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Optical properties of electron beam deposited lutetium oxide thin films

TADEUSZ WIKTORCZYK

Institute of Physics, Wrocław University of Technology, 50-370 Wrocław, Wybrzeże Wyspiańskiego 27, Poland.

Lu_2O_3 thin-film coatings of a thickness 0.1 – 1.3 μm were deposited onto quartz plates by an electron beam gun. Optical measurements were carried out for the wavelengths $\lambda = 0.2$ μm – 2.5 μm. All fabricated coatings were highly transparent in the spectral range from 0.3 μm to 2.5 μm. Optical constants of Lu_2O_3 films have been determined from the spectrophotometrically measured transmittance. The dispersion $n(\lambda)$ and extinction $k(\lambda)$ curves in the spectral range considered have been presented and analysed. The refractive index for Lu_2O_3 films has been estimated as 1.84 at 0.55 μm. The characteristics of the real and imaginary parts of the dielectric function $\varepsilon^*(\nu)$ are also presented. Values of $\varepsilon'_\infty = 3.23 - 3.53$ have been obtained as the high-frequency optical relative permittivity for Lu_2O_3 thin films.

1. Introduction

The physical properties of rare earth oxides have been a subject of intensive studies in the last years. Many publications and review articles devoted to preparation of rare earth oxides, their structure, physicochemical properties and also possible applications have appeared up to date [1] – [5]. Rare earth sesquioxides are known to belong to one of the five types of the polymorphic structures [1], [4], [5]. At normal pressure lutetium sesquioxide (Lu_2O_3) exhibits, however, only C-type structure (cubic, bixbyite type structure) with the lattice constant of 1.0391 nm [4]. At high temperatures Lu_2O_3 directly transforms to the molten state [4].The Lu_2O_3 possesses the highest melting temperature among lanthanide oxides, $T = 2467$ °C [6]. Literature data on the optical properties of this material are very limited. Only a few papers give values of the refractive index of such Lu_2O_3 (baked powder of Lu_2O_3) [7] – [9]. Optical properties of Lu_2O_3 thin-films were examined in papers [10] – [12]. Thin films of Lu_2O_3 were prepared by electron beam deposition [11], by reactive evaporation of metallic lutetium in oxygen [10], [12] and by chemical deposition [11].

The literature data which deal with optical properties of Lu_2O_3 are compiled in Table 1. It can be seen from this Table that the reported values of the refractive index for Lu_2O_3 are in the range 1.86 – 2.02. To our knowledge, due to difficulties with

Table 1. Some selected physical parameters for Lu_2O_3 (literature data).

Refractive index	Density [g/cm^3]	Energy gap E_g [eV]	Relative dielectric permittivity ε'	Type of Lu_2O_3 specimen and preparation method	Refs.
	9.49			Crystalline sample	[7]
		5.6		Monocrystals	[13]
$n(589\ nm) = 1.933$	9.41	5.2, 5.5	$\varepsilon'_0 = 12.6$		[14]
1.884	9.03		$\varepsilon'_0 = 12.9$	Baked powder	[8], [9]
$n(589\ nm) = 1.93$ $n(656\ nm) = 1.917$ $n_\infty = 1.86$	9.24		$\varepsilon'_\infty = 3.55$ $\varepsilon'_0 = 12.1$	Baked powder	[7]
$n(500\ nm) = 2.02$				Electron-beam deposition	[11]
		5.5		Evaporation of Lu in oxygen	[12]
$n(550\ nm) = 1.89$		5.52	$\varepsilon'_\infty = 3.53$ $\varepsilon'_0 = 12.6$	Evaporation of Lu in oxygen	[10]
$n(540\ nm) =$ $= 1.86-1.88$				Chemical deposition	[11]

preparation of mononocrystalline specimens, only ref. [14] contains information on the refractive index for Lu_2O_3 monocrystals. For crystalline specimens of Lu_2O_3, the highest density for this material has been determined [7], [14]. However, dispersion characteristics of the optical constants of Lu_2O_3 (for bulk specimens and for thin films) have not been known.

In this paper, a simple method of fabrication of Lu_2O_3 thin films with the help of an electron gun has been presented. Optical characteristics of Lu_2O_3 thin-film coatings on quartz substrates have been reported and discussed.

2. Fabrication of Lu_2O_3 thin film coatings

All films were prepared by evaporation of lutetium sesquioxide in vacuum at a pressure of 5×10^{-6} Tr (7×10^{-4} Pa) or as a reactive evaporation in oxygen atmosphere at the oxygen pressure of 8×10^{-5} Tr (1×10^{-2} Pa). An electron beam gun of 10 kW output power, with magnetically focused electron beam, was used as Lu_2O_3 evaporation source. Powdered Lu_2O_3 of 99.9% purity, produced by Koch-Light Lab. was pressed in a copper, water-cooled, crucible. Such "pellets" of

Table 2. Vacuum deposition parameters for Lu_2O_3.

Film thickness [nm]	Pressure [Tr]	Deposition rate [nm/s]
997	$p_{O_2} = 8 \times 10^{-5}$	0.18
1295	$p_{O_2} = 8 \times 10^{-5}$	0.24
513	$p_{O_2} = 8 \times 10^{-5}$	0.15
457	$p = 5 \times 10^{-6}$	0.15
103	$p_{O_2} = 8 \times 10^{-5}$	0.10
349	$p_{O_2} = 8 \times 10^{-5}$	0.19

Lu_2O_3 were melted and heated in vacuum chamber with the electron gun in order to degas the material before evaporation process. All films used in optical studies were deposited onto quartz substrates (quartz plates) at the substrate temperature of about 423 K with a rate in the range from 0.1 nm/s to 0.24 nm/s. Lu_2O_3 films deposited under these conditions were reproducible and stable in time. The film thickness was determined by multiple-beam interference method (the Tolansky's method). The interference microscope was used for that aim. Thickness of the deposited films was in the range from 0.1 μm to 1.3 μm. All parameters of deposited films are given in Table 2.

3. Optical measurements

Optical properties of Lu_2O_3 films were examined in the spectral range from 0.2 μm to 2.5 μm. Measurements of the transmittance T of such films were carried out for normal incidence of light using Zeiss double-beam spectrophotometers (models Specord UV-VIS and Specord 61NIR). A single beam Zeiss spectrophotometer (model VSU2-P) was also applied for the transmittance measurements. Results presented here show the relative transmittance, *i.e.*, the transmittance of a film deposited onto quartz plate related to the transmittance of the same quartz plate without any coating.

4. Optical characteristics of Lu_2O_3 thin films

4.1. Spectral characteristics of the transmittance for Lu_2O_3 films

It has been shown earlier [15] that physical properties of rare earth oxide thin film coatings depend on such technological parameters as: i) the substrate temperature during film deposition, ii) residual gas pressure at the evaporation process and iii) film annealing after deposition. All lutetium-oxide-based coatings were deposited onto quartz substrates at a temperature of about 423 K. We tested the influence of oxygen pressure during film deposition as well as specimens annealing (after their fabrication) on the film properties.

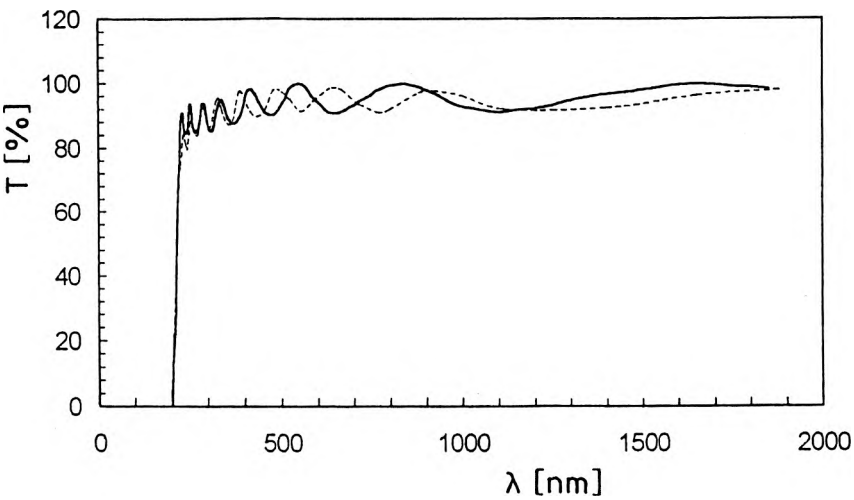

Fig. 1. Spectral dependence of the transmission coefficient $T(\lambda)$ of lutetium oxide thin films deposited under different evaporation conditions. The broken line shows the $T(\lambda)$ curve for films deposited at the oxygen presssure of 8×10^{-5} Tr (1×10^{-2} Pa) and at the substrate temperature of 423 K. Film thickness $d = 513$ nm. The solid line shows the $T(\lambda)$ curve for films deposited at the residual gas pressure of 5×10^{-6} Tr (7×10^{-4} Pa) and at the substrate temperature of 423 K. Film thickness $d = 457$ nm.

Typical spectral characteristics of optical transmittance for lutetium oxide thin film coatings on quartz plates are shown in Fig.1. These results relate to samples of a similar thickness of about 0.5 μm fabricated at different gas pressure during film deposition. Almost no difference between the transmittance characteristics for films evaporated reactively in the oxygen (at $p_{O_2} = 8 \times 10^{-5}$ Tr) and evaporated in the air (at the residual gases pressure of $p = 5 \times 10^{-6}$ Tr) was observed. A good transparency of the film starts about 0.22–0.3 μm and extends up to the near infrared. Such a behaviour suggests that optical absorption in this region is very small. A strong absorption of light below 220 nm is caused by the fundamental optical absorption and corresponds with optical energy gap for lutetium sesquioxide. Values of the energy gap for Lu_2O_3 published by different authors are in the range from 5.2 eV to 5.6 eV (see Table 1). A characteristic modulation of the transmittance in the considered spectral range is connected with the interference effects in the film.

The influence of the sample annealing on spectral characteristics of the transmittance is shown in Fig. 2. Curves in this figure present the transmittance for "as-deposited" films and for the same films annealed for 24 h at a temperature of 523 K. It is seen hat both characteristics are almost the same. Annealing causes only a small reduction of the absorption in the UV-range of spectrum.

We can conclude from these experiments that there is only negligible influence of the deposition parameters on spectral characteristics of the transmittance of Lu_2O_3 film. The results may suggest that vacuum evaporation of Lu_2O_3 with the help of electron gun enables fabrication of films with a stable state of oxidation.

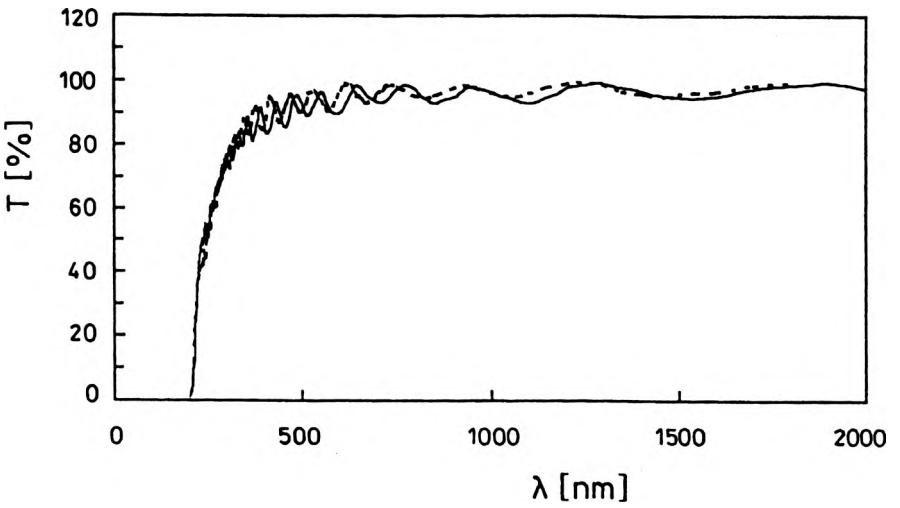

Fig. 2. Spectral dependence of the transmission coefficient $T(\lambda)$ for as-deposited oxide thin films (solid line) and for films annealed at a temperature of 523 K for 24 h (dotted line). Sample thickness – 997 nm.

4.2. Optical constants

Optical investigations of different thin film coatings have been carried out widely with the spectrophotometric method. This method enables evaluation of the complex refractive index ($n^* = n - ik$) of the homogeneous thin film specimen. In general case, even for normal incidence of the light, the transmittance is a complicated function of the sample parameters and wavelength [16]. For calculation of the optical constants simplified methods based on the interference effects in the film (registered in absorptionless region and in the region of small absorption) were used in this paper [15], [17], [18].

Typical dispersion curves of the refractive index $n(\lambda)$, and the extinction coefficient $k(\lambda)$, for lutetium oxide films are shown in Fig. 3. One can see that except of the ultraviolet region, optical constants exhibit very small dispersion in the visible and infrared range of spectrum. Films deposited by us exhibited very weak absorption for the measured wavelengths. For $\lambda < 400$ nm, the extinction coefficient was below 0.017. For different specimens of Lu_2O_3 thin films values of the refractive index were determined. Results presented in Table 3 show that values of the refractive index are in the range $1.80-1.88$ and $1.80-1.87$ for $\lambda = 0.55$ μm and $\lambda = 1$ μm, respectively. These values of the refractive index for lutetium oxide films are only slightly lower than those obtained for baked powder of Lu_2O_3 and for monocrystals (Table 1). Similar values of the refractive index have been obtained for Lu_2O_3 films prepared by chemical deposition and by reactive evaporation of metallic lutetium in the oxygen [10], [11]. The value of $n = 2.02$ at $\lambda = 0.5$ μm for electron-beam deposited Lu_2O_3 films reported in paper [11] seems to be too high., *ie.*, higher than for bulk specimens and does not reflect material properties of Lu_2O_3.

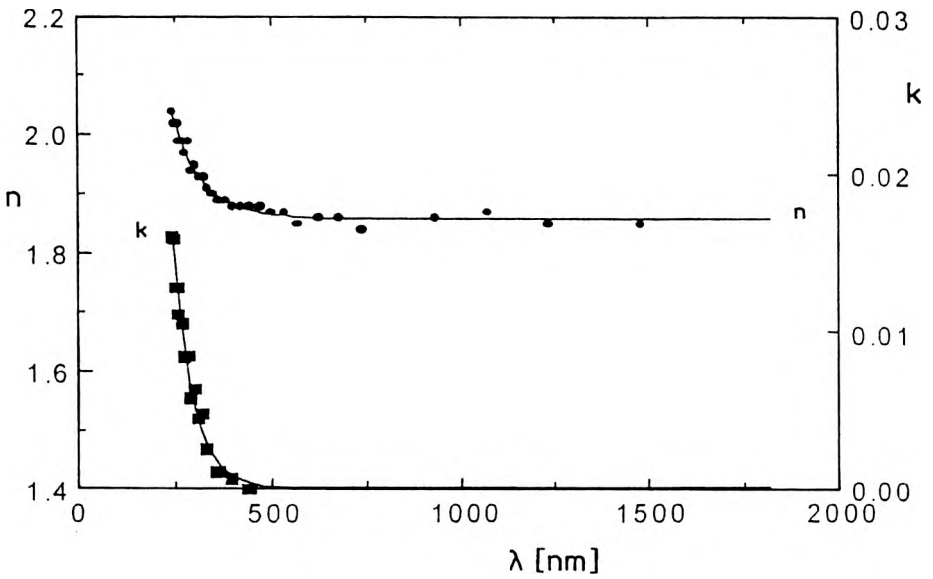

Fig. 3. Spectral dependence of the refractive index n and extinction coefficient k for Lu_2O_3 thin films deposited onto quartz substrate. Sample thickness – 997 nm.

Table 3. Values of the refractive index for Lu_2O_3 thin films of different thicknesses determined in this paper: for as deposited films and for films annealed at 523 K for 24 h.

Sample	Film thickness [nm]	Refractive index $n(\lambda = 0.55\ \mu m)$	$n(\lambda = 1\ \mu m)$
	997	1.88	1.87
As-deposited	1295	1.84	1.84
Lu_2O_3 thin films	513	1.86	1.85
	457	1.80	1.80
Lu_2O_3 thin films annealed at 523 K	997	1.86	1.86

Electron-beam deposited films obtained by us exhibited high packing density ($p = 0.93$) evaluated from the Lorentz-Lorenz relation [19]. Many different dispersion equations can be found in the literature for fitting experimental data [20]–[22]. We applied Cauchy-type expressions (Eq. (1) and (2)) and Sellmeier equation (Eq. (3)) to fit $n(\lambda)$ experimental characteristics for Lu_2O_3 films:

$$n(\lambda) = A_{n_1} + \frac{B_{n_1}}{\lambda^2}, \tag{1}$$

$$n(\lambda) = A_{n_2} + \frac{B_{n_2}}{\lambda^2} + \frac{C_{n_2}}{\lambda^4}, \tag{2}$$

$$n(\lambda) = \sqrt{1+\frac{A}{1-(B/\lambda)^2}} \tag{3}$$

where: A_{n_1}, A_{n_2}, B_{n_1}, B_{n_2}, C_{n_2}, A and B are constants. In Figure 4, the refractive index versus the wavelength for annealed Lu_2O_3 film of a thickness of 0.997 μm is shown.

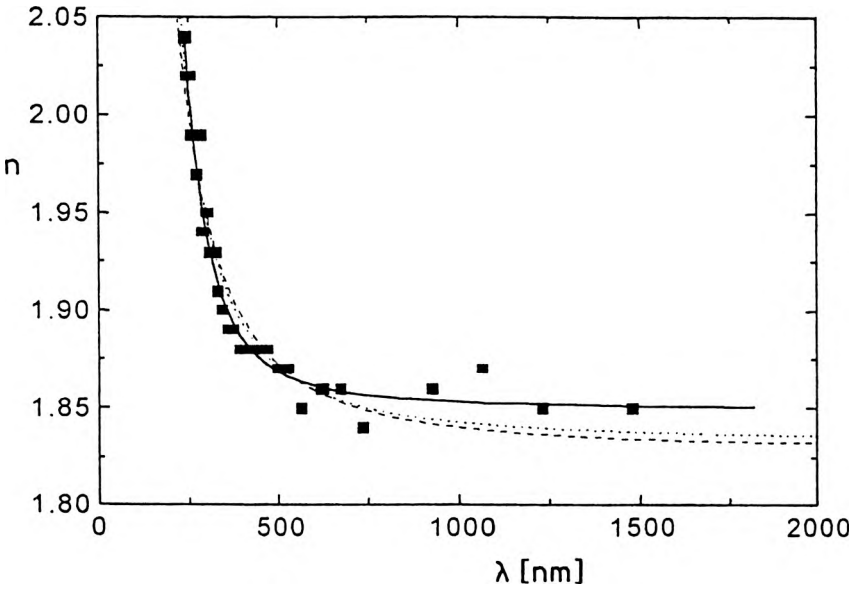

Fig. 4. Spectral dependence of the refractive index for Lu_2O_3 thin films of a thickness of 997 nm – comparison between the experimental data and the data calculated from Eqs. (1)–(3). The dotted line shows the best fit from Eq. (1). The solid line presents the best fit according to Eq. (2). The dashed line shows the best fit from Eq. (3).

In the same figure, theoretical $n(\lambda)$ curves calculated on the basis of the analytical models expressed by Eqs. (1)–(3) are shown. The NLSF method was applied for fitting experimental data. The best fit for these models has been obtained at the following values of the fitting parameters: $A_{n_1} = 1.8293$, $B_{n_1} = 1.077 \times 10^4\,(\mathrm{nm})^2$, $A_{n_2} = 1.850$, $B_{n_2} = 2.9 \times 10^3\,(\mathrm{nm})^2$, $C_{n_2} = 4.64 \times 10^8\,(\mathrm{nm})^4$, $A = 2.363$, $B = 117.2$ nm. It is seen from Fig. 4 that the best fitting results have been obtained according to Cauchy-type formula (Eq (.2)).

4.3. Dielectric function $\varepsilon^*(\nu)$ for optical frequencies

The real and imaginary parts of the complex dielectric function $\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$: were evaluated for optical frequencies from Maxwell relations:

$$\varepsilon'(\nu) = n^2(\nu) - k^2(\nu), \tag{4}$$

$$\varepsilon''(\nu) = 2n(\nu)k(\nu). \tag{5}$$

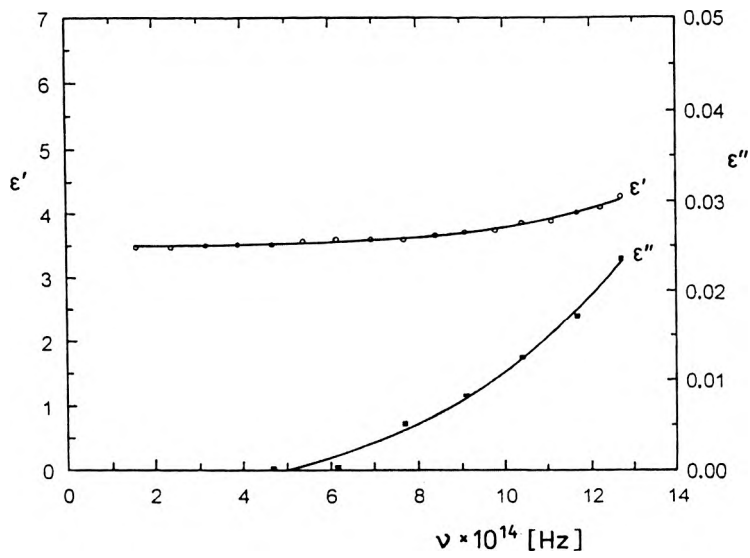

Fig. 5. Frequency dependence of the real part ε' and imaginary part ε'' of the complex dielectric function $\varepsilon^*(\nu)$ for Lu_2O_3 thin films.

In Figure 5, frequency dependence of $\varepsilon'$and ε'' is presented. Taking into account the curve of the real part of dielectric function in this figure, the high frequency limit of $\varepsilon'_\infty = \lim_{\nu = \infty} \varepsilon'(\nu)$ can be estimated. Value $\varepsilon'_\infty = 3.46$ was determined as so-called "high frequency optical relative permittivity" of Lu_2O_3 films. However, taking into account results for all specimens examined values of ε'_∞ were in the range: 3.23 – 3.53. These results are very close to the value of ε'_∞ for bulk specimens of Lu_2O_3 obtained by DULEPOV, BATSANOV and KUSTOVA [7]. The estimated value of ε'_∞ is connected with a contribution of the electronic polarization mechanism in lutetium oxide itself to the total dielectric response of the film.

5. Conclusions

1. Vacuum deposition method was applied for fabrication of lutetium oxide thin film coatings on quartz substrates. An electron beam gun source was used for evaporation of Lu_2O_3. Reproducible thin film coatings can be fabricated with this method. They exhibit a good stability in time and are mechanically resistant.

2. Optical characteristics of Lu_2O_3 coatings were examined in the wavelength region from 0.2 μm to 2.5 μm. Thin films of Lu_2O_3 exhibit interesting optical properties. They have good transparency over a wide spectral range (from 0.3 to 2.5 μm).

3. Optical constants were estimated taking into account the interference effects in the film. Dispersion and absorption characteristics for the refractive index and for extinction coefficient are presented. For $\lambda = 0.55$ μm values of the refractive index of

the films are in the range 1.80 – 1.88 and are close to the refractive index for bulk specimens of Lu_2O_3. The films exhibited only a weak absorption: $0.005 < k < 0.017$ for 200 nm $< \lambda <$ 400 nm.

4. In the visible range values of the refractive index for Lu_2O_3 films are similar to those obtained by us earlier for the other rare earth oxide films [15], [17], [18], [23].

5. The characteristics of the real and imaginary parts of dielectric function $\varepsilon^*(\nu)$ were presented for the frequency range $(1.5 \times 10^{14} - 1.3 \times 10^{15})$ Hz. Values of the high-frequency optical relative permittivity ε'_∞ were in the range: 3.23 – 3.53.

6. Electron-beam deposited Lu_2O_3 films exhibited high packing density, $p = 0.93$. Only a small influence of technological parameters (*i.e.*, oxygen pressure during film deposition and thermal annealing of coatings) on optical properties of the films was observed.

7. Taking into account all the results presented thin films of Lu_2O_3 can be considered as useful material for fabrication of the interference thin film coatings. Optical characteristics classify them as effective single-layer antireflection coatings for semiconductor substrates having high refractive index of about 3.4 (*e.g.*, for silicon substrates).

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References

[1] EYRING L., *The Handbook on The Physics and Chemistry of Rare Earths*, Vol. 3, pp.337-399, [Eds.] K. A. Gschneider, L. Eyring, North-Holland, Amsterdam 1979.
[2] GASGNIER M., Phys. Status Solidi A **57** (1980), 11.
[3] *Ibidem* **114** (1989), 11.
[4] ADASCHI G., IMANAGA N., Chem. Rev. **98** (1998), 1479.
[5] EYRING L., *High Temperature Oxides*, Part II, [Ed.] M. Alper Allen, Acad. Press, New York 1970, pp. 41 – 97.
[6] MORDOVIN O. A., TIMOFEEVA N. I., DROZDOVA L. N., Izv. Acad. Nauk Neorg. Mater. (in Russian) **3** (1967), 187.
[7] DULEPOV E. V., BATSANOV S. S., KUSTOVA G. N., Zh. Strukt. Khimii (in Russian) **13** (1972), 935.
[8] BATSANOV S. S., GRIGORIEVA G. N., SOKOLOVA N. P., Zh. Strukt. Khimii (in Russian) **3** (1962), 339.
[9] BATSANOV S. S., DULEPOV E. V., Fiz. Tverd. Tela (in Russian) **7** (1965), 1239.
[10] ANDREEVA A. F., GILMAN I. Ya., Zh. Prikl. Spektrosk. (in Russian) **28** (1978), 895.
[11] DEMENTIEV A. V., PRIDATKO G. V., KRYZHANOVSKIJ B. P., (in Russian) OMP No. 1 (1977), 41.
[12] SAMSONOV G. V., GILMAN I. YA., ANDREEVA A. F., Izv. Acad. Nauk SSSR, Neorg. Mater. (in Russian), **10** (1974), 1645.
[13] BAGDASAROV K., ZHUZE W. P., KARIN M. G., *et al.*, Solid State Physics **26** (1984), 1134.
[14] ZHUZE W. P., SZELYKH A. I., Phys. Tech. Semicond. **23** (1989), 393.
[15] MARCINÓW T., TRUSZKOWSKA K., Appl. Opt. **20** (1981), 1755.
[16] HEAVENS O. S., *Physics of Thin Films*, [Eds.] G. Hass, R. E. Thun R.E., **2** (1964), 193.
[17] MARCINÓW T., WESOŁOWSKA C., WIKTORCZYK T., Opt. Appl. **7** (1977), 135.
[18] WIKTORCZYK T., Opt. Appl. **31** (2001), 5.

[19] BORN W., WOLF E., *Principles of Optics, Electromagnetic Theory of Propagation, Interference and Diffraction of Light*, Cambridge University Press 1999, Chapt. 2.3.3.
[20] SPIGA S., TALLARIDA G., BOGHESI A., *et al.*, Thin Solid Films **325** (1998), 36.
[21] DOBROWOLSKI J.A., HO F.C., WALDORF A., Appl. Opt. 22 (1983), 3191.
[22] NENEKOV M., PENCHEVA T., Thin Solid Films **324** (1998), 305.
[23] WIKTORCZYK T., Eur. J. Solid State Inorg. Chem. **28** (1991), 581.

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