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NOTES

INDUCED THERMOLUMINESCENCE OF SOME CLAY MINERALS

Key Words—Thermoluminescence, Smectite, Kaolin, Attapulgite, Cations.

INTRODUCTION

Thermoluminescence (TL) is the release of energy in the form of light by the thermal activation of naturally occurring or artificially induced charge carriers, either "trapped electrons" or "holes" created during the ionization of elements in various compounds. Luminescence of minerals brought about through heating has been studied since the 12th century (Marfunin, 1979). Robert Boyle wrote of his observation of the luminescence of a diamond when it was warmed by body heat or by the flame of a candle (McKinley, 1981).

Currently, the primary use of TL is in radiation dosimetry, chiefly in radiotherapy, the control of health hazards, and the dating of archaeological artifacts and geological events. Because archaeological materials such as pottery are the main substances being used for TL dating, Siegel *et al.* (1968) investigated the thermoluminescence of the clay raw materials. Kaolinites, illites, and montmorillonites from the American Petroleum Institute standard clay minerals were used in that investigation because their chemical and mineralogical compositions had already been published. All of the samples used by Siegel *et al.* (1968) were studied "as received" and hence contained not only the clay mineral, but other minerals as well. The resultant TL was thus a result of all the minerals present.

In the present study the following source clays from The Clay Minerals Society were examined after sedimentation to remove non-clay components: (1) Na-montmorillonite from Wyoming (SWy-1); (2) Ca-montmorillonites from Texas (STx-1) and Arizona (SAz-1); (3) California hectorite (SHCa-1); (4) attapulgite from Florida (PFl-1); and (5) well-crystallized (KGa-1) and poorly crystallized (KGa-2) kaolin from Georgia.

The phenomenon of TL may be represented as a three-step process (Figure 1). The first step is the ionization of elements in the crystal structure when the sample is exposed to sufficiently energetic radiation. Some electrons remain in higher energy levels after the radiation has been removed until they are supplied with sufficient energy to enable them to escape and diffuse through the structure until they recombine with a hole at a "luminescence center." The energy of such recombination is released as visible light. However, the energy of recombination may be released in the form of heat, without the emission of a photon. Such recombination sites are termed "non-luminescence" or "killer" centers (Aitken, 1974).

The Schrodinger equation for electrons in a "box" of infinite dimensions assigns specific energy bands which these electrons are allowed to occupy. Because crystals are not infinite, it is necessary to introduce boundary conditions to the equations to obtain solutions forbidden in the infinite crystal. The introduction of boundary conditions gives solutions to the equation which predict the presence of energy states localized on the surface of the crystals that are capable of trapping or releasing electrons. Such surface-charge carriers are important in varying the charge region around a crystal. For a clay particle, such variations in the electrical double-layer severely regulate the physical and chemical properties of clay, and the influence of the space-charge potential barrier can be far-reaching. For semiconductors and insulators, the influence of the space-charge region is about 10^4 Å (Somorjai, 1972).

The density of this space-charge is readily determined by zeta potential measurements; however, such an analysis gives only the density of the adsorbed counter-ions and not the origin of the surface charge. Electron spin resonance (ESR) studies provide information as to the nature of crystal defects and interlayer cation positions (McBride *et al.*, 1975). However, ESR measurements only pertain to elements which contain unpaired electrons, either those elements in the crystal structure or dimagnetic exchangeable cations introduced to the clay.

The purpose of this investigation was to determine how different degrees of crystallinity and different exchangeable cations affect the TL glow curves of various clay minerals.

EXPERIMENTAL

Instrumentation

Robert Boyle's study of diamond demonstrated that some TL can be observed by the unaided eye. More often, TL signals are weak and must be amplified (Figure 2). The samples investigated here were placed on an aluminum sample pan under the photomultiplier tube. A thermocouple was positioned directly under and in intimate contact with the aluminum sample pan, and the temperature was registered on the X-axis of an X-Y plotter. Gaseous nitrogen was supplied to the sample compartment in order to remove oxygen and to cool the photomultiplier tube, thereby eliminating sample oxidation and providing the photomultiplier tube with a steady temperature state. The signals detected by the photomultiplier tube were amplified and plotted on the Y-axis of the X-Y plotter.

Three different TL curves were obtained from each sample (Figure 3). An artificial or induced-TL curve was obtained after a sample had been exposed to a known radiation source; a natural TL curve was obtained by heating a sample which had not been radiated except for those sources present in nature; and a black-body or "red-glow" curve was obtained when the sample and sample pan began to glow red at high temperatures. The black-body curve was determined on samples that had previously been bleached of their natural or induced TL by heating. The glow curves reported here are induced TL curves only.

Procedure

One percent dispersions were prepared for each clay described in Table 1 and allowed to settle for 48 hr. The top 500 ml of the two-liter suspensions were then siphoned off, converted to a sodium or calcium form as described below, oven dried at 85°C, reground to pass through a 270 mesh sieve, and allowed to equilibrate with a 50% RH atmosphere for 48 hr.

The smectites were converted to the sodium form by passing them through an exchange column of Na-charged Dowex 50 W-X8 exchange resin at 60–70°C. Calcium forms of the smectites were prepared by adding $CaCl_2$ directly to the clay suspensions, which were then placed in a high-speed Waring Blendor for 15 min. Each was then repeatedly washed with deionized water and centrifuged until no chloride ions were detected in the clear liquid by the $AgNO_3$ test. X-ray powder

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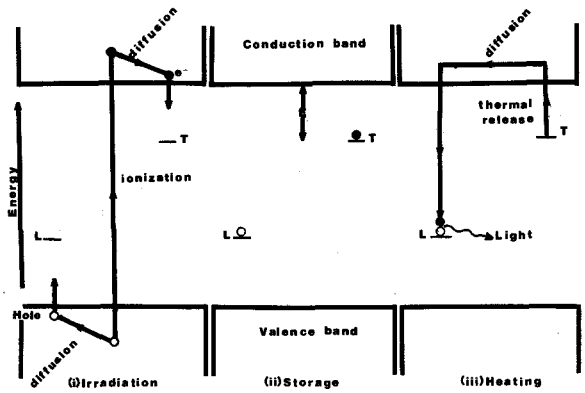


Figure 1. Schematic representation of the three-step process of thermoluminescence.

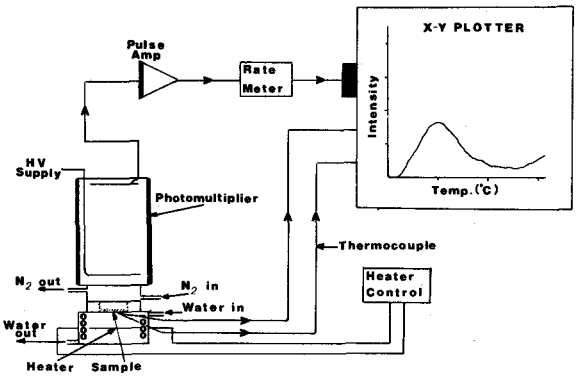


Figure 2. Schematic diagram of thermoluminescence apparatus.

diffraction studies were made on all samples to confirm the mineralogical purity of each; no crystalline impurities were detected in any of the samples. The samples were then mixed with silicone oil, producing a 1:1 oil-to-clay ratio by weight. The clay-oil mixtures were then applied to the sample pans using a fine-tipped paint brush while spinning the sample pan on a turntable. The intensity of each TL glow curve was found to be dependent on the surface area of the sample and independent of sample thickness. The temperature of the TL signal was dependent on the sample thickness. A sample thickness of $\geq$2 mm was required before a change in the temperature of a TL signal was noted.

TL is a measure of events which occur in a sample that are brought about through intense heating. In a clay sample, many TL events are irreversible (e.g., dehydration, structural collapse, alteration) when the clay is heated to 325°C in a silicone oil medium. Thus, the physical and chemical properties of the clay are different after heating, and a second TL spectrum made on the same sample will generally be different. Eight samples of each clay were therefore prepared. One sample of each clay was used to determine any natural TL. No natural TL was observed for any of the clays examined. Induced TL determinations were made on the remaining seven samples and averages calculated. Each sample was exposed for 2.5 min to tungsten X-radiation (0.9 ma, 30 kV), and glow curves were made immediately after exposure. A constant heating rate of 3.6°C/sec was maintained by using a DATA-TRAK card programmer.

RESULTS AND DISCUSSION

Three TL parameters are easily obtained from a TL glow curve: (1) peak temperature, (2) peak intensity, and (3) peak width at its half height. The trap depth, may be estimated from:

$$\bar{E} = kT^2/W_{\frac{1}{2}}$$

where $\bar{E}$ is the average energy of the electron trap, k is the Boltzmann constant (8.62×10^{-5} eV/K), T is the absolute temperature of the glow peak, and $W_{\frac{1}{2}}$ is the width of the glow curve at its half height (Marfunin, 1979).

Temperature and trap depth

Results of the thermoluminescence studies of the clays are shown in Tables 2 and 3. Most noticeable in Table 2 (smectites) is the influence of exchangeable cations on the position of a peak in a TL emission curve and on the energy of the electron traps. The peak temperatures and trap energies of all Ca-exchanged smectites are greater than those of their Na-exchanged counterparts. Because of their small particle size, electron traps in clay samples are considered as surface phenomena. Therefore, the traps are affected by surface cations and their respective hydration spheres, which implies that the stability of electron traps in clays depend, in part, on the separation between an electron trap and an adsorbed cation. Whether or not this adsorbed cation will eventually recombine with the electron and participate in the TL process as an emission center depends on the recombination process. For hydrated cations, the charge separation is a function of ionic radii and the radii of hydration spheres. Therefore, as thermal energy is supplied to the system, the sphere of hydration decreases, the charge separation between the electron trap and cation also decreases, and the Coulombic attraction increases. The rate of dehydration is a major influence in determining where a TL glow peak occurs, with respect to the temperature and the energy of the electron trap between. For Ca-smectites, complete dehydration occurs in between 100° and 150°C, whereas Na-smectites dehydrate at lower temperatures (Zettlemoyer, 1965), is in accord with our TL observations, and suggests a relationship between trap stability and the type of surface cation.

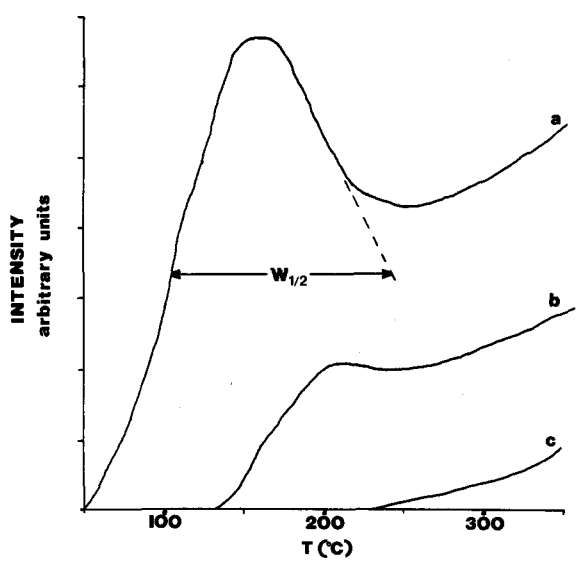


Figure 3. Representative glow curves (for clay pottery). a. induced thermoluminescence, b. natural thermoluminescence, c. black body or "red glow" thermoluminescence.

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Table 1. Description of clays investigated by thermoluminescence.

Clay	Origin	Distinguishing characteristics
Na-montmorillonite SWy-1	Newcastle Formation, Crook County, Texas	Predominantly Na exchangeable cations. CEC = 76.4 meq/100 g, Si/Al = 1.0/0.31. Moderately high Fe_2O_3 and MgO concentrations (3.35 and 3.05%, respectively).
Ca-montmorillonite STx-1	Manning Formation, Gonzales County, Texas	Predominantly Ca exchangeable cations. CEC = 84.4 meq/100 g, Si/Al = 1.0/0.23. Low Fe_2O_3 concentration (0.65%) and moderately high MgO concentration (3.69%).
Ca-montmorillonite SAz-1	Bidahochi Formation, Apache County, Arizona	Predominantly Ca exchangeable cation. CEC = 120 meq/100 g, Si/Al = 1.0/0.29. Low Fe_2O_3 concentration (1.42%). High MgO concentration (6.46%).
Hectorite SHCa-1	Red Mountain Andesite Formation, San Bernardino County, California	CEC = 43.9 meq/100 g, Si/Al = 1.0/0.02. Low Fe_2O_3 concentration (0.02%). High MgO concentration (15.3%). High CaO concentration (23.4%).
Attapulgite PFl-1	Hawthorne Formation, Gadsden County, Florida	CEC = 19.5 meq/100 g, Si/Al = 1.0/0.17. Moderate Fe_2O_3 concentration (2.98%). High MgO concentration (10.2%). CaO concentration (1.98%). Small amounts of smectite present.
Kaolin KGa-1	Tuscaloosa Formation? (Uncertain stratigraphy), Washington County, Georgia	CEC = 2.0 meq/100 g, Si/Al = 1.0/0.90. Low Fe_2O_3 and MgO concentrations (0.13 and 0.03% respectively). Well crystallized.
Kaolin KGa-2	Lower Tertiary? (Uncertain stratigraphy), Warren County, Georgia	CEC = 3.3 meq/100 g, Si/Al = 1.0/0.88. Low Fe_2O_3 and MgO concentrations (0.98 and 0.03% respectively). Poorly crystallized.

Samples from Source Clay Repository of The Clay Minerals Society. Data from van Olphen and Fripiat (1979).

The temperatures of TL glow peaks determined for the non-smectite minerals (Table 3) are similar to those of the Na- and Ca-smectites. The estimated trap depths for the kaolins are about twice that for the smectites and attapulgite, with the well-crystallized kaolinite having the highest trap energy of all of the samples investigated. The difference in trap energies between the well-crystallized and poorly crystallized kaolin samples shows clearly how degree of crystallinity can influence trap energy. The trap energies for attapulgite are similar to those estimated for smectites. The attapulgite sample may contain some smectite (van Olphen and Fripiat, 1979) which could account in part for the two peaks observed. However, the extent of the contribution to the TL spectra made by smectite in the attapulgite sample has yet to be determined.

Intensity and half-width

The intensity of a TL glow curve is indicative of the relative number of electron traps in a sample. The half-width of a TL emission spectrum provides information as to the diversity of trap energies present within a sample (Marfunin, 1979). The TL glow curve of the smectites investigated is representative of no single peak, but is a summation of several unresolved peaks. The TL emission spectrum of the attapulgite shows two partially resolved peaks, both of which have intensities and half-width values similiar to those obtained from the smectites. The intensities and half-width values of the kaolinite samples are quite small in comparison with the smectites, indicating that few defects are present, relative to the smectites, and that the electron traps established by these defects have

Table 2. Thermoluminescence emission spectra parameters of the smectite samples.

	Peak temperature (°C)		Relative intensity (%)		Half-width (°C)		Trap energy (eV)	
	Na	Ca	Na	Ca	Na	Ca	Na	Ca
Na-montmorillonite SWy-1	107	140	62	100	131	89	9.5×10^{-2}	1.7×10^{-1}
Ca-montmorillonite STx-1	110	150	62	72	111	105	1.1×10^{-1}	1.5×10^{-1}
Ca-montmorillonite SAz-1	100	147	55	48	100	104	1.2×10^{-1}	1.5×10^{-1}
Hectorite SHCa-1	108	140	60	77	146	95	8.5×10^{-2}	1.6×10^{-1}

[1] Relative intensities reported as a percentage of the Ca-exchanged Wyoming smectite.

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Table 3. Thermoluminescence emission spectra parameters of the non-smectite samples.

	Peak temperature(s) (°C)	Relative intensity (%)[1]	Half-width (°C)	Trap energy (eV)
Attapulgite PFl-1	110, 150	82, 72	80, 105	1.6×10^{-1} 1.5×10^{-1}
Kaolin (well crystallized) KGa-1	110	17	17	4.2×10^{-1}
Kaolin (poorly crystallized) KGa-2	110	2	2	3.6×10^{-1}

[1] Relative intensities reported as a percentage of the Ca-exchanged Wyoming smectite.

energy differences which are closer than those in smectites. Smectites and attapulgite have a large number of electron traps with trap depths that vary extensively in energy. With the exception of the Arizona smectite, Ca-exchanged smectites have smaller half-widths and larger TL intensities compared to Na-exchanged form. The Ca-smectite from Arizona has a lower TL intensity and a broader half-width, but the changes were small when compared to the changes involved in the other smectites, demonstrating the ability of Ca-exchangeable ions to stabilize traps over Na cations. The higher intensity of the Ca-smectites shows that the Ca cation "preserves" trapped electrons which are able to escape when the smectite is in its Na-form. Ca-exchanged smectites vary less with respect to trap energies than their Na-exchanged analogues.

SUMMARY AND CONCLUSIONS

The TL parameters of smectites are not only affected by substitution, vacancy defects, and degree of crystallinity as shown in previous TL studies of non-clay minerals (Daniels, 1968; Marfunin, 1979), but also by the type of exchangeable cation present on the clay. From the TL glow curves it is evident that Ca-exchanged clays have electron traps of higher energy than Na-exchanged clays. Ca-smectites also possess more electron traps; these traps have energies which do not vary as much as those in the Na-smectites.

Attapulgite shows a TL signal similiar to that of smectites. The signal differs from that of the other clays studied in that it has two partially resolved peaks, whereas only one peak is present in the spectra from the other clays. This is possibly due to the presence of smectite in the attapulgite sample. Kaolinites primarily show how the TL spectra of a sample depends on its degree of crystallinity. The sample of poorly crystallized kaolinite shows a barely perceptible TL signal, whereas the well-crystallized kaolinite gives a moderately intense, well-defined peak. Both kaolinites have trap energies much greater than the other clays studied. The lower intensities of the two kaolinite samples can be attributed partly to the low amount of structural substitutions in these two clays.

Further TL studies of clay minerals are needed with emphasis on correlating the TL curves with ESR and XRD data. Such studies should give new insight into the "defect" structure of clays and how these defects are related to cation exchange and surface properties.

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