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Influence of preparation conditions of gadolinium oxide films on their optical properties and structure

Optical properties of vacuum deposited films of gadolinium oxide have been studied in the infrared region from 0.6 to 50 μm. The refractive index of the films has been determined in the wavelength of 0.6–5 μm. The Gd_2O_3 films are highly transparent in the spectral region of 0.6 to 20 μm with the exception of two absorption bands at 3 and 7 μm. Interpretation of these bands is given.

1. Introduction

The investigations on optical properties of Gd_2O_3 films, conducted earlier, have indicated that these films being highly transparent within a wide spectrum, can be utilized in multilayer stacks. Further investigations, which were undertaken, concern the influence of the deposition parameters, like gas pressure and substrate temperature, on the optical properties and structure of the films, as well as the interpretation of absorption bands in the infrared region.

2. Experimental

The films of gadolinium oxide were evaporated by electron bombardment of the Gd_2O_3 powder compressed into pills and pure Gd metal in an oxygen atmosphere at 2×10^{-5} Tr. The films were condensed onto amorphous substrates (borosilicate glass, fused quartz) and crystalline substrates (CaF_2, KRS-5). The preparation of the films have already been reported in full details [1].

The transmittance was measured by using the following spectrophotometers: VSU2-P, Cary 14, Perkin Elmer 621. The reflectance was recorded on a special reflectance attachment constructed in our laboratory. The film thickness was measured by multiple beam interference (Tolansky's method).

3. Results and discussion

The refractive and absorption indices of the Gd_2O_3 films have been determined from measurements, at normal incidence, of reflectance and transmittance. The influence of the Gd_2O_3 evaporation conditions on the refractive index n is shown in fig. 1. The curve a is the average dispersion curve from several different Gd_2O_3 films deposited onto unheated CaF_2 substrates at 2×10^{-6} Tr. The values of the index are lower than those reported by Hass [2]. Evaporation in oxygen at a pressure of 5×10^{-5} Tr allowed to produce films with a refractive index higher by 5% (curve c). Gadolinium oxide films, prepared by evaporating pure Gd metal at oxygen pressure of 2×10^{-5} Tr onto an unheated substrate, have the middle values of rafractive index. Gd_2O_3 films showed a very marked dependence of the optical constants on substrate temperature. The index of refraction of the films condensed onto a quartz substrate at 200°C increased from 1.78 to 1.92 (curve d). Such high value of n can be obtained by baking the films deposited on unheated substrates in air at 400°C for 5 h after evaporation. The refractive index of all the films has a small dispersion in the studied wavelength range.

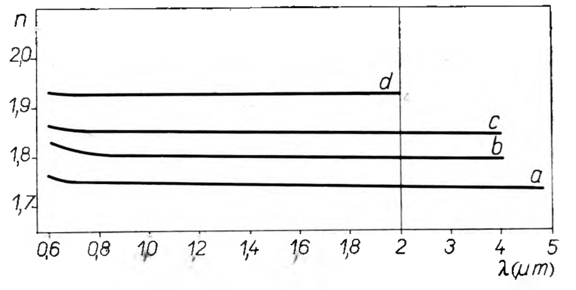

Fig. 1. Refractive index of evaporated Gd_2O_3 films
a – films deposited onto an unheated CaF_2 substrate, b – films produced by evaporating a pure Gd metal in oxygen atmosphere, c – films evaporated onto an unheated CaF_2 substrate at 5×10^{-5} Tr of oxygen, d – film on a quartz substrate heated to 200°C. The scale changes at 2 μm

The increase of the refractive index of Gd_2O_3 films is connected with the ordering of its structure and an increase of density packing. X-ray diffraction study of the films showed the films formed at room temperature were amorphous in nature, whereas those deposited at 200°C were polycrystalline with a preferred [100] orientation. Annealing of

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amorphous films on air at 400°C caused their partial crystallization. Figure 2 shows typical diffraction patterns of Gd_2O_3 powder used in evaporation (*a*), of the film deposited onto a heated substrate (*b*) and of the film baked in air (*c*).

In the investigated infrared 2–50 μm region the Gd_2O_3 films — regardless of the evaporation technique and the kind of substrate — have absorption bands localized at 3 μm, 7 μm and 25 μm (fig. 3). In the case of films thicker than 0.7 μm a very weak absorption band appears at 11.7 μm. We have determined the absorption coeficient α at the maximum of these bands: for $\lambda = 2.88$ μm, $\alpha = 1\times10^3$ cm^{-1}, for $\lambda = 6.66$ μm and 7.14 μm $\alpha = 5\times10^3$ cm^{-1}, for $\lambda = 25$ μm $\alpha = 7\times10^3$ cm^{-1}. On the basis of comparison of the transmission spectrum of Gd_2O_3 powder used in our experiment with the spectrum of the films, one may conclude that the absorption band at wavelength 25 μm concerns the centre of the lattice vibration of gadolinium oxide [3].

The rare earth oxides being hygroscopic, one would expect that some of the aforementioned bands are due to water incorporated into films. In order to see if this expectation was valid the films were enclosed in an exsiccator with a deuterium oxide for one month. In the transmission spectrum of the films after deuteration an additional absorption band appears with a maximum at 3.9 μm. This izotopic shift of the water band is illustrated by dashed line in fig. 4. The experiment confirmed that absorption band at about 3 μm is caused by that O-H stretching mode. Fig. 5 represents the transmittance of Gd_2O_3 film

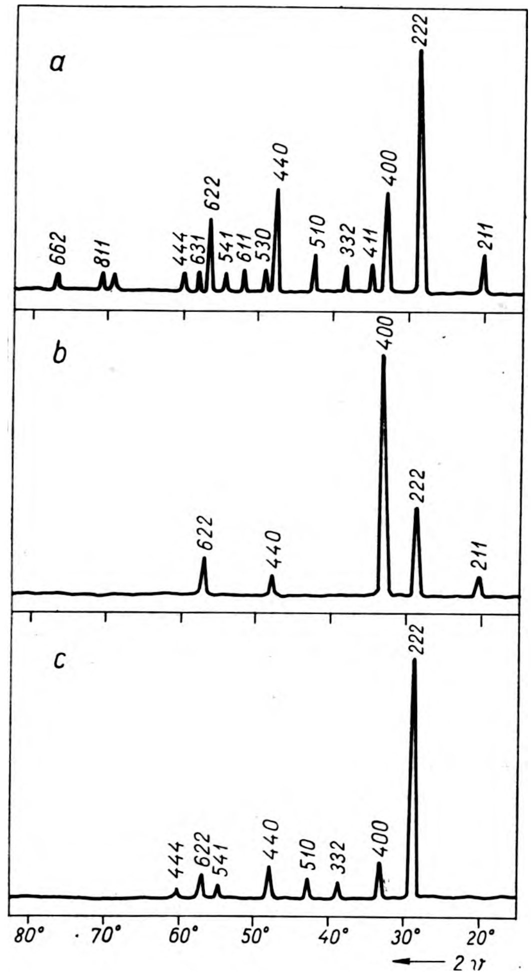

Fig. 2. X-ray diffraction pattern of Gd_2O_3 powder (*a*), film of Gd_2O_3 on a heated substrate (*b*), film baked in air (*c*)

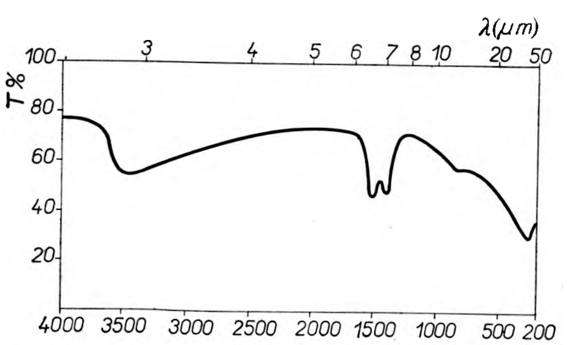

Fig. 3. I. r. transmittance of 1.0 μm thick film on an unheated KRS-5 substrate

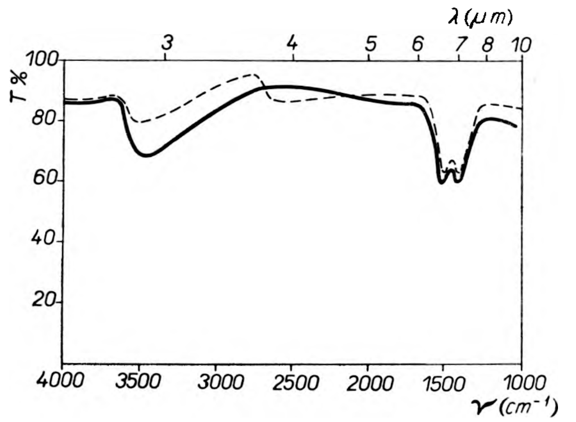

Fig. 4. I.r. transmittance of Gd_2O_3 film on an unheated CaF_2 substrate. Dashed line: the same film after deuteration

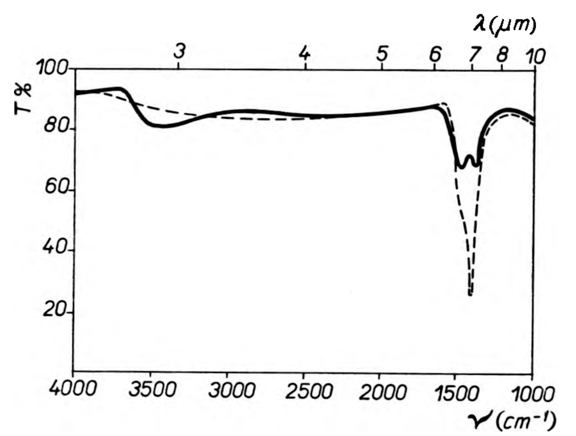

Fig. 5. I.r. transmittance of Gd_2O_3 film on an unheated CaF_2 substrate before being baked in air (continous line) and the same film after being baked (dashed line)

on the CaF_2 substrate (continuous line) and the same film after being baked in air (dashed line). The disappearance of the 3 μm band is the second proof for the origin of this band. The deformation and the great depth of the double band in the 7 μm region are visible after baking treatment.

In order to ascertain that the absorption bands, occurring at 3 μm and 7 μm, are characteristic of Gd_2O_3 films only, optical properties of other rare earth oxide films: CeO_2, Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Er_2O_3, Yb_2O_3 and Y_2O_3 have been investigated in the wavelength range of 2–10 μm. All the films examined have the absorption bands localized at the same wavelength ranges as Gd_2O_3 films. The group of lanthanides is highly reactive towards atmospheric gases, such as hydrogen, water, nitrogen and carbon-dioxide [4]. In the case of rare earth oxides it is possible to form the carbonates $Me_2(CO_3)_3$ or $Me(HCO_3)_3$.

To explain the absorption band at 7 μm several experiments have been made with Gd_2O_3 powder, including a thermogravimetric analysis at temperature ranging within 20–950°C, the measurement of infrared transmittance of the powder baked at 400°C and 900°C, and Raman spectrum. From these investigations and the literature data related to the vibration of the CO_3^- ion in carbonate compounds [5] it may be concluded that at 7 μm the double absorption band is due to the stretching vibration of the CO_3^- ion and at 11.7 μm to the bending of the same ion.

4. Conclusions

The refractive index of Gd_2O_3 films depends on evaporation condition. Its value increases with the increasing substrate temperature. This appears to be associated with the crystal growth process of the films.

Low values of α for the maximum infrared bands allow to state that the evaporated Gd_2O_3 films have a wide region of high transparency, and that they find applications in optics.

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Влияние условий приготовления плёнок из окиси гадолиния на их оптические свойства и структуру

Оптические свойства плёнок окиси гадолиния, полученных путём возгонки в вакууме, исследовались в области инфракрасной части спектра от 0,6 до 50 μм. Определили коэффициент преломления этих плёнок в диапазоне длины волны от 0,6 до 5 μм. Плёнки Gd_2O_3 являются очень прозрачными в пределах от 0,6 до 20 μм за исключением полос поглащения при 3 и 7 μм. Приводится интерпретация этих полос.

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