move towards the surfaces of the microcrystals.

(iii) During the movement of dislocations after the grinding or fracture of crystals, there is electrostatic interaction between the moving charged dislocations and charge carriers in the crystallites. Consequently, the dislocations may capture charge carriers and they may transport them to the charge carriers of opposite sign, whereby electron-hole recombination may give rise to the light emission. Also the electric field of charge dislocation may cause bend bending whereby the trapped electrons may tunnel to the conduction band, and the trapped hole may tunnel to the valance band, and subsequently, the recombination of charge carriers at the luminescence centres may give rise to the light emission. Furthermore, the charge dislocations may move to the surface of the microcrystals and the charging of surfaces may take place, in which the electric field at the surface may cause the emission of energetic electrons, whereby the electron bombardment may excite the molecules of surrounding gases and light may be produced. Moreover, the electron bombardment may
also excite cathodoluminescence at the surface of crystallites. Also, the light of gas discharge may produce photoluminescence in the microcrystallites. In addition, the ions moving with the dislocations may cause chemical reaction and subsequently the chemiluminescence may be produced. In this way, light may be produced due to several processes such as cathedoluminescence, gas discharge, photoluminescence, chemiluminescence, recombination luminescence, etc. As the relaxation of dislocations is a slow process the ML emission may take place for a long duration.

(iv) As the relaxation of dislocations is a slow process the ML emission may take place for a long duration. It has been found that, in the coloured microcrystalline powders of alkali halides, the bleaching of coloration takes place due to the slow moment of dislocations towards the surfaces of microcrystallites. Depending on the size of microcrystallites the decay time for the decrease of coloration varies from several days to several weeks (Chandra et.al. 1985, 1996 and Deshmukh et.al. 1983). The decay time of the coloration bleaching in alkali halide microcrystals decreases with decreasing size of the microcrystals because of the increase of dislocation density with decreasing size of the microcrystals. It is to be noted that, in the case of prolonged ML of clays and other materials the decay time of prolonged ML varies from several hours to several days.
5.3 THEORETICAL APPROACH TO THE PROLONGED MECHANOFLUORESCENCE INDUCED BY FRACTURE AND GRINDING OF CLAYS AND OTHER MATERIALS

5.3.1 Expression for the Time Dependence of ML Intensity Based on the Dislocations having Large Number of Relaxation Times

If \( \tau \) is the relaxation time of the dislocation moving towards the newly created surface of clay or any other material, the decrease in the number of relaxing dislocations of the relaxation time \( \tau \) can be written as

\[
- \frac{dN}{dt} = \frac{N}{\tau} = \psi N
\]

where \( \psi = 1/\tau \) is the rate constant for the relaxation of dislocations and \( N \) is the number of relaxing dislocations having relaxation time \( \tau \).

Integrating Eq. (5.1) and taking \( N=N_0 \), at \( t=0 \), we get

\[
N = N_0 \exp(-\psi t)
\]

If \( \eta \) is the ML efficiency, then the ML intensity can be expressed as

\[
I = \eta N \quad \text{where} \quad I = \eta \psi N_0 \exp(-\psi t) = I_0 \exp(-\psi t)
\]

where, \( I_0 = \eta \psi N_0 \), is the ML intensity at \( t=0 \), produced due to the relaxation of the dislocations having relaxation time \( \tau \).

Let us consider that, the relaxation times are different at different sites. If \( \psi_1, \psi_2, \psi_3, \ldots \) and \( \psi_n \) are the rate constants for the relaxation of the dislocations relaxing from different sites such as first, second, third, \( \ldots \ldots \) and \( n \) sites, respectively, and \( I_1, I_2, I_3, \ldots \) and \( I_n \) are the ML intensities at \( t=0 \), for the dislocations having relaxation times \( \tau_1, \tau_2, \tau_3, \ldots \ldots \ldots \) and \( \tau_n \), respectively, then the time dependence of the ML intensity can be expressed as

\[
I = [I_1 \exp(-\psi_1 t) + I_2 \exp(-2\psi_2 t) + I_3 \exp(-3\psi_3 t) + \ldots + I_n \exp(-n\psi_n t)]
\]

Equation (5.4) can be written as
\[ I = [I_1 + I_1 \exp(-\psi t) + I_2 \exp(-2\psi t) + I_3 \exp(-3\psi t) + \ldots + I_n \exp(-n\psi t) - 1] \]

----- (5.5)

Multiplying both the sides of Eq. (5.5) by \( \exp(-\psi t) \) we get
\[ I \exp(-\psi t) = I_1 \exp(-\psi t) + I_2 \exp(-2\psi t) + I_3 \exp(-3\psi t) + I_4 \exp(-4\psi t) + \ldots + I_n \exp(-(n-1)\psi t) - I_1 \exp(-\psi t) \]

----- (5.6)

Now subtracting Eq. (5.6) from Eq. (5.4), we get
\[ I[1 - \exp(-\psi t)] = [I_1 \exp(-\psi t) - I_n \exp(-(n-1)\psi t)] \]

or, \[ I = \frac{I_1[\exp(-\psi t) - f \exp(-\phi t)]}{[1 - \exp(-\psi t)]} \]

----- (5.7)

where \( \phi = (n+1)\psi \), and \( f = (I_n/I_1) \)

Now, we will consider the following two cases: (i) small and medium value of time, and (ii) large value of time.

**Case I: Small and Medium Values of Time**

As \( \exp[-(n+1)\psi t] \ll 1 \), after certain value of time Eq. (5.7) can be expressed as
\[ I = \frac{I_1[\exp(-\psi t)]}{[1 - \exp(-\psi t)]} = \frac{I_1}{[\exp(\psi t)-1]} \]

----- (5.8)

It is to be noted that Eq. (5.8) becomes applicable only after certain value of t, where \( \exp[-(n+1)\psi t] \ll 1 \)

For \( \psi t \ll 1 \), Eq. (5.8) can be written as
\[ I = \frac{I_1}{\psi t} = \frac{I_1}{t \psi^{t^{-1}}} \]

or, \( I = I_0 t^{-1} \)

----- (5.9)

where \( I_0 = \frac{I_1}{\psi} \)
Considering the dispersion phenomenon, it will be better to replace \( 1 \) in Eq. (5.9) by the constant \( \gamma \) related to the dispersion parameter. Thus, Eq. (5.9) can be written as
\[
I = I_0 t^{-\gamma} \quad \text{----- (5.10)}
\]

Equation (5.10) can be expressed as
\[
\log I = \log(I_0) - \gamma \log t \quad \text{----- (5.11)}
\]

It is evident from Eq. (5.11) that the plot of \( \log I \) versus \( \log t \) should be a straight line with a negative slope \(-\gamma\).

**Case II: For Large Value of Time**

For the large value of \( t \), \( \exp(\psi t) >> 1 \), therefore, Eq. (5.8) can be written as
\[
I = I_1 \exp(-\psi t) \quad \text{----- (5.12)}
\]

Equation (5.12) can be expressed as
\[
\log I = \log I_1 - \psi t \quad \text{----- (5.13)}
\]

Thus, it seems from Eq. (5.12) that, for \( \psi t >> 1 \), the ML intensity should decay exponentially with time, in which the decay time will be equal to \( 1/\psi \).

**5.3.2 Expression for the Time Dependence of ML Intensity Based on the Dislocations having Limited Number of Relaxation Times**

In this case, if the dislocations have one value, two values and three values of diffusion times, then the decay of the ML intensity can be expressed by the following expressions, respectively:
\[
I = I_1 \exp(-\psi_1 t) \quad \text{----- (5.14)}
\]
\[
I = I_1 \exp(-\psi_1 t) + I_2 \exp(-\psi_2 t) \quad \text{----- (5.15)}
\]
and,
\[
I = I_1 \exp(-\psi_1 t) + I_2 \exp(-\psi_2 t) + I_3 \exp(-\psi_3 t) \quad \text{----- (5.16)}
\]

where \( \psi_1 = 1/\tau_1 \), \( \psi_2 = 1/\tau_2 \), and \( \psi_3 = 1/\tau_3 \).
5.4 CORELATION BETWEEN THE THEORETICAL
AND EXPERIMENTAL RESULTS

Lahav et. al. (1982) have measured the ML induced by fracture and grinding of clays and other materials. For the ML measurement the sample of clays and other minerals were either ground with a mortar and pestel or fractured with a hammer and placed in pyrex vials (Lahav et.al. 1982). Samples of (1) well-crystallized kaolin, KGa-1, from Washington County, Georgia, and (2) poorly crystallized kaolin, KGa-2, from Warren County, Georgia, were obtained in the form of powders from The Clay Mineral Society's Source Clay Repository. The powders had no detectable photon emission. Samples of Mesa Alta, New Mexico, kaolinite (Ward’s Natural Science Establishment, Rochester, New York), and Umiat, Alaska, bentonite (Anderson and Reynolds, 1960) were prepared by forming cube-like chunks of known surface areas. Ground samples of chalk calcite, South England (Ward’s Natural Science Establishment, Rochester New York), sodium chloride, AR (Baker Analyzed Reagents), and quartz were filled up to half the volume of the Tricarb vials. The emitted photons caused by grinding and fracture of samples were counted using a Packard Tri-CarbLiquid Scintillation Spectrometer, Model 3320.

Fig.5.1 shows the decay curves of the ML of excited kaolin (Lahav et.al. 1982). The grinding of the well-crystallized kaolin (KGa-1) resulted in a higher photon-emission rate than that of the poorly crystallized kaolin (KGa-2). The count rate of the latter did not appreciably increase with further grinding. The decay characteristics of the emitted light (Fig.5.1) continued for at least three days, and were very similar to those described by Stranski et.al.(1955) for arsenic crystals. A rough estimate of the ML at the very first moments can be made by intrapolating the
curves in Fig. 5.1 back to time zero. It was estimated that the count rate of the well-crystallized kaolin immediately after the grinding was of the order of several million counts per minute. Fig. 5.1 shows the log-log plot of the ML intensity verses time after the grinding of the well-crystallized kaolin (KGa-1) and poorly crystallized kaolin (KGa-2). It is seen that the plots are straight line with a negative slope.

![Log-log plot of ML intensity versus time after grinding](image)

Figure 5.1. Luminescence rate as a function of time elapsed from the end of grinding: well crystallized kaolin KGa-1 and poorly crystallized kaolin KGa-2 (after Lahav et.al., 1982).

The decay curves of freshly filed, cube-like chunks of mesa Alta kaolinite and Umiat bentonite are shown in Fig.5.2. The activity of kaolinite, which greatly exceeded that of bentonite, exhibited a similar
decay characteristic in that the decay was very fast during the first few minutes following by a slower rate; in which the slower rate gave a straight line on a log-log scale (Fig. 5.2). It is seen that, for long time duration the plots are straight line with a negative slope.

Fig. 5.2 Luminescence rate as a function of time elapsed from the end of filing of kaolinite, Mesa Alta, New Mexico, and bentonite, Umiat, Alaska (after Lahav et.al., 1982).

Fig. 5.3 shows the log-log plot of the ML intensity verses time after the grinding of quartz, sodium chloride, and chalk calcite. It is seen that, for quartz and chalk calcite, for the long time duration the log-log plots of the ML intensity verses time are straight line with a negative slopes; however, for sodium chloride, for the shorter time duration the log-log plot of the ML intensity verses time is straight line with a negative slope.
Figure 5.3 Luminescence rate as a function of time elapsed from end of grinding of quartz, sodium chloride, and chalk calcite (after Lahav et.al., 1982).

It is evident that, whereas the log-log plots of the ML intensity verses time for well-crystallized kaolin (KGa-1) and poorly crystallized kaolin (KGa-2) are straight lines, the log-log plots of the ML intensity verses time plots for other samples are not the straight lines. The slopes of the straight line regions of the the log-log plots of the ML intensity verses time are given in Table 5.1 for all the samples studied in the present investigation.
Table 5.1
Slope $\gamma$ of the log-log plots of the ML intensity versus time for different materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\gamma$ (hour$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Kaolinite (well crystallized)</td>
<td>1.580</td>
</tr>
<tr>
<td>2. Kaolinite (poorly crystallized)</td>
<td>0.588</td>
</tr>
<tr>
<td>3. Kaolinite (Mesa Alta)</td>
<td>0.576</td>
</tr>
<tr>
<td>4. Bentonite</td>
<td>0.324</td>
</tr>
<tr>
<td>5. Quartz</td>
<td>0.830</td>
</tr>
<tr>
<td>6. Chalk Calcite</td>
<td>0.668</td>
</tr>
<tr>
<td>7. Sodium Chloride</td>
<td>1.204</td>
</tr>
</tbody>
</table>

Fig. 5.4 shows the semilog plot of the ML intensity versus time for well crystallized kaolin, and poorly crystallized kaolin. It is seen that, initially the ML intensity decays at a fast rate, later on it decays at a slow rate, and for large values of time it decays at a very slow rate. The values of the three rate constants for ML decay and the values of three decay times of ML for well crystallized kaolinite and poorly crystallized kaolinite are shown in Table 5.2.
Figure 5.4 Semilog plot of the ML intensity versus time for well crystallized Kaolin and poorly crystallized Kaolin.

Fig. 5.5 illustrates the semilog plot of the ML intensity versus time for mesa Alta kaolinite and Umiat bentonite. It is seen that, initially the ML intensity decays at a fast rate and later on it decays at a slow rate. The values of two rate constants for ML decay and the values of two decay times of ML for mesa Alta kaolinite and Umiat bentonite are shown in Table 5.2.
Fig. 5.6 shows the semilog plot of the ML intensity versus time for quartz, sodium chloride, and chalk calcite. It is seen that, for chalk calcite, initially the ML intensity decays at a fast rate and later on it decays at a slow rate. It is seen that, for sodium chloride and quartz, initially the ML intensity decays at a fast rate, later on it decays at a slow rate and for large values of time it decays at a very slow rate. The values of the rate constants for decay and the values of decay times for quartz, sodium chloride, and chalk calcite are shown in Table 5.2.
Figure 5.6 Semilog plot of the ML intensity versus time for Quartz, Chalk Calcite and Sodium Chloride.

It seems that the time dependence of the ML intensity of the clays and other materials studied in the present investigation have two or three values of the ML decay times and the time dependence of their ML intensity follows Eqs. (5.15) and (5.16).

As the values of the slopes of log-log plots of the ML intensity versus time for certain samples are less than one, Eq. (5.9) derived on the basis of the dislocations having large number of relaxation times are not applicable.
Table 5.2

Values of the rate constants \( \psi_1, \psi_2, \) and \( \psi_3 \) and the decay times \( \tau_1, \tau_2 \) and \( \tau_3 \) for the ML of materials

<table>
<thead>
<tr>
<th>Materials</th>
<th>( \psi_1 ) (h(^{-1}))</th>
<th>( \psi_2 ) (h(^{-1}))</th>
<th>( \psi_3 ) (h(^{-1}))</th>
<th>( \tau_1 ) (h)</th>
<th>( \tau_2 ) (h)</th>
<th>( \tau_3 ) (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Kaolin (well crystallized)</td>
<td>0.456</td>
<td>0.175</td>
<td>0.039</td>
<td>2.192</td>
<td>5.714</td>
<td>26.315</td>
</tr>
<tr>
<td>2. Kaolin (poorly crystallized)</td>
<td>2.343</td>
<td>0.319</td>
<td>0.060</td>
<td>0.426</td>
<td>3.134</td>
<td>16.666</td>
</tr>
<tr>
<td>3. Kaolinite (Mesa Alta)</td>
<td>1.800</td>
<td>0.060</td>
<td>-</td>
<td>0.555</td>
<td>16.666</td>
<td>-</td>
</tr>
<tr>
<td>4. Bentonite</td>
<td>2.340</td>
<td>0.060</td>
<td>-</td>
<td>0.427</td>
<td>16.666</td>
<td>-</td>
</tr>
<tr>
<td>5. Quartz</td>
<td>0.013</td>
<td>0.003</td>
<td>0.001</td>
<td>76.923</td>
<td>333.33</td>
<td>1000.0</td>
</tr>
<tr>
<td>6. Chalk Calcite</td>
<td>0.003</td>
<td>0.001</td>
<td>-</td>
<td>333.33</td>
<td>1000.0</td>
<td>-</td>
</tr>
<tr>
<td>7. Sodium Chloride</td>
<td>0.130</td>
<td>0.023</td>
<td>0.006</td>
<td>7.692</td>
<td>43.478</td>
<td>166.66</td>
</tr>
</tbody>
</table>

On the basis of the counting efficiency, it was estimated that the total amount of light emitted from a unit surface area of the Mesa Alta kaolinite, i.e. the light that was detected and counted by the scintillation spectrometer, was of the order of several tens of billions of photons per square centimeter of surface area. It is to be noted that, a part of the emitted light came from the surface, but the remainder originated at deeper layers in the solid phase. The total photon output of a unit mass of clay could not be estimated.

When water was added to either the kaolinite or bentonite preparations, then the count rate of emitted light was found to increase to some extent; however no effort was made to quantify this effect. It was
found that, when freshly filed chunks of Mesa Alta kaolinite were dipped into a solution of the amino acid tryptophan and carefully drained, the count rate increased above that of the same kaolinite chunk wetted with water. Though the increased count rate induced by tryptophan was significant, it could not be quantitatively measured by the method used by Lahav et al. (1982).

It is known that tryptophan, a fluorescent molecule, has excitation and fluorescence maxima at 287 nm and 348 nm, respectively (Underfriend 1962). One possible interpretation of the tryptophan effects is that part of the ML light was in the UV of near UV range and was not counted by the photomultiplier both because of the high light absorbance and scattering of the kaolinite (Lindberg and Smith, 1974) and because of the light absorbance in this range of the spectrum by the Pyrex vials. However, the fluorescence amino acid was excited by these photons and consequently the photons were emitted at a higher wavelength. Because light transmittance of both clay and glass greatly increased with increasing wavelength in the UV or near UV range, the tryptophan molecules, according to this interpretation, served as probes for photons produced in the prolonged ML process, which otherwise would not have been counted. Mechanoluminescence in the UV and near UV range has been shown earlier (Stranski, 1955, Chandra et al., 2013). Another possible interpretation for the tryptophan effect is nonradiative energy transfer between excited sites in the ground clay and the tryptophan molecules (Fendler and Fendler, 1975).

As the mechanical stress in the form of grinding was so effective in exciting ML in kaolinite and montmorillonite, freezing should have produced similar effects under conditions that brought about breaking and distortion of the crystal structures. To investigate this effect, pastes of kaolinite and montmorillonite were smeared on the inner walls of vials,
frozen in either liquid nitrogen (fast freezing) or in a -10°C salt-ice mixture (relatively slow freezing), thawed, and the emitted photons were counted. Freezing by either method excited montmorillonite to produce luminescence and produced a decay curve similar to that shown in Fig. 2 (Lahav et.al. 1982). This freezing-induced ML was repeated simply by further freezing and thawing the bentonite paste. In fact, the quantitative comparison between the two processes has not been attempted. In contrast, freezing excited no measurable ML in kaolinite. Obviously, it will be interesting to do further study to understand the difference between the two clays in their response to freezing. It seems that the different responses are related to both particle size and interparticle distances and forces, as well as to surface-water interaction (Lahav et.al. 1982).

The prolonged has been examined in many other solids, including several kaolinite and montmorillonites, quartz, pure sand, calcite, marble, illite, nontronite, talc, pyrophyllite, ilmenite, vermiculite, apatite, asbestos (Jade mine), sodium chloride, and sugar. Several examples are shown in Fig. 3. All of these materials exhibited prolonged ML; however, the apparent ML intensities of the effect differed considerably. For example, nontronite exhibited very weak activity; quartz, “pure” sand, talc, and pyrophyllite showed a considerable effect; and montmorillonite samples exhibited a rather low level of prolonged ML. Vermiculite produced no apparent ML, presumably because the method of grinding was not effective in breaking its sheets.

In fact, the intensity and decay rate of prolonged ML depend on both the properties of the material under study and on the method of sample preparation and measurement. To compare different materials and to elucidate the roles of chemical composition, crystallographic properties, environmental conditions, and method of sample preparation, the method
of excitation must be standardized as well as the measurement procedure should also be standardized. Obviously the grinding applied in study made by Lahav et.al. (1982) cannot be easily standardized. On the other hand, development of a standardized polishing technique is easier and it may permit measurements of ML excitation under comparable conditions (Lewis, 1968). It is to be noted that the effects of chemical composition and crystallographic properties on prolonged ML are not easily separated. For example, the two kaolinites shown in Fig.1 differ considerably not only in their degree of crystallinity, but also in their chemical composition, cation-exchange capacity, surface area, and thermal analysis (Van Olphen and Fripiat, 1979), and presumably, in impurities content. As such, because of light absorbance (Diehl et.al., 1968), the higher iron content of the KGa-2 Kaolinite may be at least partially responsible for its lower ML activity.

In fact, it will be interesting to study the possible significance of the prolonged in connection with processes in which it is either naturally formed or artificcally induced. An example of a natural process is rock fracturing, whether by expansion-contraction, the impact of meteorites, or during tectonic movement (Wakita et.al., 1980). It is to be noted that the artificially induced prolonged ML is probably very common in mines and quarries.

Lahav et.al.(1982) have reported that the prolonged ML and the surface phenomena related to it immediately suggest a possible connection between human exposure to freshly powdered materials such as those produced in mines (e.g. asbestos and silica) and certain respiratory diseases (e.g. asbestosis and silicosis).
5.5 CONCLUSIONS

The important conclusions drawn from the present investigation are as given below:

(i) The fracturing or grinding of certain clays gives rise to a burst of light during the time of the application of mechanical stress, and when the stress is removed a surprisingly high photon flux continues, although at a diminishing rate, for several days. The first burst of light can be observed by the unaided eye in a dark room; the latter process can be easily detected by a photomultiplier tube.

(ii) The examples of clay materials which exhibit prolonged ML are: well-crystallized kaolin, poorly-crystallized kaolin, kaolinite, bentonite, quartz, sodium chloride, chalk calcite, etc. Kaolin shows prolonged ML for nearly three days; kaolinite and bentonite show ML for nearly one week; and quartz, sodium chloride, and chalk calcite, show ML for more than one week.

(iii) The semilog plot of the ML intensity versus time curves show that, whereas well crystallized kaolin, poorly crystallized kaolin, quartz, and sodium chloride have three decay times for the ML emission; kaolinite, bentonite, and chalk calcite have two decay times for the ML emission.

(iv) During the movement of dislocations after the grinding or fracture of crystals, there is electrostatic interaction between the moving
charged dislocations and charge carriers in the crystallites. Consequently, the dislocations may capture charge carriers and they may transport them to the charge carriers of opposite sign, whereby electron-hole recombination may give rise to the light emission. Also the electric field of charge dislocation may cause bend bending whereby the trapped electrons may tunnel to the conduction band, and the trapped hole may tunnel to the valance band, and subsequently, the recombination of charge carriers at the luminescence centres may give rise to the light emission. Furthermore, the charge dislocations may move to the surface of the microcrystals and the charging of surfaces may take place, in which the electric field at the surface may cause the emission of energetic electrons, whereby the electron bombardment may excite the molecules of surrounding gases and light may be produced. Moreover, the electron bombardment may also excite cathodoluminescence at the surface of crystallites. Also, the light of gas discharge may produce photoluminescence in the microcrystallites. In addition, the ions moving with the dislocations may cause chemical reaction and subsequently the chemiluminescence may be produced. In this way, light may be produced due to several processes such as cathodoluminescence, gas discharge, photoluminescence, chemiluminescence, recombination luminescence, etc.

(v) As the relaxation of dislocations is a slow process the ML emission may take place for a long duration.

(vi) On the basis of the mechanism of ML of clays and other materials expressions are derived for different characteristics of the ML of
clays and other materials, in which a good agreement is found between the theoretical and experimental results.

(vii) Till now, the prolonged ML has been observed only after the fracture of solids. It will be interesting and useful if the intense prolonged ML will be observed after the elastic deformation of solids.

(viii) The expressions derived for the time dependence of ML intensity based on the dislocations having large number of relaxation times are as given below:

\[ I = I_0 t^{-\tau} \quad \text{(for low and medium values of time)} \]

and,

\[ I = I_1 \exp(-\psi t) \]

Expressions derived for the time dependence of ML intensity based on the dislocations having limited number of relaxation times are as given below:

\[ I = I_1 \exp(-\psi_1 t) + I_2 \exp(-\psi_2 t) \]

and,

\[ I = I_1 \exp(-\psi_1 t) + I_2 \exp(-\psi_2 t) + I_3 \exp(-\psi_3 t) \]

where \( \psi_1 = 1/\tau_1 \), \( \psi_2 = 1/\tau_2 \), and \( \psi_3 = 1/\tau_3 \).

(ix) The time dependence of the ML intensity of the clays and other materials studied in the present investigation have two or three values of the ML decay times and thus the time dependence of the ML intensity follows the expressions derived for the time dependence of ML intensity based on the dislocations having limited number of relaxation times.