# PHOTOLUMINESCENCE OF ANODIC ZrO$_2$ LAYERS

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The problem dealt with in this work is the stationary luminescence of anodic ZrO$_2$ layers, formed on zirconium in 0.5 $n$ nitric acid, induced to glow by UV light of wavelength $\lambda = 312.5$ nm. A curve of optical absorption of these layers was plotted, and the effect of temperature and UV light intensity on the total photoluminescence intensity was investigated. The thermal activation energy of the quenching process was determined to be $\varepsilon = 0.08$ eV. This work also included an analysis of intensities in the photoluminescence spectrum of the anodic layers, a comparison then being made with the photoluminescence spectrum of spectrally pure ZrO$_2$.

## 1. Introduction

Zirconium oxide is a substance which possesses interesting physical properties and widespread technical application. Luminescent properties of ZrO$_2$ had been investigated in many studies [3, 4, 5, 6, 15, 16].

In $X$-ray photography ZrO$_2$ finds use because it readily absorbs $X$-rays. Added to magnesium oxide, it intensifies its blue luminescence. ZrO$_2$ is a component of phosphors used in lamps which prevents blackening of screens and at the same time prolongs the life of the phosphors (prevents ageing).

In recent years, because of the development of reactor techniques in which zirconium rods are used for slowing down neutrons, oxide layers covering circonium have moved into the limelight [12, 13, 14]. Such layers become formed on zirconium metal due to thermal or electrolytic oxidation of zirconium.

The controversial views on the mechanism of growth of these layers, their structure and physical properties have been the topic of many researches [2, 11, 14, 16]. In the present work an attempt was made to define some photoluminescent properties of anodic ZrO$_2$ layers, for there are rather large gaps in the literature.

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## 2. Experiments and results

### 2.1 Optical absorption of $ZrO_2$ and the efect of temperature and exciting radiation intensity on photoluminescence of $ZrO_2$

In 1960 a paper by Salomon, Grawer and Adams [1] described optical absorption in anodic $ZrO_2$ layers formed in a solution of sodium borate and boric acid. It is found in this work that zirconium oxide strongly absorbs electromagnetic waves in the far ultraviolet region. The wavelength of the edge of the band of fundamental absorption is approximately 236 nm; this was found from the absorption curve by extrapolating the linear segment.

In order to compare the absorptive properties of $ZrO_2$ layers formed in a solution of nitric acid with those of oxide layers studied in Ref. [1], we plotted the optical absorption curve for anodic layers formed in $HNO_3$ in the ultraviolet and visible parts of the spectrum. Figure 1 presents the curve of relative optical absorption of these layers. On this figure the absorption of the oxide coating for light of wavelength $\lambda = 400$ nm was arbitrarily taken as unity. The absorption measurements were carried out on a Zeiss spectrophotometer, the source of radiation in the ultraviolet region being a deuterium lamp. For the tests, layers peeled off the metallic substrate were used. It is seen in Fig. 1 that
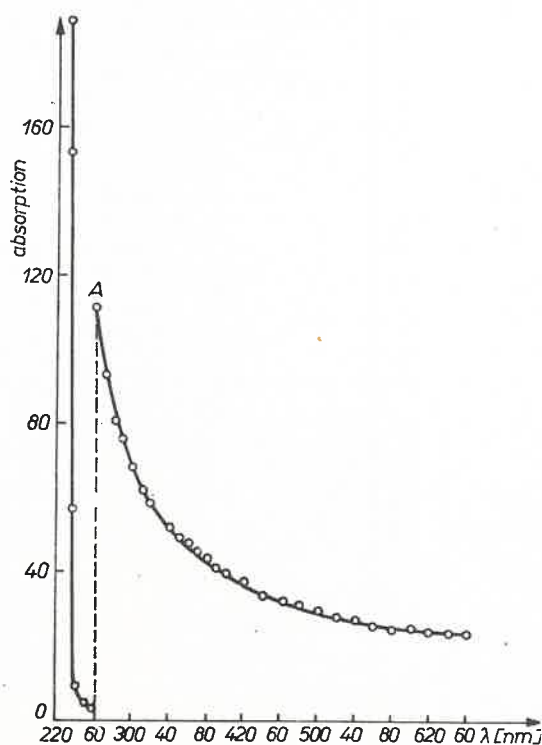


Fig. 1. Curve of relative optical absorption of anodic $ZrO_2$ layer. Absorption of layer for 400 nm is taken as unity. At point $A$ the scale on the absorption axis is magnified 40 times in order to show better the run of the curve in the visible region

by shortening of light wavelength the thin layer's absorption increases relatively slowly in the visible region, whereas it is very rapid in the UV region. The run of the curve in the ultraviolet region (Fig. 1) is identical with that of the curve obtained by Salomon and collaborators [1], while in the visible region the compatibility of the two curves is only satisfactory. The wavelength defining the edge of the band of fundamental absorption in $ZrO_2$ layers formed in $HNO_3$ (determined by extrapolating the linear segment of the curve, is approximately 240 nm,) hence, it is in very good agreement with the result cited in Ref. [1]. An energy gap of approximately 5.3 eV corresponds to this wavelength.

As Misch and Ruther [2] have shown, an aqueous solution of nitric acid of appropriate concentration is an electrolyte in which coarse and porous (grey or white) $ZrO_2$ layers become formed during oxidation, especially at higher formation voltages or large current densities. It is known [3, 4, 5, 6] that zirconium oxide obtained by thermal processes and anodic $ZrO_2$ layers alike exhibit stationary luminescence when excited by UV radiation. Our experiments have shown that radiation of wavelength $\lambda = 312.5$ nm induces intense emission from $ZrO_2$. Many phosphors exhibiting a glow under the excitation of constant intensity $E$ are characterized by a definite temperature $T$ (quenching point) above which the luminescence intensity decreases rapidly. On the other hand, at a fixed temperature (below the quenching point) the stationary luminescence $L$ for each emission band in a phosphor depends on the intensity of the exciting radiation $E$. In this work we also
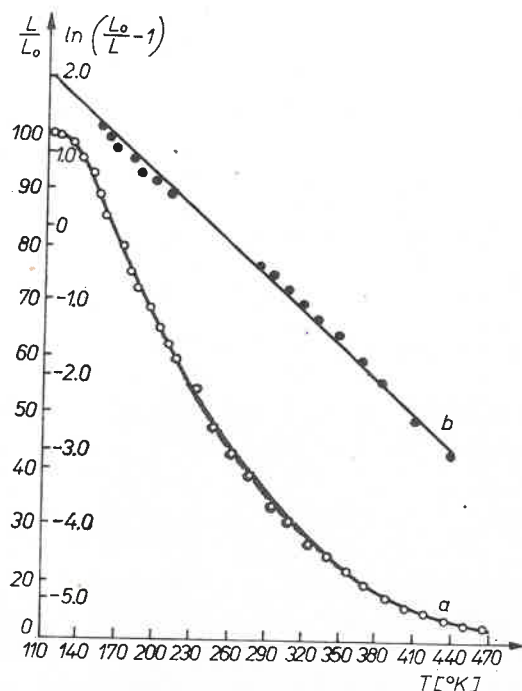


Fig. 2. The dependence of relative luminescence intensity $L$ on temperature $T$ (curve $a$) and the dependence of $\ln\left(\dfrac{L_0}{L} - 1\right)$ on reciprocal temperature (curve $b$). Intensity at $T = 103°K$ is assumed unity
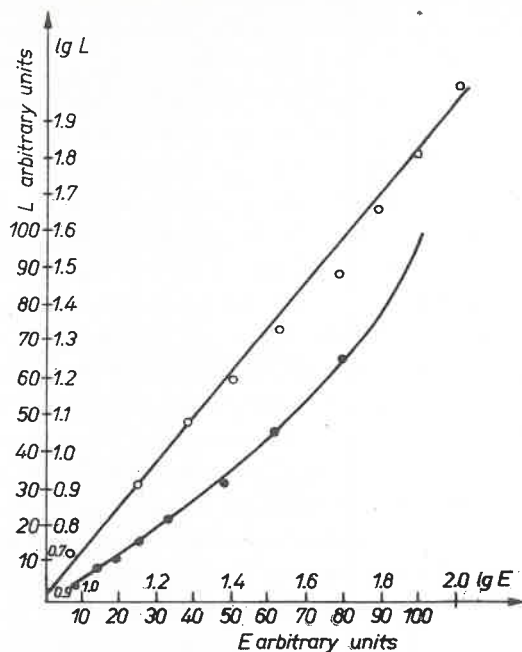
Fig. 3. Relative luminescence intensity $L$ *versus* exciting light intensity $E$ (curve —·—·—) and the dependence of lg $L$ on lg $E$ (curve —o—o—)

studied the effect of temperature and exciting light intensity on the intensity of the stationary luminescence of anodic $ZrO_2$ layers. Temperature was varied in the range from 103°K to 470°K, whereas intensity $E$ of the exciting light was variable within the limits of two orders of magnitude. The results of these experiments are shown in Figs 2 and 3.

Figure 2 illustrates the relative changes in intesity of stationary photoluminescence $L$ as a function of temperature $T$, and the dependence of $\ln\left(\dfrac{L_0}{L} - 1\right)$ on reciprocal temperature $1/T$. $L_0$ denotes the luminescence intensity at the initial temperature $T = 103°K$. As is seen in Fig. 2, the changes of photoluminescence against temperature may be represented by the relation describing the process of temperature quenching [7, 8] for luminophors in which the emission kinetics is of the first order (isolated emission centers),

$$L = L_0 \frac{1}{1 + \tau A e^{-\varepsilon/kT}}$$

where $\tau$, $A$ and $k$ are constants independent of temperature, and $\varepsilon$ is the thermal activation energy of the quenching process.

The effect of temperature on luminescence is not so simple for all substances [8]. For example, the dependence of electroluminescence on temperature for ZnS–Cu is very complicated and, in addition, from the work of Wrzesińska and Arsoba [9] it is known that it becomes somewhat altered with a change of frequency and voltage applied to the luminophors.

For the luminescence of $ZrO_2$ studied now the experimental curve presented in Fig. 2 in the system of coordinates $\ln\left(\dfrac{L_0}{L}-1\right)$ and $1/T$ is a straight line. Using the angle of inclination of this line the thermal activation energy to be determined by $\varepsilon = 0.08\ \text{eV}$.

Figure 3 shows the intensity of photoluminescence of the anodic layer at room temperature as a function of exciting light intensity $E$. This curve can be described by the equation [7]

$$L = BE^{\alpha}$$

where $B$ is a constant, and the exponent $\alpha$ is calculated from the inclination of the straight line in the coordinates $\lg E$ and $\lg L$ and equals about 1.25.

## 2.2. Distributions of intensities in $ZrO_2$ photoluminescence spectrum

In his doctor's thesis [6] Mochniak gave among other things a short communication about the spectral distribution of anodic $ZrO_2$ layers obtained with technical zirconium. In 1969 Bettinari and collaborators [10] presented their results of research on the thermoluminescence of $ZrO_2$ and gave the spectral distribution curve of photoluminescence of a sample of nucleonic purity. It is shown in the paper of the Italian researchers [10] that the photoluminescence of $ZrO_2$ gives a broad emission band with maximum emission in the vicinity of wavelength $\lambda = 498\ \text{nm}$.

In this work we measured the intensity distributions in the spectra of photoluminescence of $ZrO_2$ for 3 kind of samples produced from:

spectrally pure zirconium oxide (manuf. Johnson Matthey Chemicals Limited), which spectrographical techniques revealed a slight impurities of hafnium, iron and silicon;

zirconium oxide obtained by electrolytic oxidation of 99.96% pure zirconium;

zirconium oxide of chemical purity (imported from the USSR).

The spectral distributions of the above listed samples, normalized to one height, of maximum are shown in Fig. 4. The curves here were obtained at room temperatures by means of an arrangement consisting of a ZMR-3 prism monochromator, FEU-38 photomultiplier and G1-B1 compensating recorder. As is seen in Fig. 4, that all three kinds of samples are characterized by a spectrum comprising practically the whole visible range of electromagnetic waves, and the intensity maxima fall near the following wavelengths:

$\lambda = 490\ \text{nm}$ for the spectrally pure $ZrO_2$ sample;

$\lambda = 510\ \text{nm}$ for the sample of anodically formed $ZrO_2$;

$\lambda = 520\ \text{nm}$ for the chemically pure sample of $ZnO_2$.

It follows from photometric measurements that the sample of chemically pure $ZrO_2$ exhibits the most intense glow, while that of the spectrally pure $ZrO_2$ is the weakest. This would imply that some impurities in the former sample play the role of luminescence centers.

A comparison of the spectral distributions of the present work with similar curves given in Refs [6, 7] demonstrates that the photoluminescence spectrum depends on the

type of the sample, and their maxima are located in the blue or green regions. The changes in position of emission maxima ensuing from changes in sample type are presumably associated with a difference in concentration of luminescence centers responsible for the blue and green emissions of $ZrO_2$.
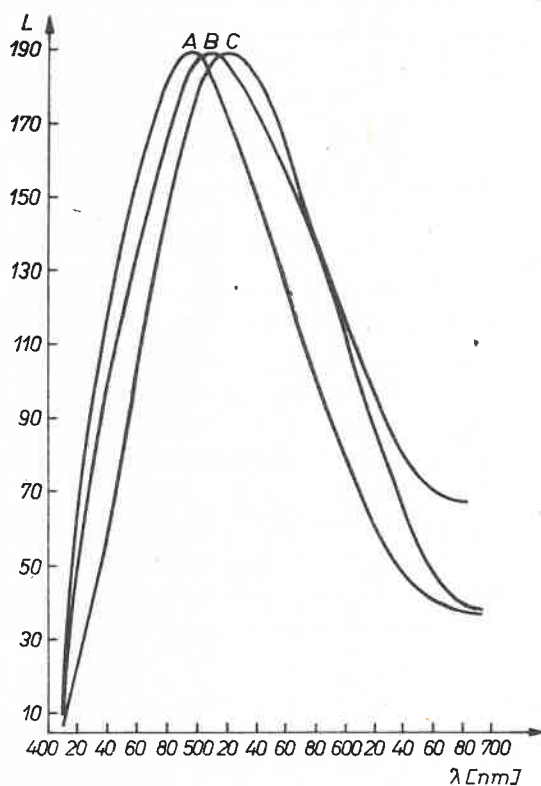


Fig. 4. Intensity distributions in photoluminescence spectra $L$ (normalized to the same height) of samples made of: curve $A$ — spectrally pure $ZrO_2$, curve $B$ — anodically formed zirconium platelet, curve C — chemically pure $ZrO_2$

As is known [2, 12, 13, 14, 18], a layer of oxide formed anodically on zirconium does not have an identical structure over its entire thickness. Near the metal substrate a $ZrO_2$ layer with a high concentration of anion defects becomes formed, whereas near the electrolyte the concentration of such defects is much lower. A test comparison of the photoluminescence spectrum of anodic $ZrO_2$ layers adjacent to the environment (outer layer) was made with the photoluminescence spectrum of the oxide region adjacent to the metal substrate (inner layer). As a result, it was found that the outer layer gives off a more intense glow than the inner layer. On the other hand, the normalized photoluminescence spectra of the outer and inner layers presented in Fig. 5 feature maxima in the neighbourhood of the same wavelength, $\lambda = 510$ nm, and the character of the wavelength dependences of the intensities is almost identical.
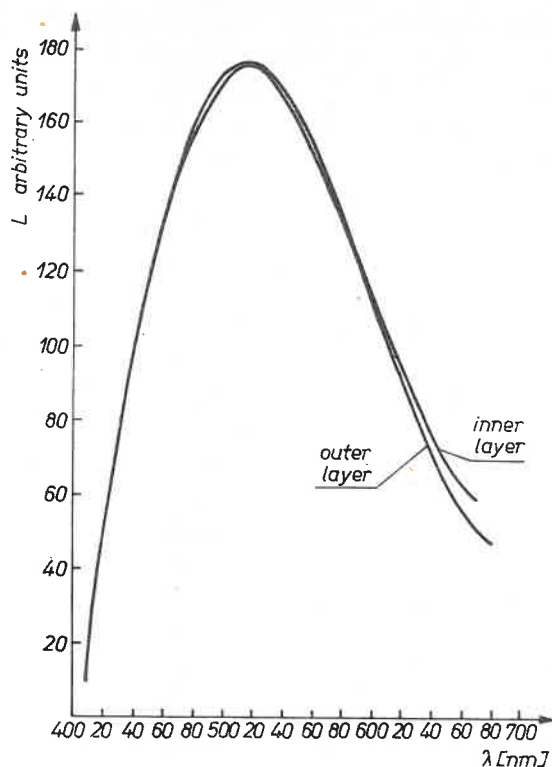
Fig. 5. Intensity distributions in photoluminescence spectra $L$ of inner and outer $ZrO_2$ layer, normalized to the same height

The observed agreement in the positions of both maxima for the outer and inner layer gives rise to the supposition that the luminescence centers of the same kind are formed in the entire region of the $ZrO_2$ layer, only their concentration changes, growing along the direction from the metal substrate towards the outer surface.

## 3. Final comments and conclusions

The results now presented regarding the photoluminescence of $ZrO_2$ show that anodic $ZrO_2$ layers glow when excited with UV light.

In the nineteen fifties Rusch and Ruther [2] discovered that when zirconium is oxidized electrolytically in nitric acid of concentration lower than 14% there forms on the metal a layer of oxide of monoclinic structure with a large content of cubic structure. The shade of this layer's colour depends on the concentration of anion defects. Chemical analysis of the $ZrO_2$ layer shows that the chemical composition over its whole thickness departs from the stoichiometric composition corresponding to the $ZrO_2$ compound.

The works of Sarkisov [7] and Parfenov et al. [14] find that the dark oxide layer adjacent to the zirconium substrate has a high concentration of anion defects (oxygen ion vacancies), as opposed to the white outer layer in which this defect concentration is very low.

Electron-microscopic studies of dark $ZrO_2$ layers performed by Cox [12, 18] revealed that at the grain boundaries in the oxide lattice regions of increased numbers of defects are formed, and they are favourable for the formation of a white layer.

Experiments described in the foregoing prove that the white $ZrO_2$ layer exhibits intense photoluminescence, as opposed to the dark layer. It is reasonable to suppose that one of the types of luminescence centers in these layers are zirconium ion vacancies, whose concentration should be higher in the white layer than in the dark one. It may be that there is a different kind of center, for instance, ions of an alien metal impurity substituting the tetravalent zirconium ion in the crystal lattice of the oxide. For example, Italian researchers [10] discovered the existence of impurity centers (Ti) in the case of $ZrO_2$ with titanium impurity. The peak of the luminescence spectrum in the case of Ti impurities, however, lies at a somewhat different wavelength (498 nm) than observed in the present study.

The implication of the newer studies [12, 13, 14, 18, 19] is that controversial opinions on the growth mechanism and structure of the oxide layer of electrolytically oxidized zirconium now have a tendency to accept the mechanism of anion defect diffusion to the oxide-environment contact surface, what is equivalent to the diffusion of oxide from the electrolyte (environment) through the oxide layer to the metallic substrate. It seems that the results of photoluminescence studies presented in the foregoing also confirm this view.

In conformity with the assumed diffusion mechanism, the concentration of zirconium ion vacancies should be lower in the volume of oxide adjacent to the substrate. Consequently, (assuming zirconium ions vacancies as luminescent centers) this should lead to a decrease in the intensity of luminescenc in the layer in contact with the substrate. This is precisely what is observed in the present work.

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