# EFFECT OF CHROMIUM IONS ON THE THERMOSTIMULATED (EXO) EMISSION OF ELECTRONS AND THE THERMOLUMINESCENCE OF $Al_2O_3$ CRYSTALS

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The thermostimulated (exo)emission of electrons and the thermoluminescence of $Al_2O_3$ and $Al_2O_3+Cr^{+++}$ (0.08% and 0.1%) crystals, previously excited by $X$-rays (Cu, 50 kV, 8 mA) for 30 minutes, were investigated. It was found that there is similitude between the curves of thermostimulated (exo)emission of electrons and the thermoluminescence glow curves.

## 1. *Introduction*

Owing to the interest in lasers, the number of papers dealing with the properties of materials displaying laser action has risen considerably during recent years and still is growing. The methods of (exo)emission of electrons and thermoluminescence has also been applied in tests of materials applied in lasers (Gourgé, Hanle 1957; Low 1965; Sujak, Niklas 1965). These methods can give information on the trap levels and on the state of the surface layer of a crystal (Sujak 1961).

Figure 1 gives by way of illustration a curve of thermostimulated (exo)emission for a sample in the form of a pill, shaped under pressure from $Al_2O_3$ powder (chemically pure). Subsequent experiments proved, however, that the polycrystalline $Al_2O_3$ material formed into pills gives rise to many difficulties during experiments performed in an atmosphere of atmospheric air because of the immense hygroscopicity of the samples. It was decided, therefore, to study single crystal samples instead.

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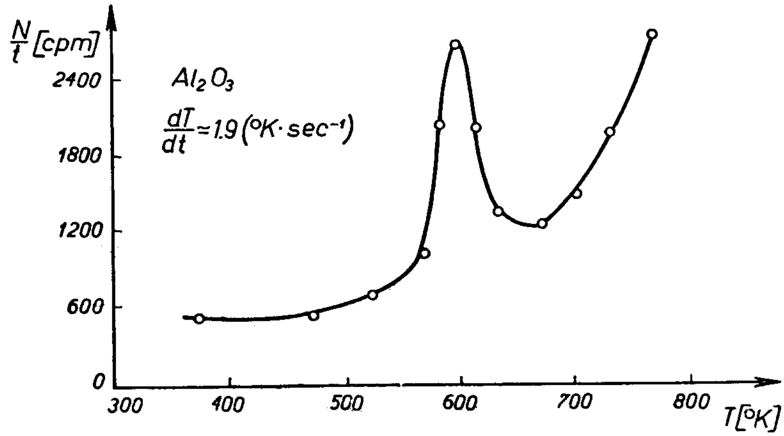


Fig. 1. Curve of thermostimulated (exo)emission of electrons $\frac{N}{t}$ for pills of $Al_2O_3$ powder after excitation by $X$-rays

## *2. Apparatus*

The (exo)electrons were detected by means of an open point counter with the quenching vapour over the free surface of ethyl alcohol. Closer details concerning the design of the counter applied can be found in the papers: Stępniowski, Piróg, Sujak (1963), Piróg, Stępniowski, Sujak (1964), Stępniowski, Sujak (1964), Podolak, Stępniowski, Sujak (1964) and Stępniowski (in press). The thermostimulated (exo)emission of electrons was investigated by means of a conventional system (Sujak 1958) with some small improvements. Thermoluminescence was measured in a separate measuring cycle, but the same furnace as in thermostimulated (exo)emission of electrons was used. A control device ensured linear increase of the furnace temperature in time. The samples were heated at a constant rate of about 1.2 degrees/sec. within the temperature range 300°K to 720°K. The accuracy of the temperature measurement was 10°K. The thermoluminescence was measured with an *FEU*-27 photomultiplier. The current intensity of the photomultiplier I, after being amplified by the *CD* amplifier, was recorded automatically and continuously on recording tape. Before measuring the thermoluminescence or thermostimulated (exo)emission of electrons, the samples were irradiated with $X$-rays (Cu, 50 kV, 8 mA) at room temperature for 30 minutes. During the measurement of (exo)emission of electrons the strength of the accelerating field between the base of the sample and the grid of the counter amounted to 100 V/cm.

## *3. The samples*

The tested samples were cut out in the form of discs, 0.6 cm in diameter and 0.15 cm high, from single crystals of $Al_2O_3$ and $Al_2O_3$ with a content of 0.08 per cent and 0.1 per cent (by weight) of $Cr_2O_3$, respectively. The $Al_2O_3$ and $Al_2O_3+Cr^{+++}$ crystals were breeded at the Aluminium Works at Skawina. In order to remove the impurities which appeared on the surfaces due to processing with abrasive powders, the samples were rinsed before use

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in measurements in nitric acid and then in distilled water, after which they were heated to a temperature of 700°K.

The samples prepared thus displayed (exo)emission of electrons after having been irradiated by $X$-quanta. In the preliminary cycle of measurements, it was found that the character of the curves of thermostimulated (exo)emission of electrons and the thermoluminescence glow curves of ground samples was the same as for cleaved samples, hence, samples which were not submitted to the grinding process.

## 4. *Result of measurements*

Th $Al_2O_3$ crystals and the $Al_2O_3+Cr^{+++}$ (0.08% and 0.1%) crystals, in the form of samples 0.6 cm in diameter and 0.15 cm high, having been previously excited by $X$-rays, exhibited thermostimulated (exo)emission of electrons $\frac{N}{t}$ and thermoluminescence $I(t)$. Figure 2 present the curves of thermostimulated (exo)emission of electrons and the thermo-

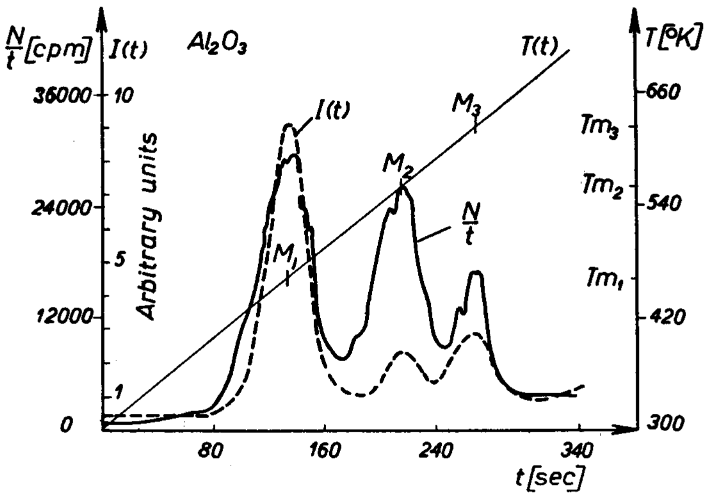


Fig. 2. Curves of thermostimulated (exo)emission of electrons $\frac{N}{t}(t)$ and thermoluminescence glow curves $I(t)$ for $Al_2O_3$ after excitation by $X$-rays (Cu, 50 kV, 8 mA)

luminescence glow curves for $Al_2O_3$ without a chromium admixture. Figure 3 gives the same curves for $Al_2O_3+Cr^{+++}$ (0.08%). As is seen, the curves of thermostimulated (exo)-emission of electrons and the thermoluminescence glow curves are parallel. This would signify electron and not hole luminescent transitions (Antonov-Romanovskii 1966). The introduction of $Cr^{+++}$ ions into $Al_2O_3$ causes the maxima $M_1$and $M_2$ to vanish in the case of thermoluminescence, whereas in the case of thermostimulated (exo)emission of electrons they are distinctly lowered. Ruby crystals with $Cr^{+++}$concentration (0.1%) were also investigated and similar plots had been obtained, as shown in Fig. 4. In the majority of the tested samples of ruby crystals with $Cr^{+++}$ (concentration 0.08% and 0.1%) it was noticed that

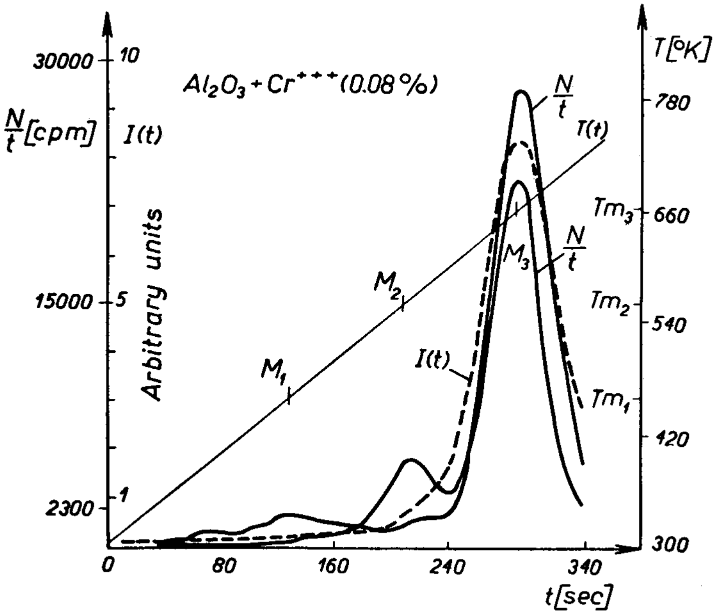


Fig. 3. Curves of thermostimulated (exo)emission of electrons $\frac{N}{t}(t)$ and thermoluminescence glow curves $I(t)$ for $Al_2O_3+Cr^{+++}$ (0.08%) after excitation by $X$-rays (Cu, 50 kV, 8 mA)

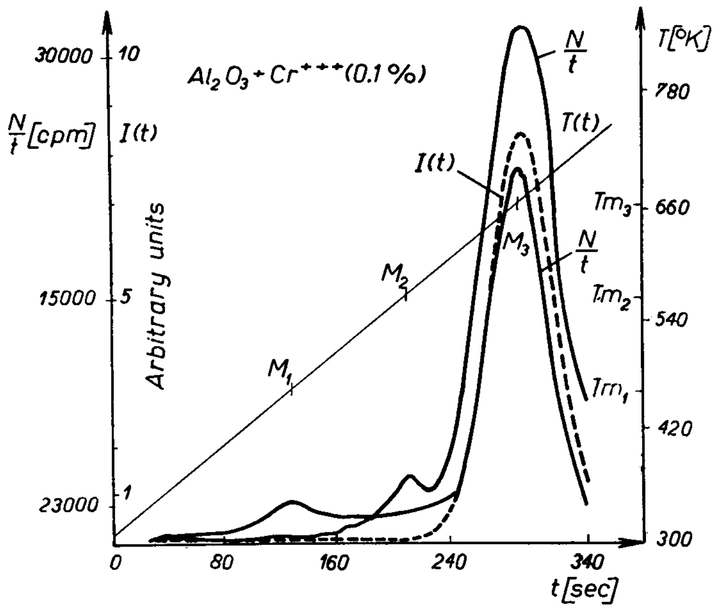


Fig. 4. Curves of thermostimulated (exo)emission of electrons $\frac{N}{t}(t)$ and thermoluminescence glow curves $I(t)$ for $Al_2O_3+Cr^{+++}$ (0.1%) after excitation by $X$-rays (Cu, 50 kV, 8 mA)

besides the distinct maximum $M_3$ the maximum $M_1$ appeared more often than $M_2$ on the curve of thermostimulated (exo)emission of electrons.

Additional measurements had been performed in order to find whether the air humidity during activation of the samples by $X$-rays affected the thermostimulated (exo)emission of electrons. Samples of $Al_2O_3$ without a $Cr^{+++}$ admixture were placed in a glass bulb evacuated to $10^{-4}$ mm Hg and irradiated by $X$-rays (Cu, 50 kV, 8 mA) for 30 minutes. Then the curves of thermostimulated (exo)emission of electrons were found. The character of these curves was identical to those of Fig. 2. Only the height of the maxima were changed ($X$-rays absorption of the glass).

In the Table I there are the temperature corresponding to the positions of the maxima $M_1$, $M_2$ and $M_3$, and the activation energies for the observed processes. The energies were calculated from the relationship

$$E_i(\text{eV}) = \frac{T_{max}}{500}\ (^0\text{K})$$

TABLE I

| $M_i$ | $Al_2O_3$ | | $Al_2O_3+Cr^{+++}$ (0.08% i 0.1%) | |
|---|---|---|---|---|
| | $T_{max}$(°K) | $E_i$ (eV) | $T_{max}$(°K) | $E_i$ (eV) |
| $M_1$ | 463 | 0.92 | 463 | 0.92 |
| $M_2$ | 563 | 1.12 | 563 | 1.12 |
| $M_3$ | 626 | 1.25 | 663 | 1.32 |

## 5. *Conclusion*

We see from Figs 2, 3 and 4 that the phenomena of thermostimulated (exo)emission of electrons and thermoluminescence are parallel. This would signify electron and not hole transitions with emission of light quanta (Antonov-Romanovskii 1966). The maxima $M_1$ and $M_2$ apprearing in the curves of thermostimulated (exo)emission of electrons in the case of some samples of $Al_2O_3+Cr^{+++}$ (0.08% and 0.1%) are presumably associated with uneven distribution of the $Cr^{+++}$ admixture in the ruby pear from which the samples had been cut. Research on the thermostimulated (exo)emission of electrons and the thermoluminescence of appropriately excited $Al_2O_3$ crystals is being continued.

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