MINERALOGIA POLONICA
Vol. 12, No 1 — 1981

Czesław OSTROWSKI *, *Jan MOCHNIAK* **

THERMOLUMINESCENT STUDIES AND IDENTIFICATION OF POINT DEFECTS IN $Al(OH)_3$ AND Al_2O_3

UKD 546.621—36+546.621:541.45:548.4.001.5.001.11:535.377

Abstract. Upon UV excitation, aluminium hydroxides display four thermoluminescent peaks at −140, −50, +30 and +150°C. Thermoluminescent curves for Al_2O_3 samples obtained by heating of $Al(OH)_3$ at 900°C show pronounced changes, although the position of peaks is identical with that in aluminium hydroxide. The defects that give rise to trapping levels in the structure of Al_2O_3 are the same as in the structure of $Al(OH)_3$.

INTRODUCTION

The stable crystal structures of Al_2O_3 are α-Al_2O_3 and γ-Al_2O_3 phases. The α-Al_2O_3 phase crystallizes in the trigonal system. An admixture of some elements gives it different colours (sapphire, ruby). The α-Al_2O_3 phase forms during the heating of aluminium hydroxide at temperatures higher than 900°C. The γ-Al_2O_3 phase, with a regular structure, is obtained at 600—900°C from aluminium hydroxide or its derivatives, or from some aluminium salts. The transition γ-$Al_2O_3 \rightarrow \alpha Al_2O_3$ takes place at temperatures above 1200°C. The crystallochemical properties of these phases depend not only on the reaction conditions but also on the purity of the initial substances. For example, in synthetic hydrargillite there is always 0.2—0.4% Na_2O. Admixtures of alkali metal oxides determine the amount of lattice defects in α-Al_2O_3.

The pioneer work on the thermoluminescence of various structural modifications of Al_2O_3 is the publication of Rieke and Daniels (1957), who made thermoluminescent studies of over 30 crystal forms of alumina. They found that the shape of thermoluminescent curves of alumina depended on the degree of hydration, the heating temperature, and their chemical purity. The investigations were carried out over the temperature range between 5 and 420°C, and the samples were excited with γ (Co^{60}) or UV radiation. It was found that UV excitation generated thermoluminescence in Al_2O_3 samples containing hydrates. The thermolumi-

* Institute of Binding Building Materials, Opole, ul. Oświęcimska 21.
** Institute of Physics, Pedagogical University, Opole, ul. Oleska 48.

nescent peak at 160°C was attributed to $Al(OH)_2^+$ group, while the peak at 226°C was associated with the presence of alkali metal ions. The papers of Gabrysh et al. (1962, 1963) deal with the thermoluminescence of α-Al_2O_3 samples irradiated with γ rays and subjected to pressure. These authors determined the depth of local traps, basing themselves on the theory advanced by Lushchik (1955), and found that the thermoluminescent peak at 146°C was also associated with the degree of hydration of samples. Optical and luminescent properties, the temperature and heat of phase transition and enthalpy are given by Kantor et al. (1962) and Neustuev (1974), who discuss several physical parameters determining the lattice energy and crystal structure of the α-Al_2O_3 phase.

EXPERIMENTAL AND RESULTS

This paper aims to investigate the distribution of electron traps in $Al(OH)_3$ and Al_2O_3 by thermoluminescent methods. Investigations were carried out on powdered hydrargillite $Al(OH)_3$ samples obtained for the purposes of ceramics for electronic capacitors, or for the growing of corundum or ruby crystals. Two series of samples (8 samples each) were used, and measurements of thermoluminescence were expected to systematize the samples according to the degree of their purity (Table 1). The results are presented in figures 1—6. All the measurements were made over the temperature range from −190 to 250°C, and the samples were heated at a constant rate of 0.3°/sec. UV excitation was carried on at the liquid nitrogen temperature for 10 minutes. Each portion of powdered $Al(OH)_3$ or Al_2O_3 was investigated three times, and the diagrams show the average values of each series of three measurements.

Figures 1 and 2 show thermoluminescent curves for $Al(OH)_3$ samples numbered from I to VIII and normalized to a common peak height at −50°C. As is evident from the figures, upon UV excitation, aluminium hydroxides display four thermoluminescent peaks at −140, −50, +30 and +160°C. The height of peaks is different and does not show any regularity that could be related to sample numbers, while maximum luminescence temperatures remain constant within the experimental error limits. The repeated constant positions of thermoluminescent peaks indicate that the eight $Al(OH)_3$ samples numbered from I to VIII derive from the same initial substance, and that the process of chemical purification has no effect on the position of peaks and their amplitudes.

The second series of thermoluminescent measurements was carried out on eight alumina obtained by heating $Al(OH)_3$ for 4 hours at a

Table 1

Content of alkalis in the Al_2O_3 samples *

Sample	Na_2O	K_2O
	wt. %	
I	0.46	0.02
II	0.22	0.01
III	0.13	0.01
IV	0.14	0.02
V	0.20	0.02
VI	0.20	0.01
VII	0.11	0.01
VIII	0.11	0.01

* The samples were obtained by heating of $Al(OH)_3$. The samples II—VIII were leached with distilled water in 80°C.

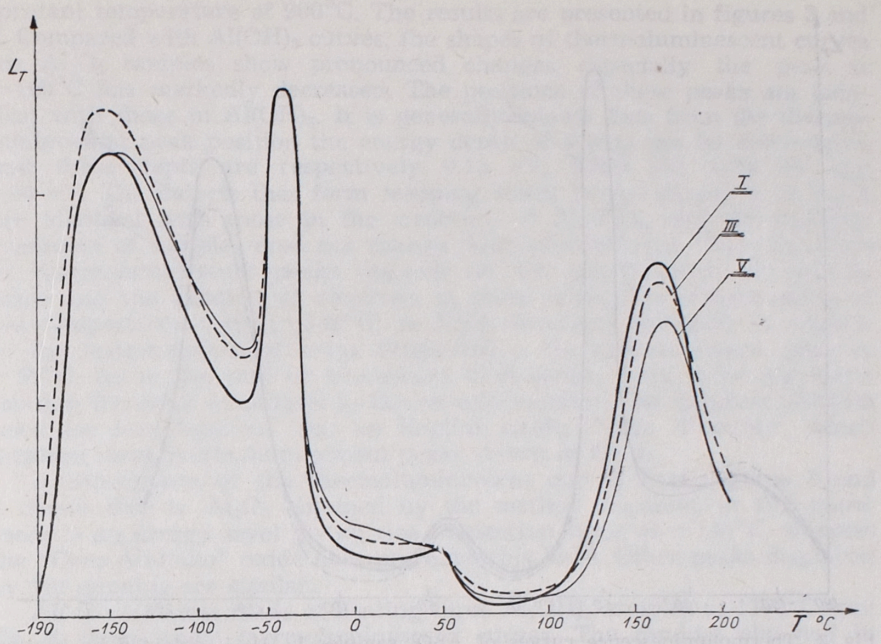

Fig. 1. Thermoluminescence curves of $Al(OH)_3$ samples I, III, V

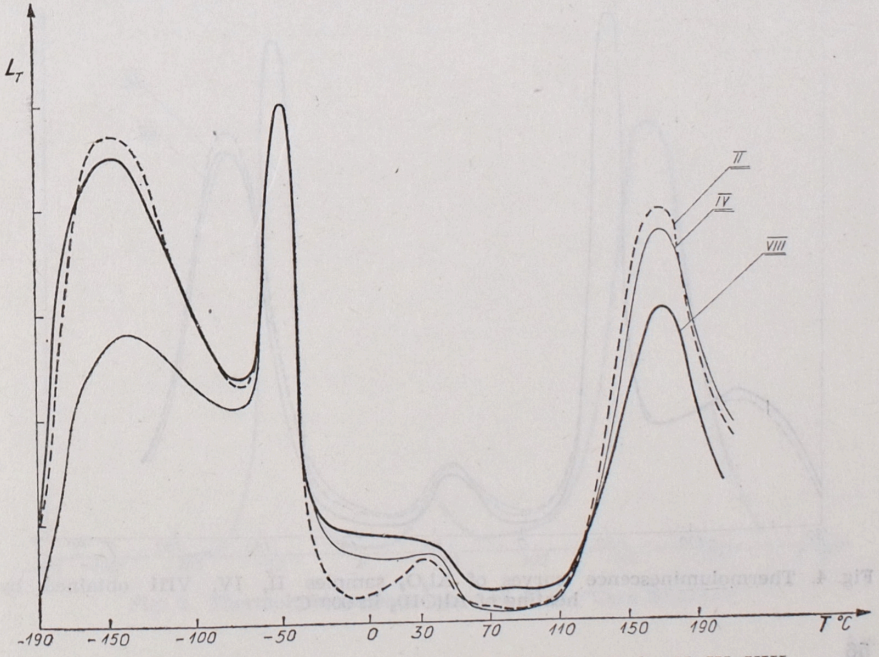

Fig. 2. Thermoluminescence curves of $Al(OH)_3$ samples II, IV, VIII

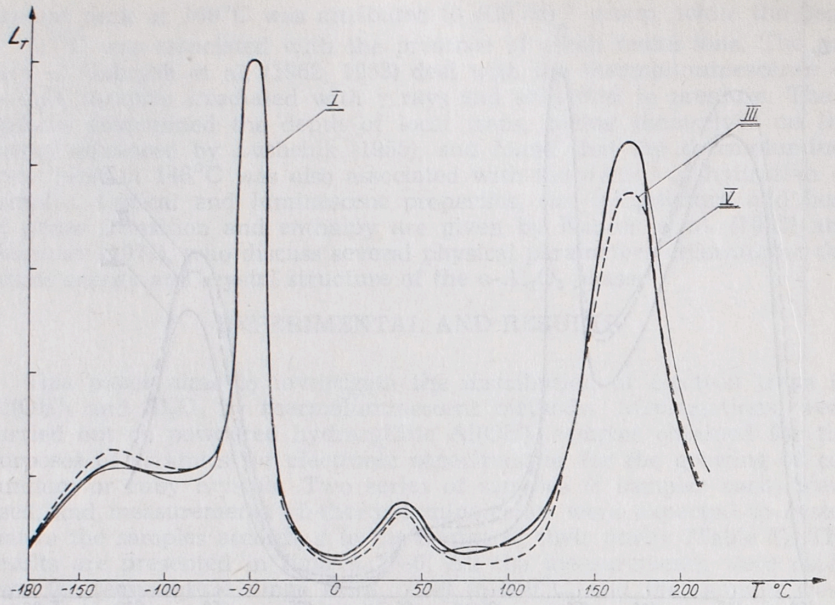

Fig. 3. Thermoluminescence curves of Al_2O_3 samples I, III, V obtained by heating of $Al(OH)_3$ in 900°C

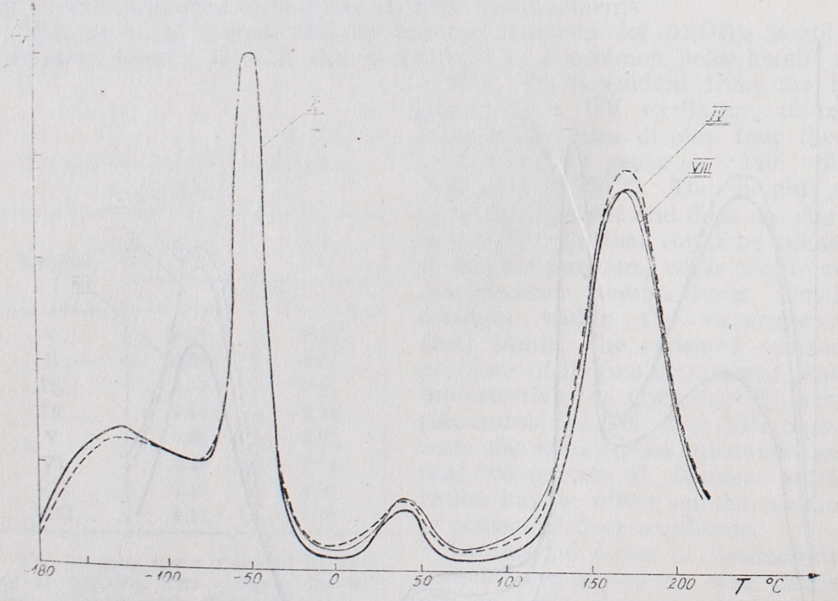

Fig. 4. Thermoluminescence curves of Al_2O_3 samples II, IV, VIII obtained by heating of $Al(OH)_3$ in 900°C

constant temperature of 900°C. The results are presented in figures 3 and 4. Compared with $Al(OH)_3$ curves, the shapes of thermoluminescent curves for Al_2O_3 samples show pronounced changes, especially the peak at −140°C has markedly decreased. The positions of these peaks are identical with those in $Al(OH)_3$. It is generally known that from the thermoluminescent peak position the energy depth of a trap can be determined, and these depts are respectively 0.13 eV, 0.295 eV, 0.56 eV and 0.68 eV. The defects that form trapping states in the structure of Al_2O_3 are identical with those in the structure of $Al(OH)_3$, and the chemical treatment of samples does not change their energy depth. The amplitude of thermoluminescent peaks depends on the concentration of electron traps and the location of electrons in these traps. The concentration of low-temperature traps (−140°C) in Al_2O_3 decreases markedly in relation to the concentration of traps displaying a thermoluminescent peak at −50°C. As in the case of aluminium hydroxides, there is no regularity relating the peak amplitude to the sample number. The standard alumina used for investigations was an English oxide, "Cera Alumina", which displays three thermoluminescent peaks shown in fig. 5.

A comparison of the thermoluminescent curves from figures 3 and 5 shows that in Al_2O_3 obtained by the method discussed in this paper there is an energy level giving rise to electron traps at −140°C, whereas the "Cera Alumina" oxide does not have this level. Other peaks displayed by the alumina are similar.

An attempt was made at heating three $Al(OH)_3$ samples at 1300°C, and fig. 6 shows their thermoluminescent curves. The product obtained in this way does not much differ from the English alumina. It is feasible

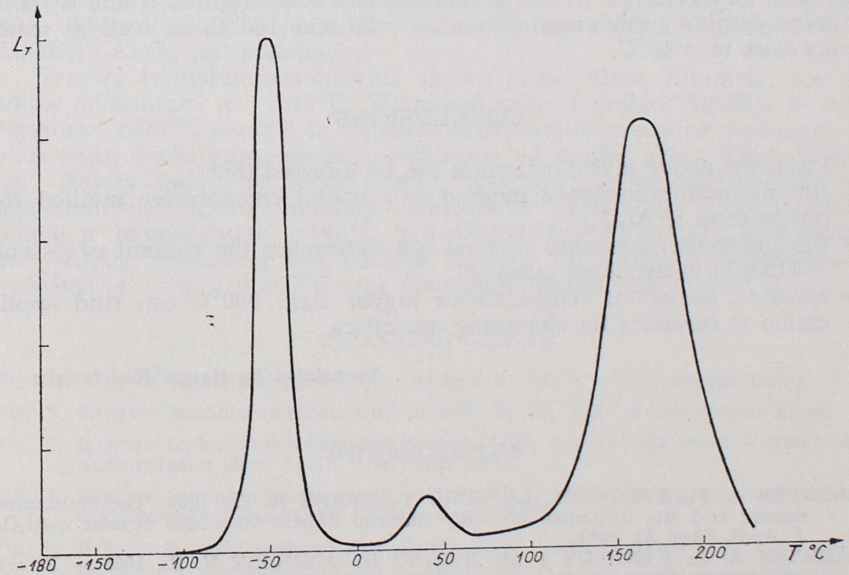

Fig. 5. Thermoluminescence curve of Al_2O_3 "Cera Alumina"

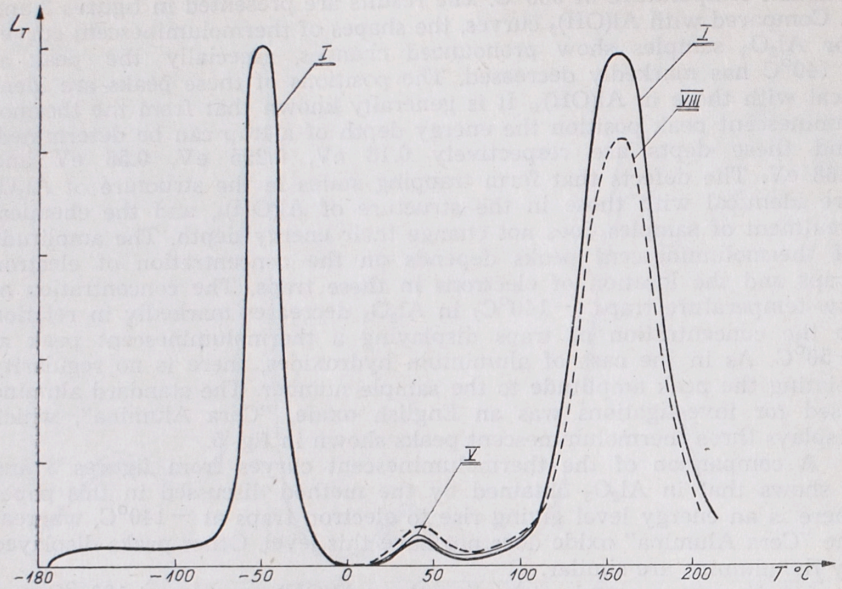

Fig. 6. Thermoluminescence curves of Al_2O_3 samples I, V, VII obtained by heating of $Al(OH)_3$ in 1300°C

that longer heating would eliminate completely the traps responsible for thermoluminescence at −140°C. As appears from figures 5 and 6, both alumina display pronounced peaks at −50 and 160°C, as well as small peaks close to +40°C.

CONCLUSIONS

From the above investigations it can be inferred that:

— the thermoluminescence method is a useful comparative method for purity tests of Al_2O_3;
— the thermoluminescence method can determine the content of α- and γ-Al_2O_3 in heterophase samples;
— alumina heated at temperatures higher than 900°C can find application in ceramics for electronic capacitors.

Translated by Hanna Kisielewska

REFERENCES

GABRYSH A. F., EYRING H., LEFEBRE V., EVANS M. D., 1962: Thermoluminescence and the influence of γ-ray induced defects in single crystal α-Al_2O_3. *J. Appl. Phys.* 33, 3389.

GABRYSH A. F., KENNEDY J. M., EYRING H., JOHNSON V. R., 1963 — Effects of high pressure on the thermoluminescence of γ-irradiated α-Al_2O_3 single crystals. *Phys. Rev.* 131, 1543.

[LUSHCHIK C. B.] ЛУЩИК Ц. Б., 1955: Исследования центров захвата в щелочно-галлоидных кристаллах. *Тр. АН Эст. ССР* 3, 3.

[KANTOR J. L. et al.] КАНТОР Й. Л., ЛАЗАРЕВА Л. С., КАНДИБА В. В., ФОМИЧЕВ Е. М., 1962: Экспериментальные вызначения энтальпии, температуры и теплоты фазового переходу α-Al_2O_3 при температурах 1200—1500 К. *Укр. Физ. Журн.* 7, 205.

[NEUSTUYEV V. V.] НЕУСТУЕВ В. В., 1974: Оптические свойства корунда. *Труды ФИАН* 79, 3.

RIEKE J. K., DANIELS F., 1957: Thermoluminescence studies of aluminium oxide. *J. Phys. Chem.* 61, 629.

Czesław OSTROWSKI, Jan MOCHNIAK

BADANIE I IDENTYFIKACJA DEFEKTÓW PUNKTOWYCH W $Al(OH)_3$ I Al_2O_3 METODĄ TERMOLUMINESCENCYJNĄ

Streszczenie

Wykonano badania termoluminescencyjne 8 próbek wodorotlenków glinu, które zostały poddane procesowi „odsodowania" (przez przemycie wodą destylowaną w 80°C). Zmieniająca się zawartość Na_2O i K_2O nie wpływa na położenie 4 maksimów termoluminescencyjnych w −140, −50, +30 i +160°C. Następnie 6 próbek wygrzano w 900°C przez 4 h. Kontury krzywych termoluminescencyjnych próbek Al_2O_3 w stosunku do $Al(OH)_3$ uległy wyraźnej zmianie, zwłaszcza amplituda maksimum w −140°C. Z położenia maksimów termoluminescencyjnych wyznaczono głębokości energetyczne poziomu pułapkowego, które wahają się w granicach 0,13—0,68 eV. Natura defektów, które tworzą poziomy pułapkowe w $Al(OH)_3$ i Al_2O_3, jest podobna.

Krzywa termoluminescencyjna tlenku glinu "Cera Alumina" nie zawiera maksimum w −140°C. Wygrzano więc 3 próbki $Al(OH)_3$ w temperaturze 1300°C przez 4 h. Pomiary termoluminescencyjne wykazały, że otrzymane tlenki glinu niewiele odbiegają od tlenku glinu "Cera Alumina". Należy sądzić, że przez dłuższe wygrzewanie próbek mogłoby się wyeliminować zupełnie pułapki elektronowe powodujące termoluminescencję w temperaturze −140°C, prawdopodobnie związane z domieszkami γ-Al_2O_3. Natomiast oba rodzaje tlenków mają dobrze wykształcone maksima w −50° i +160°C oraz niewielkie maksimum w +40°C.

OBJAŚNIENIA FIGUR

Fig. 1. Krzywe termoluminescencyjne próbek I, III, V wodorotlenku glinu

Fig. 2. Krzywe termoluminescencyjne próbek II, IV, VIII wodorotlenku glinu

Fig. 3. Krzywe termoluminescencyjne próbek Al_2O_3 uzyskanych przez wygrzewanie wodorotlenku glinu I, III, V w temp. 900°C

Fig. 4. Krzywe termoluminescencyjne próbek Al_2O_3 uzyskanych przez wygrzewanie wodorotlenku glinu II, IV, VIII w temp. 900°C

Fig. 5. Krzywa termoluminescencyjna tlenku glinu "Cera Alumina"

Fig. 6. Krzywe termoluminescencyjne próbek Al_2O_3 uzyskanych przez wygrzewanie wodorotlenku glinu I, V, VII w temp. 1300°C

Чеслав ОСТРОВСКИ, Ян МОХНЯК

ИССЛЕДОВАНИЕ И ИДЕНТИФИКАЦИЯ ПУНКТОВЫХ ДЕФЕКТОВ В $Al(OH)_3$ И Al_2O_3 ТЕРМОЛЮМИНЕСЦЕНТНОМ МЕТОДОМ

Резюме

Были выполнены термолюминесцентны исследования 8 проб гидрокиси алюминия, из которых устранялся натрий путем промывки дестилированной водой в температуре 80°C. Изменяющееся содержание Na_2O и K_2O не влияет на положение 4 темрмолюминесцентных максимумов при −140°, −50°, +30° и +160°C. Затем 6 проб подогревалось через 4 часа в температуре 900°C. Контуры темролюминесцентных кривых проб Al_2O_3 по отношению к $Al(OH)_3$ четко изменились, особенно амплитуда максимума при −140°C. Из расположения термолюминесцентных максимумов были определены горизонта — ловушки, которые колеблются в пределах 0,13—0,68eV. Природа дефектов, которые образуют горизонтны-ловушки в $Al(OH)_3$ и Al_2O_3, является похожей.

Термолюминесцентная кривая окиси алюминия „Cera Alumina" не содержит максимума при −140°C. Поэтому 3 пробы $Al(OH)_3$ подогревались в течении 4 часов в температуре 1300°C. Термолюминесцентные измерения показали, что полученные окиси алюминия на немного отличаются от окиси алюминия „Cera Alumina". Следует считать, что длительное подогревание проб могло обусловить отсутствие электронной ловушки, которые обуславливают термолюминесценцию в температуре −140°C, повидимому связанные с примесью γ-Al_2O_3. В это время оба вида окисей имеют четкие максимумы при −50°C и +160°C, а также небольшой максимум при +40°C.

ОБЪЯСНЕНИЯ ФИГУР

Фиг. 1. Термолюминесцентные кривые проб I, III, V гидрокиси алюминия

Фиг. 2. Термолюминесцентные кривые проб II, IV, VIII гидроокиси алюминия

Фиг. 3. Термолюминесцентные кривые проб Al_2O_3 полученных при подогреве гидроокиси алюминия I, III, V в температуре 900°C

Фиг. 4. Термолюминесцентные кривые проб Al_2O_3 полученных при подогреве гидроокиси алюминия II, IV, VIII в температуре 900°C

Фиг. 5. Термолюминесцентная кривая окиси алюминия „Cera Alumina"

Фиг. 6. Термолюминесцентная кривая проб Al_2O_3 полученных при подогреве гидроокиси алюминия I, V, VII в температуре 1300°C