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THERMOLUMINESCENT PROPERTIES OF MICA

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Abstract—Natural as well as β-induced thermoluminescence (TL) of mica of the muscovite type $KAl_2(AlSi_3O_{10})(OH)_2$ was investigated. Two main glow peaks were found, as about 150° and 260°C. The 260°C peak is the prominent one in the natural TL curve while the 150°C peak is dominant in the laboratory induced TL. Both curves could be interpreted in terms of two traps with activation energies of 0.75 and 0.97 eV, which are exhausted through a second order process. u.v. phototransfer experiments indicated the existence of additional, deeper traps, undetectable by the regular TL measurements. Dose dependence studies showed a slightly superlinear behaviour. Possible applications to dating in archeology are discussed.

1. INTRODUCTION

MICA is a group of silicate minerals with a layered structure. Its general formula is $(K, Na)X_nALSi_3O_{10}(OH, F)_2$ where X may be Al^{3+}, Mn^{2+}, Mn^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Ti^{4+}, or Li^+ (Pauling, 1960). Muscovite is a common mica of a dioctahedral structure. Its formula is $KAl_2(AlSi_3O_{10})(OH)_2$. It was classified by McDougall (1968) as a very weakly thermoluminescent mineral. Indeed, little has been published so far on the thermoluminescence (TL) of mica despite the possible dating applications which will be mentioned below. Nishita *et al.* (1974) investigated natural TL in muscovite and found a very weak peak at about 220°C and a slightly stronger one at 350°C. Mukhlya *et al.* (1977) suggested that by studying the thermoluminescent properties of muscovite, its stage of mineralization can be determined.

TL studies of mica might be interesting from a fundamental point of view as well. Because of its layered structure, the comparison to other types of silicate, such as quartz and feldspars, may provide information about the motion of charge carriers in anisotropic crystals. The purpose of this work was to study the basic features of the natural and laboratory-induced TL in muscovite and to evaluate the kinetic parameters of the TL peaks.

2. EXPERIMENTAL

The samples were extracted from a granite-pegmatite pre-cambrian rock, and identified with a polarizing microscope as mica of the muscovite type. The age of the rock was estimated by radioactive measurements as 597 ± 1 My (Halpern and Tristan, 1981). For our measurements single crystals in the form of flat flakes, of about 0.25 cm^2 cross section and 0.1–0.2 mm thickness were used. The mass of each flake was 7–14 mg. Several such flakes, of a total mass of about 50 mg were used for each measurement. The samples were heated in a dry nitrogen atmosphere, from room temperature to 500°C, at a constant heating rate (usually 5°C/s). The TL signal was detected by a photomultiplier (EMI 6255), amplified by a Kiethley 410 micro-microammeter and recorded by an X–Y recorder as function of temperature. Both natural and laboratory-induced TL were studied. A ^{90}Sr-^{90}Y beta-source (10 mCi) was used for the irradiation. The dose rate at the sample was about 20 rad/h. For the u.v. irradiations a low pressure Hg lamp with appropriate filters for the 254–365 nm region was used.

3. RESULTS

3.1. *Natural and beta-induced TL*

All the samples were found to exhibit strong "natural" TL when first heated from room temperature to about 500°C. For a heating rate of 5°C/s

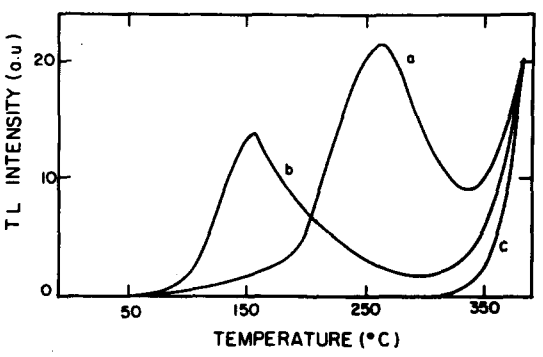

FIG. 1. Natural TL of muscovite (a), TL following 1 krad β-irradiation (b), and the black body radiation of the sample (c).

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Table 1. The kinetic parameters of the two main TL peaks in muscovite. E is the activation energy, s the frequency factor and b the order of reaction

Peak	T(°C)	E(eV)	$s(s^{-1})$	b
1	150 ± 10	0.75 ± 0.04	$5 \times 10^7 - 5 \times 10^8$	2
2	262 ± 5	0.97 ± 0.1	$1 \times 10^8 - 1 \times 10^9$	2

the main peak appeared at about 260°C. This TL peak is shown in Fig. 1a. Figure 1b presents a laboratory-induced glow curve of the same sample, following a 1 krad beta-irradiation. This curve contains a prominent peak with a long high temperature tail. The peak temperature was found to depend slightly on the sample, and varied between 140 and 160°C. The intensity of both the natural and beta-induced TL was too low to enable a proper spectral analysis, however, by using optical filters we found that a large portion of the light output was in the blue region. Figure 1c shows the black body radiation of the sample.

The dependence of the TL intensity on the radiation dose was investigated over two orders of magnitude (20–2000 rad) and was found to be slightly superlinear: $I_m = \alpha D^{1.08}$, where I_m is the maximum TL intensity and D is the irradiation dose. This behaviour is characteristic of second order peaks when n_0 is proportional to the dose (Chen and Kirsh, 1981).

3.2. *Kinetic analysis*

The kinetic parameters of each peak, namely the activation energy, E, frequency factor, s, and order of reaction, b, were evaluated by a best-fit programme (Chen and Kirsh, 1981). This programme seeks the parameters by which the peak can be optimally described if a "general-order" equation

$$-dn/dt = n^b s' \exp(-E/kT), \qquad (1)$$

is assumed. The light intensity I is proportional to $-dn/dt$, where n is the number of trapped charge carriers. The solution for $I(T)$ contains the parameters E, b, β (the heating rate) and the frequency factor s, where $s = s' n_0^{(b-1)}$ and has the dimensions of s^{-1}.

Applying the best-fit procedure to many TL curves yielded activation energies of 0.87–1.07 eV for the 260°C "natural" peak and 0.71–0.79 eV for the 150°C "artificial" peak (see Table 1). The reaction order was fitted by the programme in the range 0.7–2.5 and was found to be 2 for both peaks. The frequency factors, s, computed for different samples, were found to vary within an order of magnitude for both peaks (Table 1). It should be remembered, however, that for a second-order peak s is not a constant, but rather depends on n_0 which might vary with the sample and the irradiation dose.

The best-fit procedure is very useful for the separation of overlapping peaks and the study of small "satellites" covered by a major peak. Indeed it enabled us to show that the 150°C peak appears in the natural glow curve as well, covered by the rise of the strong 260°C peak. This is demonstrated in Fig. 2 where the dots represent the experimental results (the black body radiation subtracted) the continuous line is the theoretical expression for the 150 and 260°C peaks, and the dotted line their sum. The agreement is good, except for the 300–370°C region where the difference between the experimental and theoretical curves implies the existence of an additional small peak at about 350°C. However, due to the rise of the black body radiation, this temperature range appeared to be difficult to study.

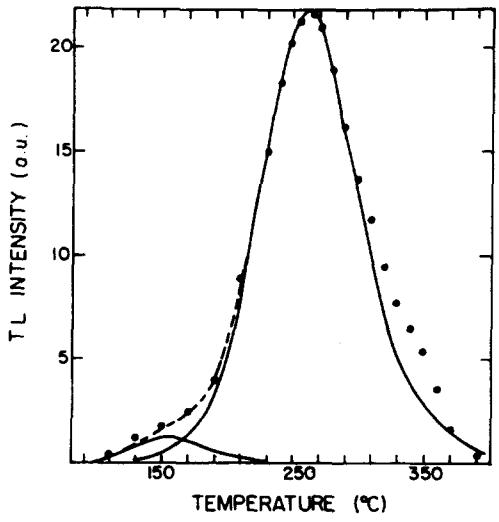

FIG. 2. The best-fit of the "natural" glow curve to the theoretical expression for general order kinetics. The dots represent the experimental results after the subtraction of the black body radiation. The continuous line describes theoretical peaks with the parameters appearing in Table 1, and the dotted line their sum in the range 110–220°C.

Figure 3 shows the result of applying the best-fit procedure to the 150°C peak. The fit is very good over the temperature range 50–170°C, but the long

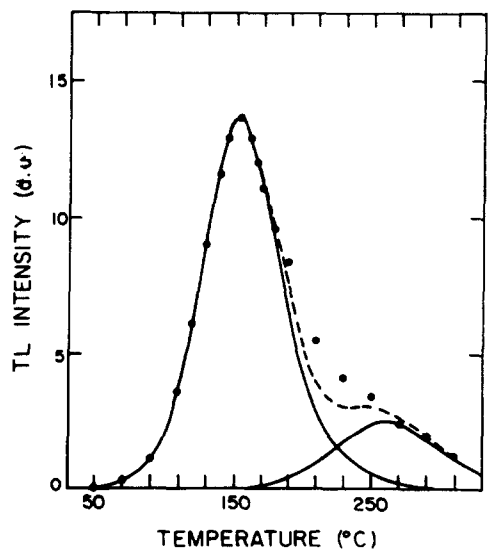

FIG. 3. The best-fit of the β-induced TL curve to the theoretical expressions.

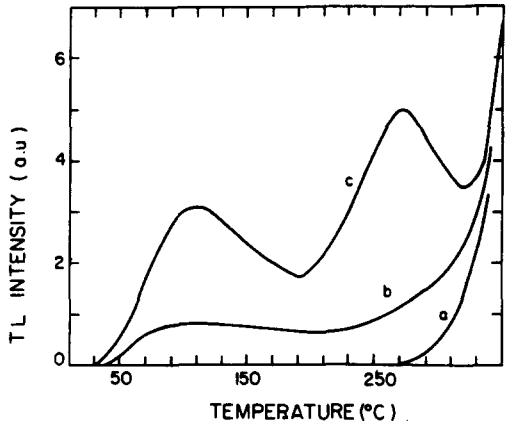

FIG. 4. Glow curves of samples exposed to u.v. light for 3 h, (a) after heating to 700°C, (b) after β-irradiation and heating to 400°C, and (c) of natural samples prior to heating and to the first TL measurement.

high-temperature "tail" is only partly explained by the 260°C peak; at least one additional small peak should be there to account for the discrepancy at the 190–250°C range.

3.3. *Effects of u.v. irradiation*

The irradiation of the samples by low energy u.v. light induced no detectable TL, provided that the sample was annealed at a temperature higher than 500°C prior to the u.v. irradiation. This is shown in Fig. 4a. However, when the sample was β-irradiated at room temperature, heated to about 400°C, and then irradiated by u.v. at room temperature, TL was observed on the subsequent heating. The resulting glow curve is depicted on Fig. 4b. The TL is quite weak, and consists of a broad structure between 70°C and the rise of the black body radiation. A similar glow curve appeared when a sample was exposed to u.v. light after measuring the natural TL, providing that it was not heated to a temperature higher than 450°C in the first measurement.

The exposure of a sample to u.v. light for several hours after the β-irradiation, was found to reduce the TL intensity and to change the shape of the curve to a somewhat broader peak. When an untreated sample was illuminated by u.v. prior to its first run, the 260°C peak was weaker but the lower temperature peak was more prominent. This is shown in Fig. 4c, in which the TL curve of a sample which was illuminated by u.v. light for 3 h before the first measurement, is described. The height of the 260°C peak is only 5 units compared to more than 20 in Fig. 1a, although the samples were similar. The low temperature peak became somewhat stronger and its temperature shifted to about 110°C.

4. DISCUSSION

Both the laboratory induced TL in muscovite and its natural TL (apparently due to radioactive isotopes in the granite-pegmatite rock matrix) can be interpreted in terms of the same discrete spectrum of traps. The two main peaks at about 150 and 260°C are associated with traps having the activation energies 0.75 and 0.97 eV, respectively.

In the lab-induced curve the 150°C peak is about five times more intense than the 260°C one (Fig. 3). If we assume that for both peaks the TL is proportional to n_0, the initial number of trapped charge carriers, it means that the first trap is filled more efficiently by the irradiation. This might be due to different cross-sections for traping charge-carriers, or to the different concentrations of the two traps in the crystal. In the natural TL curve, on the other hand, the 260°C peak is the main one and the 150°C peak is barely detectable (Fig. 2). This is readily explained by the difference in activation energies. At room temperature, the ratio between the factors $\exp(-E/kT)$ for the two traps is 2×10^{-4}. From the values of s in Table 1 and from estimations for n_0 we deduced that s' for the 0.97 eV trap cannot be larger than that of the 0.75 eV trap by more than ~ 5. Thus, for a given population of trapped charge carriers, the escape-probability from the deep trap is smaller by more than three orders of magnitude than from the shallower one. This explains why the 0.75 eV trap is thermally agitated at ambient temperatures, while the 0.97 eV trap, related to the 260°C peak, remains stable.

The fact that the u.v. irradiation by itself (~ 5 eV photons) failed to stimulate any observable TL in our samples, is in accord with the known value of about 9 eV for the energy gap in muscovite (Davidson and Vickers, 1972).

The results of the phototransfer experiments (Fig. 4) can be accounted for by assuming a third, deeper, trap which is thermally stable up to 500°C (where the black body radiation prevents TL measurements). This trap can be filled by the natural radiation, as well as by laboratory β-irradiation. In both cases, the subsequent illumination of the sample with 5 eV photons causes phototransfer of charge carriers, from this trap to the shallower traps associated with the 150 and 260°C peaks. This explains the fact that the u.v. illumination was found to induce TL in samples which had been heated to 400°C following β-irradiation (Fig. 4b), but not in samples which had been heated to 500°C.

The shift of the first peak to a lower temperature following the exposure to u.v. light (~ 110°C in Fig. 4c) might be explained as follows. The u.v. causes the transfer of charge carriers from a defect "X", which is stable up to 500°C, to another defect "Y" which forms the 0.75 eV trap. It seems that this process preferably fills a sub-class of the Y traps, which are close to X defects. Due to this proximity the Y traps are now somewhat shallower on the average and the TL peak occurs at a lower temperature.

The fact that the TL intensity of untreated samples (Fig. 4c) or β-irradiated samples, was found to reduce

by exposure to u.v., indicates that the u.v. light frees charge carriers not only from the "deep" putative trap, but from the 0.75 and 0.97 eV traps as well.

4.1. *Possible applications in dating*

In geology, mica is usually found in magmatic rocks. Our samples were collected from rocks which were formed $\sim 6 \times 10^8$ years ago. This is much longer than the periods which are considered suitable for TL dating. Since no thermal events are known which could drain the traps and enable the dating of younger occurrences, the TL of mica seems to have no direct use in geochronology.

As for archaeology, mica was found in ancient objects from different periods and locations. For example, Srirath and Fremlin (1968) found mica grains in stones which were used as "pot boilers" in the Birmingham area around 400 BC. Porat (1984) found mica in pottery cooking pots of the 3rd millenium BC, from the Negev in southern Israel. It should be mentioned, however, that mica is usually less abundant than other crystalline minerals embedded in the clay. We have found, for example, that mica (muscovite and biotite) amounts to only $\sim 5\%$ of the crystals in the surface of a typical pottery sherd from the Negev; about 60% were quartz and 30% feldspars. This, and the low thermoluminescent efficiency of mica compared to common minerals such as quartz, calcite and feldspars, will not make it the first choice of a dating practitioner. However, it might be useful for double checking, or when other minerals fail to give consistent answers.

Our results indicate that the 260°C peak might be suitable for archaeological dating, although more research is needed in order to establish the fading properties of this peak, for example.

Phototransfer seems to be less appropriate as a dating technique, since the u.v. light used by us was found not only to transfer charge carriers from the trap of the assumed 500°C peak to the two shallower traps, but to deplenish these two traps as well. This influence of the u.v. light should be remembered if the dating of samples which have been exposed to sunlight is attempted.

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