

QUANTITATIVE DETERMINATION BY DIFFERENTIAL THERMAL
ANALYSIS OF THE HEAT LIBERATED
IN THE THERMOLUMINESCENCE OF NATURAL CALCITE

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The paper presents results of the experimental determination of the quantity of heat liberated during the thermoluminescence (TL) of natural calcite.

As the method for experimental investigation, quantitative differential thermal analysis was used, in which the reference was natural calcite which had previously been thermally treated at 623 K for 60 min to eliminate the TL effect.

It was established that during the TL of natural calcite 7.11 J/g is liberated, which is in accordance with results obtained by estimating possible values of the concentration of charge carriers at trapping centers and the energy liberated by elementary recombination process.

It is widely known that natural calcite has the capability of thermoluminescence (TL), which is manifested by emission of light during heating of the mineral, before the temperature of red heat [1]. During the TL process, the energy of ionized radiation accumulated in calcite is transformed into heat and optical radiation [2]. Depending on the optical properties of the mineral and the conditions under which the light is emitted, a part of the light energy is always transformed into heat, because of absorption in the mineral itself. It must be borne in mind, too, that the heating of calcite mineral leads in certain cases to changes in the position and the structure of trapping centers, which may also be followed by liberation of heat [3, 4].

In this paper the authors have tried to determine quantitatively the quantity of heat liberated in the TL process, using differential thermal analysis (DTA) as a method of experimental investigation.

Experimental

For experimental investigations natural calcite was used from a copper-bearing deposit in the vicinity of Bor, Yugoslavia. The sample studied consisted of calcite (99%) and quartz (0.5%). For recording of TL curves, an RCA 6199 photomultiplier was used. The sample heating rate was 5°/s.

Quantitative DTA was carried out with equipment in which the reaction spaces are situated in a Ni-block [5]. All experiments with the DTA equipment were carried out at the heating rate of 45°/min in an atmosphere of air.

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Results and discussion

Figure 1 shows the TL curve of the calcite mineral sample studied; it was obtained at a heating rate of 5°/s and a photomultiplier mains voltage of 1 kV. The investigation showed that the sample studied has a very strong natural TL. The colour of the light emitted is orange, which reveals the fact that the activator is Mn^{2+} ion [6]. The content of Mn in the sample was 850 ppm.

In the TL curve (Fig. 1) two peaks appear, the maxima of which lie at 566 and 668 K, respectively. It may also be seen from the Figure that the TL process takes place between 453 and 817 K.

The sample DTA curve was recorded against a reference of calcite which had previously been thermally treated at 623 K for 60 min, so that the TL effect had been completely eliminated. In order to provide for uniform thermal conductivity from the well of the Ni block to the tops of the thermocouples, in all investigations the same sample granulation was used. At the same time, with the purpose of preventing the loss of heat liberated in the TL process, both the sample and the reference were covered by a layer of calcined alumina. This also provided for practically a complete transformation of the emitted light energy into heat.

Figure 2 shows the DTA curve obtained in this way. A clearly defined exotherm may be seen at 769 K, the result of the heat liberated during the TL of the calcite sample studied. It may also be seen from the Figure that the DTA peak is shifted

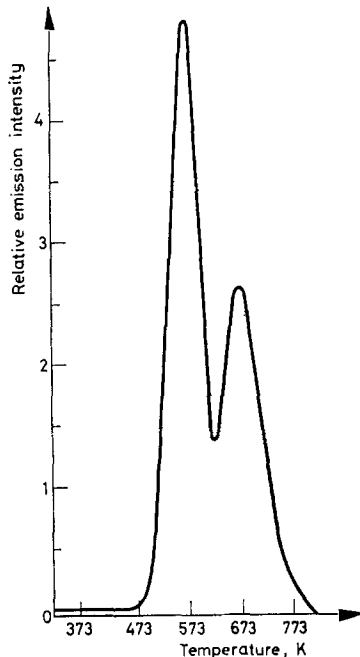


Fig. 1. TL glow curve of natural calcite

towards higher temperatures with regard to the TL peaks, which is explained by the higher inertness of the process of transformation of accumulated energy into heat, as compared to the radiation process [2].

Relatively, large sample masses, a high heating rate, as well as a low thermal conductivity in the sample, result in the appearance of a temperature gradient, so that instead of two DTA peaks, only one is observed.

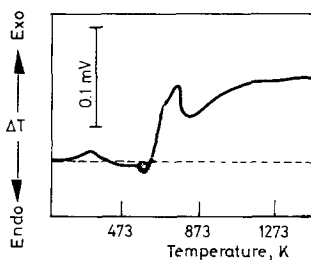


Fig. 2. DTA curve which shows TL of natural calcite (heating rate 45°/min in air)

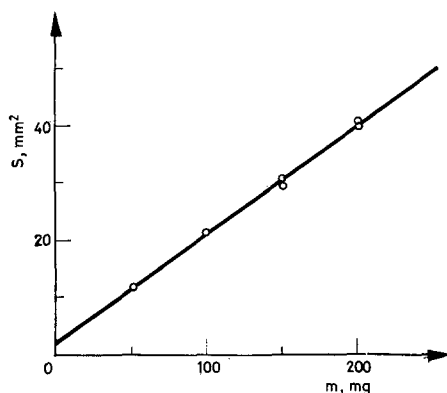


Fig. 3. Relationship between peak area and mass of sample for DTA curve which shows TL of natural calcite (heating rate 45°/min in air)

Since the DTA curve displays a peak which is a result of TL, several DTA curves were recorded with different calcite masses, i.e. 50, 100, 150 and 200 mg.

Figure 3 shows the relationship between areas of the DTA peaks obtained (S) and the masses of thermoactive calcite (m). A linear relationship exists, which may be represented analytically in the following way:

$$S = 0.188 m + 2.50 \quad (1)$$

where:

S = area of DTA peak, mm^2 ,

m = sample mass, mg.

To determine quantitatively the amount of heat liberated during the TL process, calibration of the DTA equipment used was carried out with samples with known thermal effects. These were natural calcite and magnesite minerals with a purity of 99.5% and the same granulation as the calcite sample investigated ($-400 + 160 \mu\text{m}$). For these samples DTA curves were recorded with sample masses of 5 to 15 mg, and the areas of the DTA peaks obtained, which characterize the processes of their thermal decomposition, were compared with the heats ΔH_T° calculated for

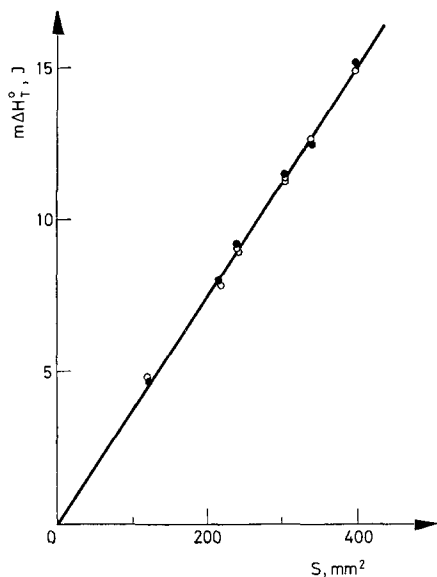


Fig. 4. Relationship between $m\Delta H_T^\circ$ and area of DTA peak for magnesite and calcite (heating rate $45^\circ/\text{min}$ in air); o MgCO_3 ; ● CaCO_3

these processes on the basis of thermodynamic data for the reaction temperatures. From the theory of Speil *et al.* [7, 8] for quantitative DTA, which gives the relationship between the reaction heat and the area of the DTA peak, it follows that

$$m\Delta H_T^\circ = gK_s \int \Delta T dt \quad (2)$$

where:

- m = sample mass,
- ΔH_T° = specific heat of reaction,
- g = constant of geometric shape,
- K_s = thermal conductivity of the sample,
- $\int \Delta T dt = S$ = area of DTA peak.

Figure 4 shows the relationship between the reaction heat (Q) and the area of Fe DTA peak for the thermal decompositions of magnesite and calcite.

With small sample masses the same relationship $Q = f(S)$ is valid for all minerals, while with large sample masses a particular relationship corresponds to each mineral because the calibration constants gK_s [5] are different. The relationship $Q = f(S)$ from Fig. 4 may be given analytically in the following way:

$$Q = 0.162 + 0.03649 S \quad (3)$$

where:

Q = reaction heat, J,
 S = area of DTA peak.

If Eq. (1) is introduced into Eq. (3), a relationship will be obtained between the quantity of heat liberated during the TL of calcite and the mass of the sample studied:

$$Q = 0.253 + 0.00686 m. \quad (4)$$

From expression (4) one obtains that the quantity of heat liberated during the TL of the calcite sample studied amounts to 7.113 J/g.

On the basis of the model of the TL process [9], the total liberated energy per unit mass may be expressed in the following way:

$$Q = \frac{n \cdot \varepsilon}{\rho} \quad (5)$$

where:

n = concentration of charge carriers at trapping centers, cm^{-3} ,
 ε = energy liberated by elementary recombination process, J,
 ρ = density of the sample, g/cm^3 .

Since experimental determination of concentration n and energy ε is very complex, in the following text the validity of the result obtained by DTA will be estimated, based on data mentioned in literature.

The concentration of trapping centers varies in a broad range from 10^{15} to 10^{20} cm^{-3} , and filling up to 10^{19} cm^{-3} , while the energy values vary from $4 \cdot 8 \times 10^{-19}$ to 14×10^{-19} J (3 to 10 eV) [2]. Taking the upper value of the total concentration of charge carriers at trapping centers as $n = 10^{19}$ cm^{-3} , which is in accordance with the prominent TL effect, taking the energy as $\varepsilon = 9.6 \times 10^{-19}$ J (6 eV), and knowing that the density of the calcite sample studied is $\rho = 2.7$ g/cm^3 , we obtain that the heat liberated in the TL process is $Q = 3.8$ J/g. However, if we take $n = 2 \times 10^{19}$ cm^{-3} , considering that during the TL process two peaks are observed, as shown in Fig. 1, we obtain $Q = 7.6$ J/g, which is very close to the result obtained by quantitative DTA.

It should be pointed out that in the quantitative DTA experiment, since the sample was covered by calcined alumina, the conditions favoured transformation of the bulk of the energy liberated as light into heat, because of absorption. It was

assumed in the previous analysis relating to the values of n and ϵ that the total energy liberated during the TL process is transformed into heat.

Such agreement may be considered satisfactory because it is possible that in the liberation of heat during the TL process the mechanism mentioned in the introductory part of the article [3, 4] also takes part; it is not possible to give any reliable data for the contribution of this.

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ZUSAMMENFASSUNG — Die Ergebnisse der experimentellen Bestimmung der während des TL-Prozesses von natürlichem Calcit freigesetzten Wärmemenge werden vorgestellt.

Bei den Versuchen wurde die quantitative Differentialthermoanalyse mit natürlichem Calcit als Referenzsubstanz eingesetzt, welcher vorher bei 623 K 60 Minuten zur Eliminierung des TL-Effekts thermisch behandelt worden war.

Es wurde festgestellt, dass während des TL-Prozesses von natürlichem Calcit 7.11 J/g freigesetzt wurden. Dies stimmt mit den durch Schätzung der möglichen Konzentrationswerte der Änderungsträger in den Einschlusszentren und der durch elementare Rekombinationsprozesse freigesetzten Energie erhaltenen Ergebnissen überein.

Резюме — Представлены результаты экспериментального определения количества тепла, выделяющегося во время термолюминесценции природного кальцита. В экспериментах были использованы количественные методы дифференциального термического анализа, где в качестве образца сравнения был использован природный кальцит, термически обработанный в течении 60 мин. при температуре 623 К для удаления эффекта термолюминесценции. Установлено, что во время термолюминесценции выделяется 7.11 Дж/г тепла и это значение согласуется с результатами, полученными путем оценки возможных значений концентрационного изменения носителей при центрах захвата и энергией, выделяющейся при элементарном процессе рекомбинации.