Lithuanian Journal of Physics, Vol. **47**, No. 3, pp. 309–314 (2007)

ELLIPSOMETRIC STUDIES OF $ErMnO_3$ SINGLE CRYSTALS *

G.-J. Babonas [a], J.-C. Grivel [b], A. Rėza [a,c], and R. Girkantaitė [c]

[a] *Semiconductor Physics Institute, A. Goštauto 11, LT-01108 Vilnius, Lithuania*
E-mail: jgb@pfi.lt

[b] *Materials Research Department, Risø National Laboratory, Technical University of Denmark, DK-4000 Roskilde, Denmark*

[c] *Faculty of Physics and Technology, Vilnius Pedagogical University, Studentų 39, LT-08106 Vilnius, Lithuania*

Received 8 June 2007

Ellipsometric studies of $ErMnO_3$ single crystals have been carried out in the spectral range of 1–5 eV by means of photometric ellipsometers. Experimental ellipsometric data were analysed in the uniaxial crystal model. For the first time, the components of dielectric function of $ErMnO_3$ were determined. The fine structure of dielectric function spectra was analysed and the origin of the optical features was discussed taking into account the possible mechanisms of electronic excitations. It was shown that intra-configuration optical transitions of d–d and f–f types in Mn^{3+} and Er^{3+} ions, respectively, and charge-transfer transitions O($2p$)→Mn($3d$) contribute to the optical response of $ErMnO_3$. The optical spectra and electronic energy band structure of $ErMnO_3$ was compared with those for other manganites.

Keywords: manganites, optical properties, electronic energy band structure

PACS: 75.47.Lx, 78.20.-e

1. Introduction

Undoped $RMnO_3$ (R = La, Nd, Pr, Er) and doped $R_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba) manganites [1] have attracted a lot of attention due to their colossal magnetoresistance. The double exchange model was used to explain the ferromagnetism and metallicity of manganites. Two additional models were developed for the interpretation of colossal magnetoresistance. The models take into account the polarons due to Jahn–Teller effect for Mn^{3+} ions and the orbital fluctuations. In order to determine the microscopic mechanism of these phenomena, the optical properties of manganites were studied along with magnetic interactions.

The structural difference between $LnMnO_3$ (Ln is a lanthanide) compounds should be emphasized. On the one hand, manganites containing large ionic radius lanthanides (La, Ce–Dy) crystallize in a distorted orthorhombic perovskite structure [1]. On the other hand, manganites with small ionic radius lanthanides (Ho–Lu) crystallize in a hexagonal structure. The coordination polyhedra for Mn differ in crystal lattices of various symmetry leading to different physical properties of manganites. While manganites with perovskite structure possess a colossal magnetoresistance effect, manganites of hexagonal symmetry are of interest because of the combination of ferroelectric and magnetic ordering [2]. In order to reveal the correlation between crystal structure and electronic energy band structure of manganites, the optical spectra of compounds from two groups, e. g., $NdMnO_3$ [3] and $ErMnO_3$, are to be compared.

The optical properties of $ErMnO_3$ were not widely investigated. Nonlinear optical spectroscopy and Faraday rotation were studied in [4]. In the present work, ellipsometric studies of $ErMnO_3$ have been carried out and the mechanism of the electronic transitions responsible for corresponding optical features is discussed.

2. Experimental

The $ErMnO_3$ single crystals were grown in Risø National Laboratory by means of the travelling solvent floating zone (TSFZ) technique. The starting reagents, MnO_2 and Er_2O_3 powders (Alfa Aesar, 99.9% purity), were mixed in ethanol and dried under stirring. After calcination at 900 °C in air, the powders were mixed with polyvinyl alcohol that acted as a binder. Rods were isostatically pressed and sintered at 1350 °C in air in a vertical furnace. After sintering, the rods had

* The report presented at the 37th Lithuanian National Physics Conference, 11–13 June 2007, Vilnius, Lithuania.

ISSN 1648-8504

a diameter of about 8 mm and a length of 3 cm (seed) and 9 cm (feed). The composition of the feed rod was $ErMn_{1.01}O_x$ to compensate for Mn evaporation from the melt during the growth process. The growth was performed in flowing air in a mirror furnace (Crystal Systems Inc) equipped with 4 lamps of 1500 W maximum power. The molten zone was moved upwards at a rate of 5 mm/h, while the rods were counter rotated at 25 rpm.

The XRD analysis of obtained $ErMnO_3$ single crystals was performed. From the Laue diffraction pattern, a hexagonal symmetry, the space group $P6_3cm$, and lattice parameters $a = 6.117$ Å and $c = 11.435$ Å were determined. The unit cell contains six formula units. In hexagonal lattice Er^{3+} ions are located in $2a$ positions (local symmetry $3m$) and $4b$ sites (symmetry 3). Magnetic Mn^{3+} ($3d^4$) ions occupy $6c$ positions (symmetry m) coordinated by O^{2-} ions. The structural parameters were in a good agreement with previous structural data [5].

The characteristic structural units in $ErMnO_3$ cell are Mn–O and Er–O polyhedra. The Mn ions are situated in a trigonal bipyramid (Fig. 1(a)), which is sharing the corners with neighbouring Mn–O polyhedra. The ordering of polyhedra results in a two-dimensional nature of the structure. The distance from Mn atom to the nearest five O atoms varies from ∼1.85 to ∼2.09 Å [5] and it is shortest to apical O atoms and longest for the bonds in the basal plane. The striking structural anisotropy for in-plane and out-of-plane Mn–O bond lengths is a particular feature of $ErMnO_3$ lattice as compared to that of $NdMnO_3$ [6]. In $NdMnO_3$ the Mn–O distance is largest for apical O atoms in MnO_6 octahedron. In $ErMnO_3$ both Er atoms are eightfold coordinated with polyhedron in the shape of distorted bicapped trigonal antiprism (Fig. 1(b)). Both Er–O polyhedra are similar in shape though 180°-rotated around b axis with respect to each other. The distortion of Er–O polyhedra is responsible for ferroelectric properties of $ErMnO_3$ [2]: dipole moments of four Er(*2*)–O polyhedra are antiparallel to those of two Er(*1*)–O polyhedra resulting in a ferrielectric configuration.

Several samples with polished surfaces were prepared for optical studies. In ellipsometric measurements, the surface of area 3×8 mm^2 was used with the c axis oriented along the short side of the sample. The optical transmission measurements have been carried out on the platelet of 1.2 mm thickness and ⌀ 6 mm with c axis in the surface plane.

Two spectroscopic ellipsometers were used, a standard SOPRA GES5 ellipsometer with rotating polarizer and home-made photometric ellipsometer with rotating analyzer. In the latter case, the ellipsometric parameters were determined with ∼0.02° accuracy. The systematic errors due to wandering of light spot on the photomultiplier cathode and nonlinearity of the detector response were taken into account. The ellipsometric data were obtained in the spectral range of 1–5 eV. The complex reflectivity ρ was determined from ellipsometric measurements

$$\rho = \frac{r_\parallel}{r_\perp} = \tan\Psi\, \exp(\mathrm{i}\Delta)\,, \tag{1}$$

where $r_\parallel$ and $r_\perp$ are Fresnel coefficients for light polarized parallel and perpendicular to the plane of light incidence, Ψ and Δ are ellipsometric parameters.

Two independent components $\varepsilon_x = \varepsilon_y = \varepsilon_o$ and $\varepsilon_z = \varepsilon_e$ of complex dielectric function $\varepsilon = \varepsilon_1 + \mathrm{i}\varepsilon_2$ (where $\varepsilon_1 = \mathrm{Re}(\varepsilon)$ and $\varepsilon_2 = \mathrm{Im}(\varepsilon)$) for $ErMnO_3$ were determined in the uniaxial crystal model. Two experimental runs of the measurements were carried out in order to obtain two pairs of Fresnel coefficients:

$$r_\parallel = \frac{\sqrt{\varepsilon_o\varepsilon_e}\cos\theta - \sqrt{\varepsilon_o - \sin^2\theta}}{\sqrt{\varepsilon_o\varepsilon_e}\cos\theta + \sqrt{\varepsilon_o - \sin^2\theta}}\,,$$

$$r_\perp = \frac{\cos\theta - \sqrt{\varepsilon_o - \sin^2\theta}}{\cos\theta + \sqrt{\varepsilon_o - \sin^2\theta}} \tag{2}$$

for c axis in the incidence plane and

$$r_\parallel = \frac{\varepsilon_o\cos\theta - \sqrt{\varepsilon_o - \sin^2\theta}}{\varepsilon_o\cos\theta + \sqrt{\varepsilon_o - \sin^2\theta}}\,,$$

$$r_\perp = \frac{\cos\theta - \sqrt{\varepsilon_e - \sin^2\theta}}{\cos\theta + \sqrt{\varepsilon_e - \sin^2\theta}} \tag{3}$$

for c axis perpendicular to incidence plane. In (2) and (3) θ is the angle of light incidence, which has been equal to 70° in a typical ellipsometric run.

3. Results and discussion

Figure 2 presents the spectral dependence of dielectric function components of hexagonal $ErMnO_3$. As is seen, a rich fine structure is observed in the optical spectra of $ErMnO_3$. As in the other manganites [3], several main peaks are to be noted in the region of ∼1.5, 2.2, and 3.4 eV. A particular feature of $ErMnO_3$ is a strong anisotropy of the peak at 1.5 eV. The

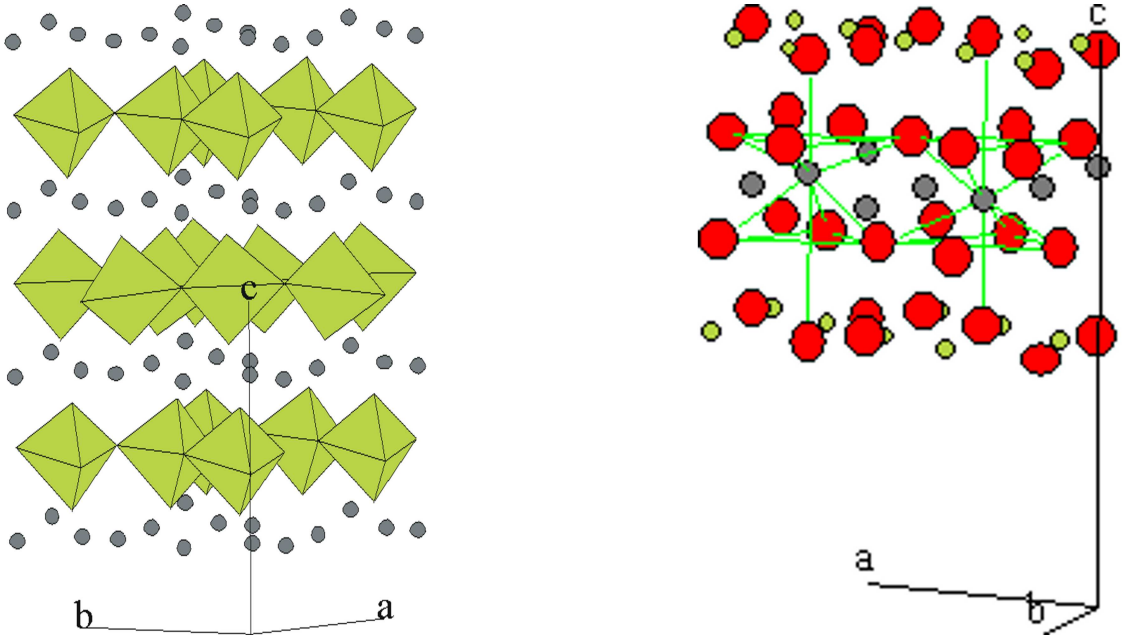

Fig. 1. (a) Mn–O and (b) Er–O polyhedra in the structure of hexagonal $ErMnO_3$. In (a) dark circles are Er atoms; in (b) small, middle, and big circles are Mn, Er, and O atoms, respectively.

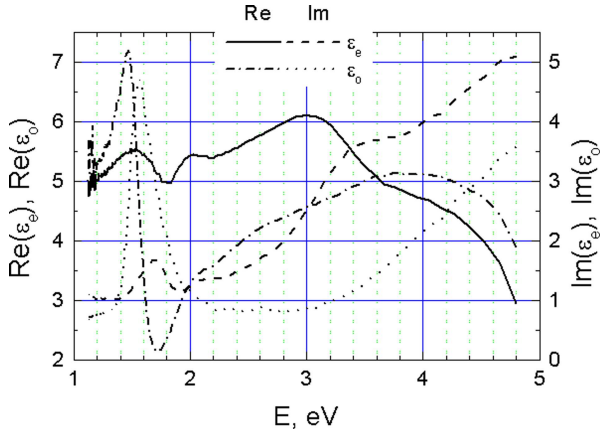

Fig. 2. Spectral dependences of the dielectric function components of hexagonal $ErMnO_3$.

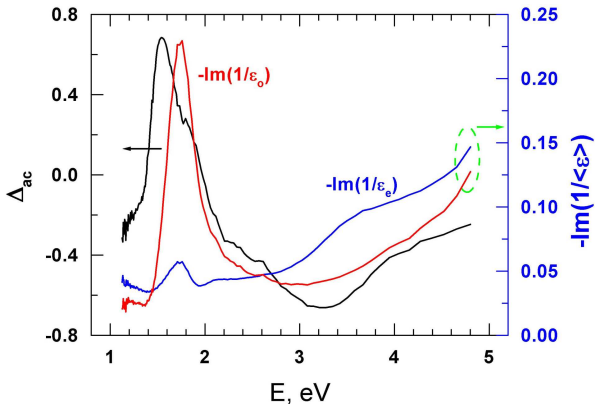

Fig. 3. Spectra of the parameter of anisotropy Δ_{ac} and energy loss functions $-\mathrm{Im}(1/\varepsilon_i)$ (where $i = e, o$).

fine structure in the spectral dependence of anisotropy (Fig. 3) is better resolved for anisotropy parameter

$$\Delta_{ac} = \frac{\varepsilon_{o2} - \varepsilon_{e2}}{\sqrt{\varepsilon_{o2}^2 + \varepsilon_{e2}^2}}\,. \qquad (4)$$

In particular, as it follows from Fig. 3, at least two optical transitions at ∼1.55 and 1.8 eV contribute to the main peak.

The edge of the fundamental absorption band is clearly seen from the absorption measurements of $ErMnO_3$ (Fig. 4). The constant refraction index $n = 2.4$ was assumed in the calculations of absorption coefficient. As is seen, the onset of absorption occurs at 1.4–1.5 eV and it is slightly different for polarizations $e\|a$ and $e\|c$. Sharp absorption lines observed in the region of relative transmittance is unambiguously assigned to the f–f intra-configuration transitions in $Er^{3+}(f^{11})$ ions ($L = 6$ and $S = 3/2$). In accordance with the Er^{3+} spectra in various rare earth compounds [7], the series of lines at ∼0.85, 1.3, and 1.55 eV are due to electronic excitations from the ground level $^4I_{15/2}$ to the excited multiplets $^4I_{13/2}$, $^4I_{11/2}$, and $^4I_{9/2}$, respectively. It is interesting to note that the structure of Stark-split components of multiplets is slightly different for two main light polarizations. A possible reason for this observation is occurrence of two non-equivalent Er sites in $ErMnO_3$. It is interesting to note that Faraday rotation was observed [4] in the region of

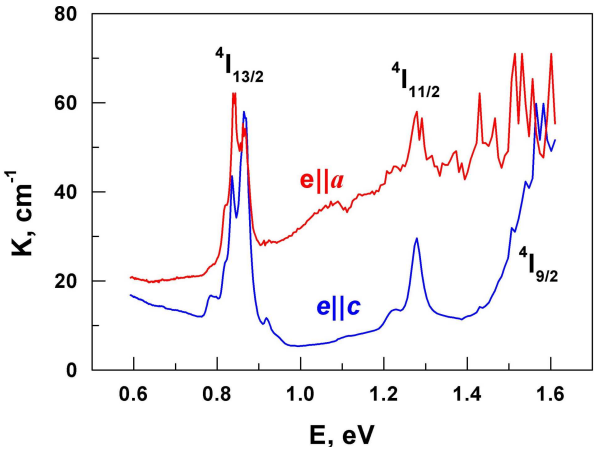

Fig. 4. Spectra of absorption coefficient $K(E)$ of $ErMnO_3$ for light polarized along the main directions of hexagonal lattice.

$^4I_{15/2} \rightarrow ^4I_{11/2}$ transitions along with a strong contribution of the electronic excitations in the fundamental absorption band with the resonance energy 1.67 eV, which is close to the low-energy peaks observed in the spectra of dielectric function (Fig. 2).

It is reasonable to analyse the fine structure of dielectric function spectra of manganites as a set of contributions originated from Lorentzian-like terms [3]. In this model, the energies of Lorentzian lines correspond to the electronic optical transitions between the levels in the energy scheme (see Fig. (5)).

The electronic energy band structure was analysed theoretically in several studies. In electronic structure of ferromagnet $YMnO_3$ [8] calculated in local density approximation, the absorption edge (at 1.1 eV) was attributed to charge transfer transitions. In the local spin-density approximation [9], the ferroelectromagnetic $YMnO_3$ was found to be a semiconducting compound with the band gap at 1.5 eV. It was also found [9] that the lowering of symmetry in hexagonal $YMnO_3$ is not connected with a Jahn–Teller instability, in contrast to perovskite manganites. In [4] the data on second harmonic spectroscopy on hexagonal manganites were interpreted by means of intraband dipole-allowed d–d transitions in the visible range. The onset of strong absorption at 1.3–1.5 eV in manganites was attributed to spin-allowed transitions within t_{2g} and e_g orbitals of Mn^{3+} ions split in local crystalline field of hexagonal manganites. These intraband transitions were assumed to have a high intensity because of acentric $6c$ positions of Mn^{3+} ions in the unit cell and their high concentration. Below, the ellipsometric data on $ErMnO_3$ will be considered in this approximation.

In hexagonal lattice, the crystal field symmetry ($\bar{6}m2$) of $Mn^{3+}(3d^4)$ ions situated in trigonal bipyramidal polyhedra causes the splitting of the ^{5}D state into three components (Fig. 5), single $^5\Gamma_1$ ground state and two doubly degenerate excited states, $^5\Gamma_5$ (lower) and $^5\Gamma_6$ (higher) [9]. The d-type wave functions of the $^5\Gamma_5$ state are mixed with the p-type x and y wave functions [4]. As compared with the octahedral crystal field splitting Δ_o in perovskite manganites, in hexagonal manganites the overall splitting is $1.25\Delta_o$ with $0.87\Delta_o$ for $^5\Gamma_1 \rightarrow^5 \Gamma_5$ and $0.38\Delta_o$ for $^5\Gamma_1 \rightarrow^5 \Gamma_6$. A further splitting of the levels occurs in the low-temperature phase with a local symmetry m for $6c$ sites lifting degeneracy of $^5\Gamma_5$ and $^5\Gamma_6$ states. The charge transfer transitions O($2p$)→Mn($3d$) are assumed [4] to occur at $E > 3$ eV.

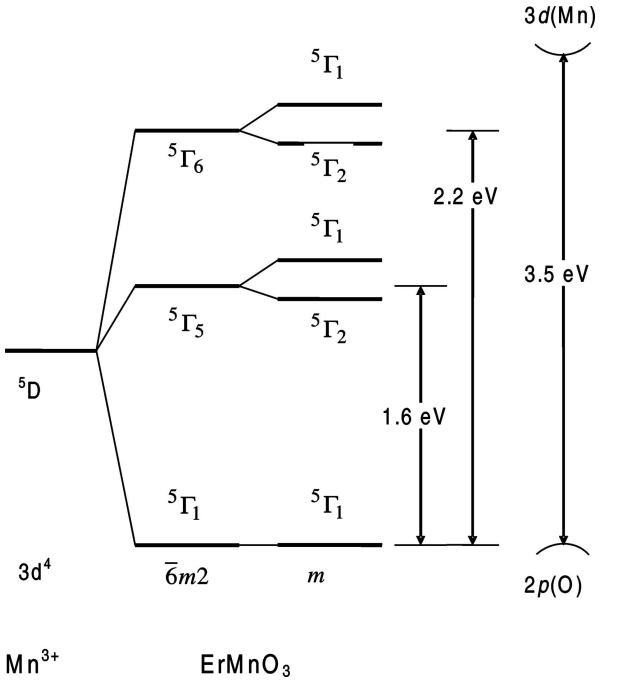

Fig. 5. Scheme of energy levels and optical transitions in $ErMnO_3$ (modified from [4]).

The experimental data (Figs. 2, 3) on $ErMnO_3$ are in a good agreement with the model described above. At first, the optical characteristics at ∼1.6 eV are strongly polarized, the intensity being larger for $e\|a$ in accordance to the predictions of the model. Therefore, they can be attributed to the $^5\Gamma_1 \rightarrow^5 \Gamma_5$ transitions. Secondly, in this model the optical features at ∼2.2 eV are assigned to the $^5\Gamma_1 \rightarrow^5 \Gamma_6$ transitions. Thus, the energy gap $^5\Gamma_6$–$^5\Gamma_5$ equals to 0.6 eV, the latter value agrees well with the crystal field splitting (0.7 eV) between these states estimated from the distance $^5\Gamma_1$–$^5\Gamma_5$. Thirdly, the mixing of p-type wave functions to $^5\Gamma_5$ state is most probably responsible for the high intensity of the peaks at 1.6 eV. Finally, the sign of the anisotropy parameter at 1.6 eV (Fig. 3) is opposite to that determined for peaks at 2.2 eV.

Comparison of optical spectra in $ErMnO_3$ and $NdMnO_3$ [3] reveals the general regularities and particular features of manganites of hexagonal and perovskite structure. The $NdMnO_3$ crystals of orthorhombic symmetry (space group $Pbnm$, $a = 5.4505$ Å, $b = 5.743$ Å, $c = 7.566$ Å [3]) can be considered in the pseudo-cubic system because of a small crystal anisotropy along the a and b axes. Indeed, a slight difference in the localization of Mn–O polyhedra along the a and b axes causes a small optical anisotropy in the basal plane. Therefore, the spectrum of anisotropy parameter Δ_{ab} is different from Δ_{ac} and Δ_{bc} [3]. The latter two are similar to each other and to Δ_{ac} in $ErMnO_3$ (Fig. 3). The lowest-energy peak of orthorhombic $NdMnO_3$ at ∼1.2 eV could be assigned to the ${}^5\Gamma_3 \rightarrow {}^5\Gamma_5$ transitions corresponding to the octahedral crystal field splitting Δ_o, in a good agreement with crystal field splitting in hexagonal $ErMnO_3$. The common feature of the dielectric function spectra of several manganites is the wide band at 3.5–4.0 eV, which in the present model is assigned to charge transfer transitions with a polarization being opposite to that of d–d transitions ${}^5\Gamma_1 \rightarrow {}^5\Gamma_5$ developed for $e \| a$. As compared to the data for $NdMnO_3$ [3], a particular feature of $ErMnO_3$ is a strong peak in the energy loss function spectra corresponding to the ${}^5\Gamma_1 \rightarrow {}^5\Gamma_5$ transitions.

The f–f transitions in $NdMnO_3$ [3] as well as in $ErMnO_3$ (Fig. 4) correspond to those in other rare earth compounds [7].

4. Conclusions

Experimental data and their analysis have shown that common features in optical spectra of both hexagonal and perovskite manganites is a higher-energy (3.5–4.0 eV) peak, which can be attributed to the charge transfer transitions. The fine spectral structure at lower energies (1–2.6 eV) can be assigned to the optical transitions between the states originated from $3d^4$ levels of Mn^{3+} which are split in octahedral and trigonal bipyramid crystal fields in perovskite and hexagonal manganites, respectively. A particular feature of $ErMnO_3$ is a strong peak at ∼1.6 eV. The f–f transitions in manganites correspond to those obtained in other rare earth compounds.

Acknowledgements

The work was partially supported by the EU project PHOREMOST (N 511616) and Danish Technical Research Council.

References

[1] J.M.D. Coey, M. Viret, and S. von Molnár, Mixed-valence manganites, Adv. Phys. **48**, 167–293 (1999).

[2] G.A. Smolenskii and I.E. Chupis, Ferroelectromagnets, Sov. Phys. Usp. **25**, 475–493 (1982).

[3] G.J. Babonas, A. Reza, R. Szymczak, M. Baran, S. Shiryaev, J. Fink-Finowicki, and H. Szymczak, Ellipsometric studies of $NdMnO_3$ single crystals, Acta Phys. Pol. A **105**, 197–208 (2004).

[4] C. Degenhart, M. Fiebig, D. Fröhlich, Th. Lottermoser, and R.V. Pisarev, Nonlinear optical spectroscopy of electronic transitions in hexagonal manganites, Appl. Phys. B **73**, 139–144 (2001).

[5] B.B. Van Aken, A. Meetsma, and T.T.M. Palstra, Hexagonal $ErMnO_3$, Acta Cryst. **E57**, i38–i40 (2001).

[6] S. Quezel-Ambrunaz, Parametres des manganites de terres rares Perovskites et structure magnetique du manganese dans $MnPrO_3$ et $MnNdO_3$ par diffraction neutronique, Bull. Soc. Franc. Mineral. Crist. **91**, 339–343 (1968).

[7] G.H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals* (Interscience Publishers, New York, 1968).

[8] M. Qian, J. Dong, and Q. Zheng, Electronic structure of the ferroelectromagnet $YmnO_3$, Phys. Lett. A **270**, 96–101 (2000).

[9] J.E. Medvedeva, V.I. Anisimov, M.A. Korotin, O.N. Mryasov, and A.J. Freeman, The effect of Coulomb correlation and magnetic ordering on the electronic structure of two hexagonal phases of ferroelectromagnetic $YMnO_3$, J. Phys. Cond. Matter **12**, 4947–4958 (2000).

$ErMnO_3$ MONOKRISTALŲ ELIPSOMETRINIAI TYRIMAI

G.J. Babonas [a], J.-C. Grivel [b], A. Rėza [a,c], R. Girkantaitė [c]

[b] *Puslaidininkių fizikos institutas, Vilnius, Lietuva*
[a] *Danijos technikos universitetas, Roskildė, Danija*
[a] *Vilniaus pedagoginis universitetas, Vilnius, Lietuva*

Santrauka

1–5 eV spektrų ruože, panaudojant fotometrinius elipsometrus, atlikti $ErMnO_3$ monokristalų elipsometriniai tyrimai. Eksperimentiniai elipsometriniai duomenys analizuoti remiantis vienašio kristalo modeliu. Pirmą kartą nustatyti $ErMnO_3$ dielektrinės funkcijos komponentų spektrai. Išnagrinėta dielektrinės funkcijos spektrų smulkioji sandara ir aptarta optinių ypatumų kilmė, atsižvelgiant į galimus elektroninių sužadinimų mechanizmus. Nustatyta, kad $ErMnO_3$ optinį atsaką sukelia nekeičiantys jonų Mn^{3+} ir Er^{3+} konfigūracijų, atitinkamai d–d ir f–f, šuoliai ir O($2p$)→Mn($3d$) šuoliai su krūvio pernaša. Palyginti $ErMnO_3$ ir kitų manganitų optiniai spektrai ir elektroninių juostų sandara.