

# Optical properties of thin praseodymium oxide films\*

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In the paper the results of examinations of both production of thin praseodymium oxide films and their optical properties are presented. It has been stated that the  $\text{Pr}_6\text{O}_{11}$  layer can be obtained by the reactive evaporation at the oxide atmosphere. After reduction of these layers in the hydrogen furnace at the  $700^\circ\text{C}$  temperature the  $\text{Pr}_2\text{O}_3$  layers were obtained. For the layers of both the oxides, the refractive indices  $n$  as well as the absorption coefficients  $k$  have also been determined, in the spectral  $0.2\text{--}2.5\ \mu\text{m}$  range.

## 1. Introduction

Praseodymium is of valency III or IV and it belongs to a not numerous group of elements which may create the oxides of  $\text{MeO}_x$  type ( $2.5 \geq x \geq 1.5$ ). The up to now published examinations of the conditions of obtaining various oxides of praseodymium for the powdered material [1] indicate that the praseodymium oxides  $\text{PrO}_x$  exist for  $x = 1.5, 1.65, 1.714, 1.778, 1.800, 1.818, 1.826, 1.833$  and  $2.0$ . From the analysis of these data it may be concluded that different oxides may appear during the evaporation in vacuo (with the exception of  $\text{Pr}_2\text{O}_3$  and  $\text{PrO}_2$ ) depending on the substrate temperature and the oxide pressure. From the literature data [1–4], it follows that the oxides  $\text{Pr}_6\text{O}_{11}$  and  $\text{Pr}_2\text{O}_3$  may be stable in the form of layers.

The present paper concerns the technology of production and optical properties of the praseodymium oxide layers.

## 2. Experimental

The praseodymium oxide layers were evaporated by using both the electron gun and the tungsten and molybdenum boats. The examinations of layers evaporated from the boat have shown the content of significant quantities of metal phase. This was manifested in the metallic appearance of the layers after the process of

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reduction in the hydrogen atmosphere. Therefore the main examinations concerned the layers evaporated on the quartz substrate with the help of the electron gun. The powdered  $\text{Pr}_6\text{O}_{11}$  material of purity 99.9<sup>0</sup>/<sub>0</sub> has been used for evaporations. In order to establish the influence of the evaporations on the layer properties the substrate temperature was changed from the room temperature up to 300°C, while the evaporation speed ranged from 3 to 12 nm/min and the oxide pressure from  $10^{-4}$  to  $10^{-6}$  Tr.

After evaporation of layers the measurements of reflection coefficients  $R$  and the transmission coefficients  $T$  were performed on Specord UV VIS and 61 NIR spectrophotometers. The thickness of layers determined by using a multi-ray interference method ranged from 185 nm to 920 nm. Next, the layers were subject to thermal treatment in the air atmosphere and in the hydrogen furnace. The annealing in the air aimed at increasing the oxidization degree of the layers while the reduction in the hydrogen furnace made it possible to obtain the  $\text{Pr}_2\text{O}_3$  layers. The conditions of complete reduction of  $\text{PrO}_x$  layers to  $\text{Pr}_2\text{O}_3$  form have been established from optical measurements and from the dependence of the transmission coefficient  $T$  both on the wavelength  $\lambda$  and the annealing time of the layers.

The process of reduction has been recognized as being finished after the saturation of the curve  $T = T(t)$  was reached.

### 3. Results of examinations

The performed examinations have shown the possibility of obtaining the thin layers of two praseodymium oxides. The layers evaporated on the substrates of 250°C temperature at the oxide pressure of  $10^{-4}$  Tr and the evaporation speed 3–8 nm/min, subject to long annealing in the air atmosphere at the 400°C temperature, do not change their spectral characteristics  $T = T(\lambda)$ . Based on literature data [1], [2], [4] it may be supposed that these are  $\text{Pr}_6\text{O}_{11}$  layers, as this oxide is the most stable of the other praseodymium oxides. The layers evaporated on the substrate of lower temperature or at lower oxide pressure are not stable during the annealing in the air. It appeared that the  $\text{Pr}_2\text{O}_3$  layers cannot be obtained by applying different parameters used in evaporation technique in vacuo.

In Figure 1 some exemplified spectral characteristics  $T = T(\lambda)$  are presented for the layers  $\text{Pr}_6\text{O}_{11}$  and  $\text{Pr}_2\text{O}_3$  of 545 nm thickness. The curve 1 concerns the layer  $\text{Pr}_6\text{O}_{11}$  immediately after evaporation. This layer was annealed also in the air at the 400°C temperature but this caused no changes in the transmission coefficient  $T$ . Significant absorption of these layers in the ultraviolet and visual part of the spectrum, like in the case of the terbium oxide is caused by the transmissions of valence electrons to the levels  $f$  of the four-valence praseodymium ions. The curve 2 refers to the same layer after the 4 hour reduction in the hydrogen furnace at the 700°C. The layers  $\text{Pr}_2\text{O}_3$  have the transmission similar to that of the remaining

sesquioxides of the rare earths but the edge of absorption is shifted toward the red as far as possible.

The optical constants  $n$  and  $k$  of the examined layers were determined on the base of the measured coefficients  $R$  and  $T$  and the thickness  $d$ . In Fig. 2 the

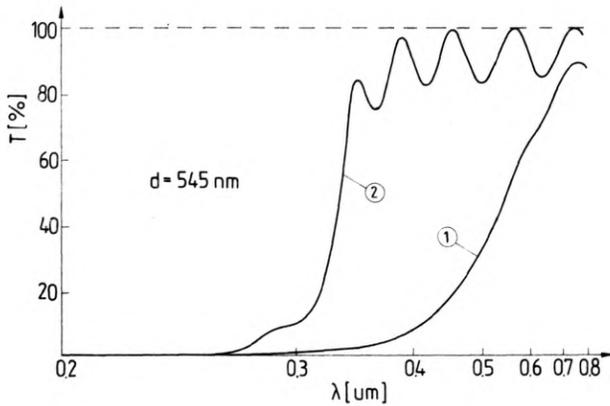


Fig. 1

optical constants of the  $\text{Pr}_2\text{O}_{11}$  and  $\text{Pr}_2\text{O}_3$  layers are shown. From this figure it may be seen that the optical constants of these layers differ significantly. The various values of the refractive indices  $n$  for the praseodymium oxide layers found in the literature range between those for  $\text{Pr}_2\text{O}_3$  and  $\text{Pr}_6\text{O}_{11}$  [3], [5], [6]. Based on

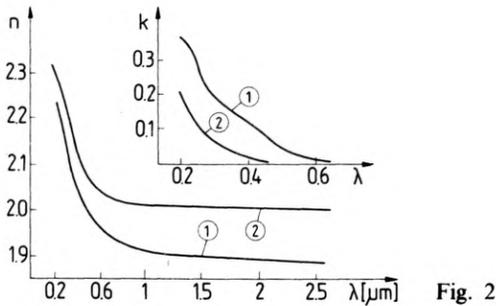


Fig. 2

examinations it has been stated that refractive indices of  $\text{Pr}_2\text{O}_3$  layers have the highest values of all the other oxides of rare earths (curve 2). A small dispersion of the refractive index for  $\text{Pr}_2\text{O}_3$  layers may be seen within the range 0.8–2.5 nm. The region of good transmittivity for these layers starts with  $\lambda \approx 400$  nm toward the infrared.

The  $\text{Pr}_6\text{O}_{11}$  layers have a wide absorption band in ultraviolet and visual parts of the spectrum. This band has no distinct extremes and the absorption of these layers within the 250–500 nm interval changes only slightly, which follows from the almost straight line representing the course of the coefficient of absorption  $k$  within this interval (curve 1 in Fig. 2).

#### 4. Conclusions

The performed examinations of the optical properties of the praseodymium oxide allow us to state that there exists a possibility to produce both the  $\text{Pr}_6\text{O}_{11}$  layers by immediate reactive evaporation in vacuo and the  $\text{Pr}_2\text{O}_3$  layers by reduction of the evaporated layers in the hydrogen furnace.

The  $\text{Pr}_6\text{O}_{11}$  layers may be applicable to the multilayer systems used in infrared ( $\lambda > 650$  nm) as well as to the filters cutting off the visual and ultraviolet parts of the spectrum. The praseodymium layers, like the other rare earths oxides, belong to the zero group with respect to their mechanical resistance [5]. They are also chemically resistant – they are only slightly reactive to the concentrated nitrogen acid.

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#### Оптические свойства тонких слоев окислов празеодима

В работе представлены результаты исследований возможностей получения тонких слоев окислов празеодима и их оптических свойств. Отмечено, что путем реакционного испарения в атмосфере кислорода возможным является получение слоев  $\text{Pr}_6\text{O}_{11}$ . После редукиции этих слоев в водороде в температуре  $700^\circ\text{C}$  получены слои  $\text{Pr}_2\text{O}_3$ . Определены также коэффициенты преломления  $n$  и показатели поглощения  $k$  слоев обоих окислов в спектральном пределе 0,2–2,5  $\mu\text{m}$ .