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Optical Properties of Thin PbO Films in Ultraviolet, Visible and Near Infrared Range

Optical properties of thin yellow and red PbO films in the ultraviolet, visible and near infrared range, were investigated. Energetical coefficients of reflectance R and transmittance T of the films were measured by means of a Zeiss spectrophotometer. Optical constants of the films (refraction and absorption coefficients) were determined in the considered wavelength range.

I. Introduction

Thin PbO films are an interesting subject for optical studies due to their high refraction index and relatively small absorption in the visual spectrum [1].

It is known [2-6] that there are two variants of PbO films — the yellow and the red one.

The yellow variant is obtained by the evaporating of the PbO films on the substrate kept in room temperature, whereas the red variant comes from the evaporating of the PbO films on the heated substrate. These variants are of different structure and have different refraction and absorption coefficients. The absorption and refraction coefficients for particular wavelengths are smaller for films of the yellow variant than those for the red one.

II. Experimental procedure

The yellow variant of the PbO films was evaporated in the Edwards Vacuum Coating Unit (type 17 E) on the substrate of Bk-7 glass, and quartz "Ultrasil" from platinum boat. Before evaporating, substrates were ion-cleaned for about 10 minutes. The film evaporation took place under the pressure $p = 1.5 \times 10^{-4}$ Tr in the oxygen atmosphere dosed by a valve. During the ion-cleaning and evaporation the substrate was rotated. The evaporation speed was about 30 Å/s. During the evaporation the thickness was checked for control by the photometric method with the filter for $\lambda_0 = 5100$ Å wavelength. Using this

technology the yellow variant of the PbO films of thickness from 7000 to 2500 Å was obtained.

The red variant of the PbO films was also evaporated in the Edwards apparatus on the Bk-7 and KBr glass substrates but this time the substrate temperature varied from 215 to 195°C. Before evaporating the substrates were ion-cleaned for about 10 minutes. The evaporation took place under the pressure $p = 3 \times 10^{-5}$ Tr in the air atmosphere dosed by a valve. The substrate was rotated both during the ion-cleaning and the evaporation. The speed of the evaporation was about 5.5 Å/s. During the evaporation thickness was checked using the filter for $\lambda_0 = 5530$ Å wavelength.

By means of a Zeiss spectrophotometer with reflection unit, the film energetic coefficients of reflectance (R) and transmittance (T) for the yellow and the red variants of the PbO films were measured in the range 210-2500 nm. In ultraviolet (210-400 nm) investigations, substrates of two types were used — quartz and KBr. Reflectance coefficients were measured with regard to Al standards of precisely determined evaporation parameters. The values of the reflectance coefficients for Al films for given parameters were taken from [7]. Transmittance of the film was measured with regard to quartz wedges or KBr plates, depending on the type of the base used.

For investigations in the near infrared and visible range, the yellow and red variants of the PbO films were evaporated on optical wedges of Bk-7 glass. Reflectance was measured with regard to Ag standard, while transmittance — to a wedge of Bk-7 glass.

In a near infrared range (1000-2500 nm) energetical coefficients of the yellow variant were measured by means of the type 203 micro-voltmeter in a modulated light. Radiation was detected by a PbS photo-resistor

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coupled with a Zeiss monochromator VSU-1. The film thickness was measured by multiple beam interference.

III. Experimental results

The values of the reflectance and transmittance coefficients for the yellow variant of the PbO films in the infrared and visible range are presented in Figs 1 and 2. The distinct minima and maxima appearing there, are the evidence that in the considered wavelength region the value of the refraction coefficient is higher than that of absorption ($n_1 \gg k$). Decrease of the distance between the neighbouring minima and maxima in the violet range indicates a normal dispersion. The behaviour of the R and T coefficients in the visible range for the red variant is similar, i.e. there appears extrema thickening in the violet part of the spectrum. On the basis of the

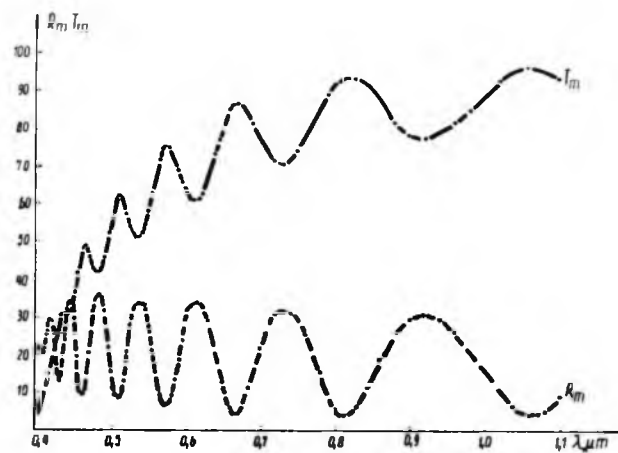


Fig. 1. Dependence of measured reflectance (R_m) and transmittance (T_m) coefficients on wavelength λ for a yellow PbO film of the thickness $d = 6700 \text{ \AA}$

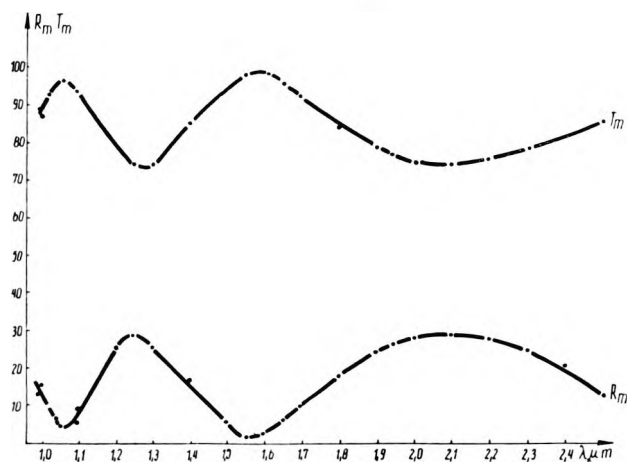


Fig. 2. Dependence of measured reflectance (R_m) and transmittance (T_m) coefficients on wavelength λ for a yellow PbO film of the thickness $d = 6700 \text{ \AA}$ (in the infrared range)

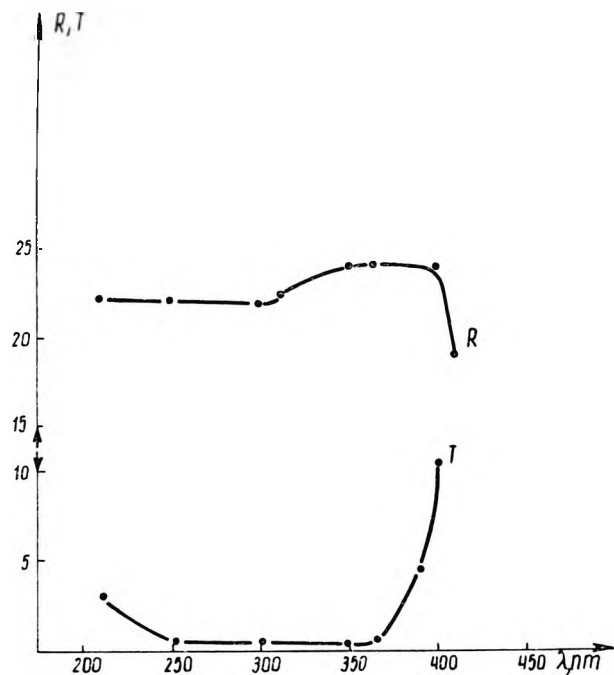


Fig. 3. Dependence of reflectance (R) and transmittance (T) coefficients on wavelength λ for a yellow PbO film in the ultraviolet range

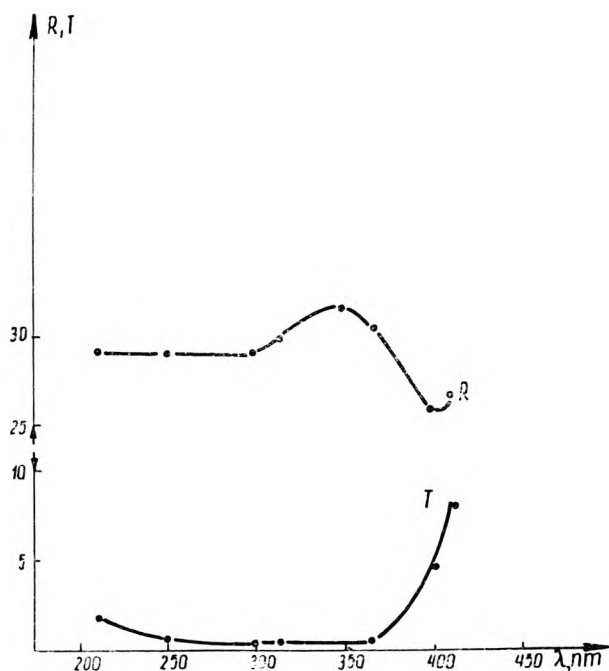


Fig. 4. Dependence of reflectance (R) and transmittance (T) coefficients on wavelength λ for a red PbO film in the ultraviolet range

results obtained constants optical of the films have been calculated using an approximate method presented in [8].

The behaviour of the reflectance and transmittance coefficients for yellow and red variants of the PbO films in ultraviolet range is different from that in visible range (Figs 3 and 4). Here, R and T depend

monotonically on wavelength, and for $\lambda = 350$ nm reflectance has a maximum for the yellow as well as the red variant. In the region 350-250 nm transmittance of variants of both kinds drops below 1%. The behaviour of the energetical coefficients indicates that for $\lambda = 350$ nm there appears an absorption band of the investigated films. Optical constants in this region have been determined with the help of a new method presented in detail in [9]. By this method, the zeroth-order approximation is determined either graphically, or from simplified formulae, and by means of the successive approximation method the exact values of n_1 and k are obtained. Numerical calculations based on this method were performed on ODRA-1204 computer at the Numerical Centre of the University of Wrocław.

Calculated coefficients n_1 and k for the yellow variant of the PbO film are presented in Fig. 5. Refraction coefficient increases from the value 2.2 in infrared, to 2.9 for $\lambda = 350$ nm (absorption band), and then decreases. In Fig. 6 the values of the coefficients n_1 and k for the red variant of the PbO film

are plotted against the wavelength. General features of the respective curves of both variants are the same. The refraction coefficient increases from the value 2.6 in infrared to 3.5 for $\lambda = 350$ nm, and then decreases. In the absorption band the value of the absorption coefficient is about 0.46, and decreases with decreasing wavelength. Absorption coefficient in the ultraviolet range has been also determined on the base of the Lambert's rule. Exact values of n_1 and k for yellow and red variants of the PbO films are given in Table I and II. From the analysis of the results obtained it can be concluded that the red variant of the PbO film has higher refraction and absorption coefficients than the yellow one. Optical properties of both variants are of repeating character. Optical constants obtained by different evaporations are, within the experimental error, equal.

Comparison of the optical properties of the films investigated by us with the data already known shows the optical constants within the experimental error, to be equal in the visible range.

In the ultraviolet part of the spectrum the films investigated by us have lower optical constants than the values given in [3]. The reason for this discrepancy may lie in different film structure. Also the behaviour of the absorption coefficient in the ultraviolet range is different from that reported in [3], where an increase with decreasing wavelength has been observed.

In [9] the accuracy of the determining of the optical constants was analysed according to the accuracy of measuring the R and T coefficients, and the film

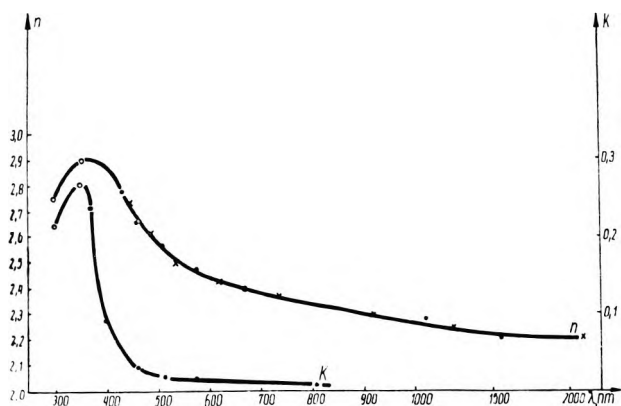


Fig. 5. Dependence of the refraction (n_1) and absorption (k) coefficients on wavelength λ for a yellow PbO film

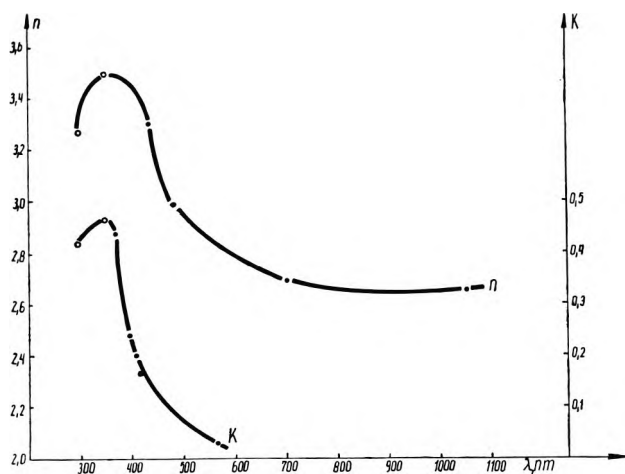


Fig. 6. Dependence of the refraction (n_1) and absorption (k) coefficients on wavelength λ for a red PbO film

Table 1

nm	n_1	k
300	2.734	0.214
350	2.906	0.26
365	—	0.23
400	—	0.09
415	2.84	—
430	2.78	—
448	2.74	—
462	2.66	0.033
485	2.62	—
510	2.57	0.023
535	2.50	—
575	2.48	0.015
615	2.43	—
668	2.41	—
735	2.38	—
815	2.34	0.005
920	2.30	—
1060	2.29	—
1250	2.25	—
1550	2.22	—
2100	2.21	—

thickness d . As the dependence of n_1, k on R, T, d, λ, n_2 is rather involved, it is not clear at all if the maximal errors $\Delta n_1, \Delta k$ correspond to the maximal errors $\Delta R, \Delta T, \Delta d$.

Table 2

nm	n_1	k
300	3.286	0.417
350	3.497	0.466
365	—	0.44
400	—	0.24
404.7	—	0.20
437	3.30	—
475	2.98	—
565	2.85	0.032
700	2.65	—
1000	2.64	—

Some information can be gained by discussing the error for certain sets of parameters R, T, d, λ, n_2 . The errors $\Delta n_1, \Delta k$ have been evaluated by systematic investigation of the n_1, k change while the parameters varied in the range $R \pm \Delta R, T \pm \Delta T, d \pm \Delta d$. In all considered cases it turned out that the extremal values of the optical constants do not correspond to the parameters values of maximal errors. Taking the experimental errors as $\Delta R/R \times 100 = 3\%, \frac{\Delta T}{T} 100 = 10\%, \frac{\Delta d}{d} 100 = 5\%$, respectively, the maximal relative errors for optical constants have been $\frac{\Delta n_1}{n_1} 100 = 2\%, \frac{\Delta k}{k} 100 = 6\%$.

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Propriétés optiques de couches minces de PbO dans le domaine de longueur d'onde de 220 nm à 2500 nm

On a étudié des propriétés optiques des couches minces de PbO de la modification jaune et rouge dans le proche ultraviolet, le visible et l'infrarouge. On a mesuré des facteurs de réflexion R et de la transmission T de couches minces. On a déterminé les constantes optiques (l'indice de refraction et d'absorption) dans ce domaine de longueur d'onde.

Оптические свойства плёнок PbO в области спектра от 220 нм до 2500 нм

Исследованы оптические свойства плёнок PbO — жёлтой и красной модификации в ультрафиолетовой, видимой и близкой инфракрасной областях. С помощью спектрофотометра Цейсса измерены энергетические коэффициенты отражения R и пропускания T плёнок. Определены оптические постоянные плёнок (коэффициент преломления и поглощения) в рассматриваемой области спектра.

References

- [1] ENNOS A. E., J. Opt. Soc. Amer., 52 (1962) 261.
- [2] NABOJKIN J. W., Pribory Techn. Eksp. No. 2 (1965) 189.
- [3] KRAMARENKO H. L., MIŁOŚLAWSKIJ W. K., Optika i Spekr. 24 (1968) 972.
- [4] KIYOTAKA WASA, Japan Journ. Appl. Phys. 8 (1969) 276.
- [5] IZWOCZNIKOW W. A., ŻURN. Prikl. Spekr. 4, (1966) 282.
- [6] MULCHER B. J., Solid State Comm. 4, (1966), 293.
- [7] HASS G., WAYLONIS J. E., J. Opt. Soc. Amer. 51 (1961) 719.
- [8] LIASZENKO S. P., MIŁOŚLAWSKIJ W. K., Optika i Spekr. (1964) 151.
- [9] DOBIERZEWSKA-MOZRZYMAS E., LEWANOWICZ S., MOZRZYMAS J., Acta Phys. Pol., Vol. A 41, No. 3 (1972), 251.

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