Materials Chemistry and Physics 147 (2014) 1191–1194

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

# Synthesis and luminescence properties of $Li_2O–Y_2O_3–TeO_2:Eu^{3+}$ tellurite glass

V.V. Atuchin [a, b, c, *], A.P. Yelisseyev [d], E.N. Galashov [e], M.S. Molokeev [f]

[a] Laboratory of Optical Materials and Structures, Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russia
[b] Functional Electronics Laboratory, Tomsk State University, Tomsk 634050, Russia
[c] Laboratory of Semiconductor and Dielectric Materials, Novosibirsk State University, Novosibirsk 630090, Russia
[d] Laboratory of High Pressure Minerals and Diamond Deposits, Institute of Geology and Mineralogy, SB RAS, Novosibirsk 630090, Russia
[e] Department of Applied Physics, Novosibirsk State University, Novosibirsk 630090, Russia
[f] Laboratory of Crystal Physics, Kirensky Institute of Physics, SB RAS, Krasnoyarsk 660036, Russia

## HIGHLIGHTS

- Tellurite glass $0.25Li_2O–0.20Y_2O_3–0.5TeO_2–0.05Eu_2O_3$ has been synthesized.
- Photoluminescence properties have been evaluated at UV and X-ray excitation.
- PL intensity is significant up to ~500 K.

## ARTICLE INFO

*Article history:*
Received 13 February 2014
Received in revised form
7 July 2014
Accepted 7 July 2014
Available online 22 July 2014

*Keywords:*
A. Glasses
B. Heat treatment
C. Photoluminescence spectroscopy
D. Optical properties

## ABSTRACT

The $Eu^{3+}$-doped red-orange emitting phosphor of tellurite glass $0.25Li_2O–0.20Y_2O_3–0.5TeO_2–0.05Eu_2O_3$ has been synthesized by the melt quenching method. The amorphous nature of the glass has been verified by XRD measurements. The photoluminescence excitation and emission spectra, the luminescence decay curves have been investigated for the composition. The phosphor can be efficiently excited by the near UV light to realize the intense narrow red emission line (611 nm) corresponding to forced electric dipole transition $^5D_0 \rightarrow {}^7F_2$ of $Eu^{3+}$ ions. The $Li_2O–Y_2O_3–TeO_2:Eu^{3+}$glass phosphor is a potential red-orange emitting candidate for the application in WLEDs.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Tellurite glasses based on $TeO_2$ as a heavy network former possess such unique properties as high chemical durability, a wide range of transparency, low phonon losses, high refractive indices and comparatively low melting points [1–4]. The glasses have recently attracted wide attention because of their high potential to be used as efficient hosts for rare earth element activators [1,5–10]. It should be emphasized that tellurite glasses can accommodate a large quantity of rare element oxides with the persistance of the amorphous state [1,10–13]. However, for several oxide compositions, the crystallization behavior was reported at ~1 mol% $Ln_2O_3$ addition [5,13]. The $Eu^{3+}$ ion is among the most interesting activators due to possible applications as a red emitting phosphor agent with the intense emission in several bands over the spectral range of 580–720 nm [6,7,12–22]. A lot of different chemical compositions were evaluated to see the effects of different metals and glass-forming agents combination on the structural, mechanical, thermal and luminescence parameters of the tellurite glasses. However, the $Y_2O_3$-containing compositions were not reported up to now. In the present study, the glass-forming and spectroscopic properties of the $Li_2O + Y_2O_3 + TeO_2 + Eu_2O_3$ oxide combination are tested for the first time.

## 2. Experimental methods

The glass composition, $0.25Li_2O–0.20Y_2O_3–0.5TeO_2–0.05Eu_2O_3$, was prepared by the conventional melt quenching method. The

* Corresponding author. Laboratory of Optical Materials and Structures, Institute of Semiconductor Physics, SB RAS, Novosibirsk 630090, Russia. Tel.: +7 383 3308889; fax: +7 383 3332771.
*E-mail addresses:* atuchin@thermo.isp.nsc.ru, atuchin@isp.nsc.ru (V.V. Atuchin).

http://dx.doi.org/10.1016/j.matchemphys.2014.07.003
0254-0584/© 2014 Elsevier B.V. All rights reserved.

mixture of high purity grade tellurium dioxide ($TeO_2$, 99.999%, NSU, Russia), lithium carbonate ($Li_2CO_3$, 99.999%, Sigma–Aldrich), yttrium trioxide $Y_2O_3$ and europium trioxide $Eu_2O_3$ (99.999%, GREEN RESOURCE CO., LTD) reagents was used as a starting charge. The well mixed materials were placed into a platinum crucible, heated slowly (2–3 h) in electric furnace up to temperature $T = 500$–$550$ K to avoid the powder eruption due to lithium carbonate decomposition. Then, the temperature was increased to $T = 1100$ K during 4 h and the melt was kept at this temperature for 2–3 h for homogenization. After this, the melt portion was poured onto a steel plate heated at $T = 700$ K, and the quenched ingot was cooled slowly to room temperature. The crystallinity of the final product was tested by XRD measurements at room temperature using a D8 ADVANCE Bruker diffractometer (VANTEC liner detector, $CuK_\alpha$ radiation). Detailed information on the set up can be found elsewhere [23,24].

The transmission (absorption) spectra were recorded over the spectral range of 200–600 nm. A 50 W incandescent and 25 W deuterium lamps were taken as light sources, whereas a diffraction monochromator MDR2 and FEU100 were used to detect the transmitted light. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were obtained using a luminescence spectrometer SDL-1 with excitation from a 1 kW Xe lamp; the emission of the latter was passed through a diffraction monochromator MDR2. The spectra of X-ray excited luminescence (XL) were obtained with a monochromator MDR2 at $T = 300$ K at the excitation from a 1 kW table X-ray set-up URS 1.0. The temperature dependence of photoluminescence spectra was measured over the range of $T = 80$–$600$ K, and the samples were heated at the rate of 0.3 K sec. In this experiment, the PL spectral range was separated by special glass filters.

## 3. Results and discussion

The appearance of a batch of glass pieces in transmitted white light and their luminescence under UV 365 nm excitation are shown in Fig. 1. A typical size of these pieces is about 1 mm. The irregular shape of the pieces is provided by vitreous fracture. Under white light illumination, the glass is colorless and transparent. The intense red-orange luminescence, however, is observed at UV excitation. The diffraction pattern shown in Fig. 1S does not contain sharp peaks, and this confirms the amorphous nature of the samples.

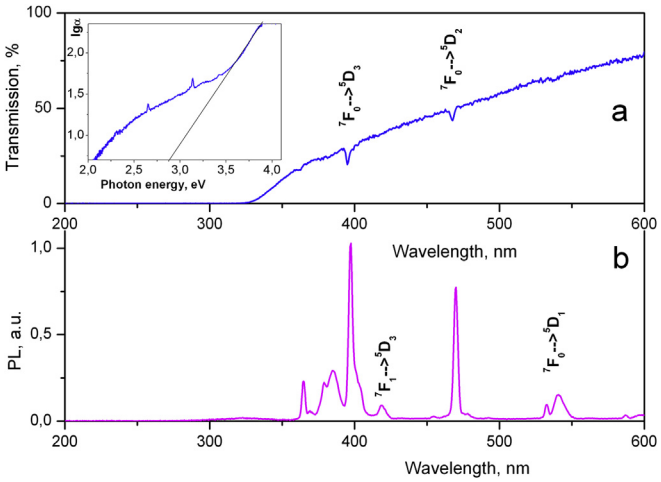


**Fig. 2.** Transmission and PLE spectra recorded from the glass plate at $T = 300$ K. In the inset, the (lg $\alpha$) dependence on photon energy is shown. Some of the 4f-4f electronic transitions in the $Eu^{3+}$ are indicated.

The transmission spectrum measured at $T = 300$ K for the glass plate, which was of about 1 mm in diameter and 300 μm thick, is shown in Fig. 2a. This glass material is transparent over a wide spectral range, and the shortwave absorption edge is located near 330 nm. One can see that an increase in transmission on the wavelength growth is smooth enough, and this character is typical of the glass state. At the absorption edge, there is a range where optical absorption coefficient $\alpha$ depends exponentially on photon energy in accordance with the empirical Urbach rule [25]. The spectrum range is shown in the inset in Fig. 2a. The exponential shape of the absorption edge is a result of a statistical disorder in the structure and electronic transitions between the tails of valence and conduction bands. Also, there are narrow absorption lines detected at 362, 394, 467 and 537 nm, and the features are associated with the 4f-4f transitions in the $Eu^{3+}$ ions [26].

The photoluminescence excitation (PLE) spectrum of the emission over the range of 550–650 nm is shown in Fig. 2b. In PLE spectrum, the 4f-4f transitions in $Eu^{3+}$ ions at 362, 383, 394, 419, 467, 532 and 540 nm groups/lines are the most intense. Here, the underlined spectral components are present also in the absorption

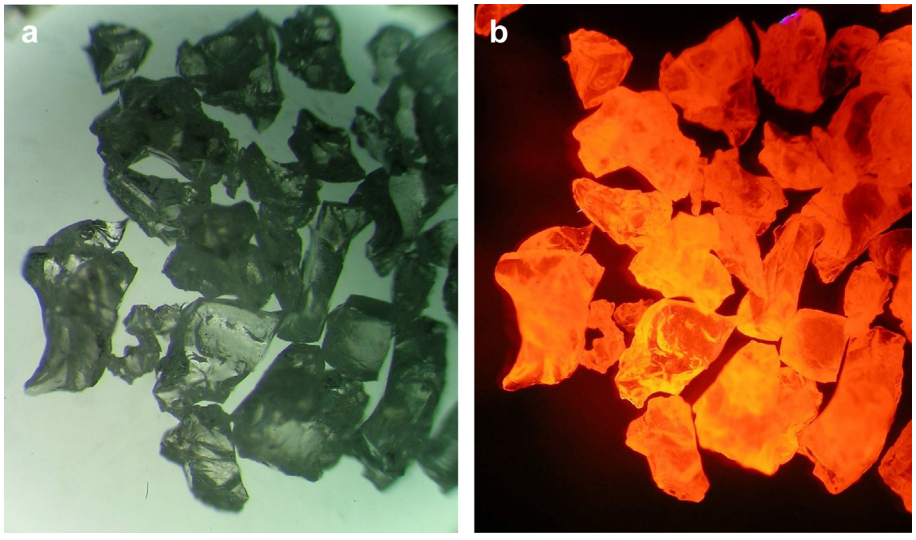


**Fig. 1.** A batch of glass pieces: (a) pattern in white transmitted light and (b) photoluminescence under UV excitation at 365 nm (Hg lamp).

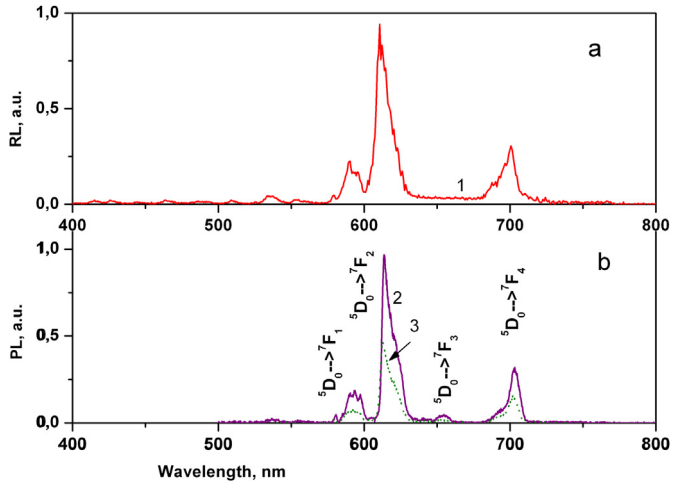


**Fig. 3.** XL (1) and PL (2, 3) spectra recorded at 300 K (1, 3) and 80 K (2) for the glass sample. PL was excited by the 390 nm light source. The spectral resolution is 1 nm.

spectra shown in Fig. 2a. These are mainly the transitions from the lower ground state multiplet $^7F_0$ to excited state $^5D_i$: 540, 467 and 394 nm bands correspond to $i = 1$, 2 and 3, respectively. Thus, red emission from the glass is excited mainly by direct absorption in the $Eu^{3+}$ ions. A very weak broad band near 320 nm corresponds to band-to-band excitation in the glass matrix, and further some excitation is transferred to a rare earth impurity ion. The luminescence spectra recorded at the photoexcitation by UV light 390 nm are shown in Fig. 3a. In both cases, the 4f-4f transitions in the $Eu^{3+}$ ions are dominant. The main line groups centered at ~590, 610, 655 and 703 nm correspond to the transitions from the excited $^5D_0$ state to the ground state multiplets $^7F_i$, where $i = 1$, 2, 3, 4, respectively. The individual lines can not be resolved at 300 K (dotted line in Fig. 3b), and the situation does not change significantly when the temperature was decreased to 80 K (solid line). Very similar spectra are recorded at X-ray excitation (Fig. 3b). This means that matrix excitation is transferred to a dopant (Rare Earth) ion, where the radiative relaxation takes place. There are no emissions associated with the band-to-band or excitonic radiative transitions in the matrix, and this, supposedly, is a result of a nonradiative multiphonon relaxation via the states in the tails of valence/conduction bands in the forbidden band.

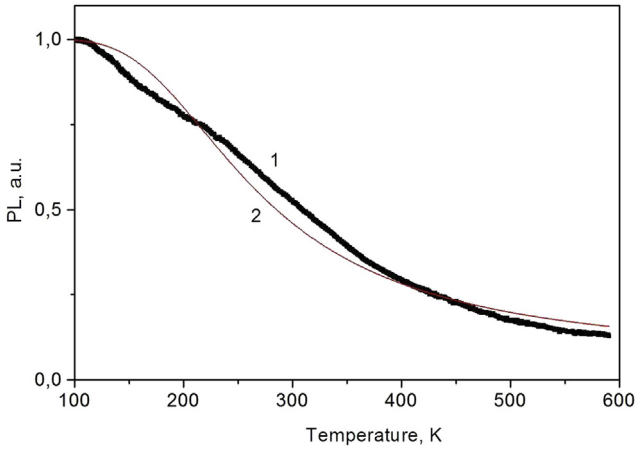


**Fig. 4.** Temperature dependence of the PL intensity of the of $Eu^{3+}$ emission over the 550–650 nm range at 400 nm excitation (curve 1). The result of approximation following the Mott law (1) is shown with the thin curve (2).

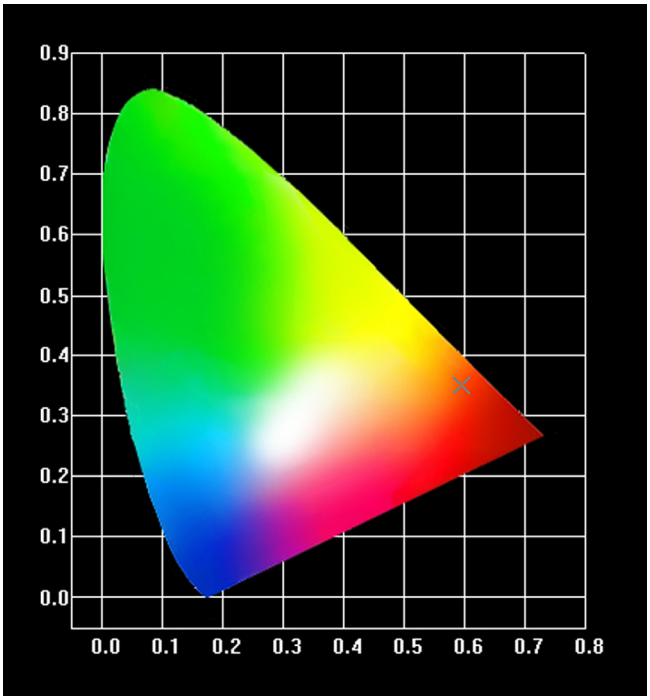

**Fig. 5.** CIE chromaticity diagram of $Li_2O$–$Y_2O_3$–$TeO_2$:$Eu^{3+}$glass phosphor under 390 nm excitation.

The temperature dependence of intensity of the red PL emission over the spectral range of 550–650 nm is shown in Fig. 4. The PL intensity measurements have been produced at the intracenter $Eu^{3+}$ excitation. The 550–650 nm emission range was separated using the combination of ZhS18 and SZS23 glass filters. It is seen that PL intensity decreases continuously on the temperature increase from $T = 80$–600 K. At $T = 300$ K, the PL intensity is only a half from that obtained at liquid nitrogen temperature, whereas at $T = 600$ K only the level of ~20% remains.

Generally, the PL dependence versus temperature may be described well with Mott law for the case of two, radiative and nonradiative, recombination channels [26]:

$$I(T) = I_0/(1 + S\exp(-E/kT)) \quad (1)$$

where $I_0$ is the PL intensity in the absence of quenching, $S$ is the dimensionless preexponential factor, $k$ is the Boltzmann factor and $E$ is the thermal activation energy for quenching. The following values of these parameters for quenching were obtained using (1): $S = 3 \cdot 10^2$ and thermal activation energy $E = 0.08$ eV. The obtained $E$ value corresponds to the thermal activation energy for the nonradiative transition from the excited to ground state. The CIE chromaticity diagram for the glass composition of $0.25Li_2O$–$0.20Y_2O_3$–$0.5TeO_2$–$0.05Eu_2O_3$ at 390 nm excitation is shown in Fig. 5. The calculated color coordinates (0.594, 0.350) indicates a good color purity for the phosphor in the red-orange region.

## 4. Conclusions

The novel tellurite glass with basic composition $0.25Li_2O$–$0.20Y_2O_3$–$0.5TeO_2$ is found in this study. The presence of $Y^{3+}$ ions provides good conditions for the incorporation of rare-earth elements, and red-orange photoluminescence is demonstrated in the glass doped with $Eu^{3+}$. The thermal quenching experiment shows a high photoemission up to $T$ ~500 K. Such glass is considered to be a promising host for phosphor creation, and photoluminescence

properties can be controlled by optimal doping rare-earth elements selection.

## Acknowledgment

This study is partly supported by the Ministry of Education and Science of the Russian Federation.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.matchemphys.2014.07.003.

## References

[1] M.J. Weber, J.D. Myers, D.H. Blackburn, Optical properties of $Nd^{3+}$ in tellurite and phosphotellurite glasses, J. Appl. Phys. 52 (4) (1981) 2944–2948.
[2] Takao Sekiya, Norio Mochida, Atsushi Ohtsuka, Mamoru Tonokawa, Raman spectra of $MO_{1/2}$–$TeO_2$ (M = Li, Na, K, Rb, Cs and Tl) glasses, J. Non-Cryst. Solids 144 (1992) 128–144.
[3] J. Heo, D. Lam, G.H. Sigel, E.A. Mendoza, D.A. Hensley, Spectroscopic analysis of the structure and properties of alkali tellurite glasses, J. Am. Ceram. Soc. 75 (2) (1992) 277–281.
[4] V. Dimitrov, T. Komatsu, Electronic polarizability, optical basicity and non-linear optical properties of oxide glasses, J. Non-Cryst. Solids 249 (2-3) (1999) 160–179.
[5] K. Hirano, Y. Benino, T. Komatsu, Rare earth doping into optical nonlinear nanocrystalline phase in transparent $TeO_2$-based glass ceramics, J. Phys. Chem. Solids 62 (2001) 2075–2082.
[6] P. Giridhar, S. Sailaja, M. Bhushana Reddy, K. Vemasevana Raju, C. Nageswara Raju, B. Sudhakar Reddy, Spectroscopic studies of $RE^{3+}$ (RE = Eu, Tb, Sm & Dy): lithium lead boro tellurite glasses, Ferroelectr. Lett. 38 (2011) 1–10.
[7] P. Giridhar, Hyo Jin Seo, S. Sailaja, M. Bhushana Reddy, C. Nageswara Raju, B. Sudhakar Reddy, Spectroscopic investigations of $Eu^{3+}$ and $Tb^{3+}$: cadmium lead boro tellurite glasses, Glass Phys. Chem. 38 (1) (2012) 77–84.
[8] M. Kochanowicz, D. Dorosz, J. Zmojda, J. Dorosz, P. Moluski, Influence of temperature on up conversion luminescence in tellurite glass with $Yb^{3+}$/$Er^{3+}$ and $Yb^{3+}$/$Tm^{3+}$, J. Lumin. 151 (2014) 155–160.
[9] E. Culea, I. Vida-Simiti, G. Borodi, E.N. Culea, R. Stefan, P. Pascuta, Effects of $Er^{3+}$:Ag codoping on structural and spectroscopic properties of lead tellurite glass ceramics, Ceram. Int. 40 (2014) 11001–11007.
[10] Shengxi Peng, Fengjing Yang, Libo Wu, Yawei Qi, Shichao Zheng, Dandan Yin, Xunsi Wang, Yaxun Zhou, $Tm^{3+}$/$Ho^{3+}$/$Yb^{3+}$ codoped tellurite glass for multicolor emission – structure, thermal stability and spectroscopic properties, J. Alloys Compd. 609 (2014) 14–20.
[11] Shi-Chao Zheng, Ya-wei Ql, Sheng-Xi Peng, Dan-Dan Yin, Ya-Xun Zhou, Shi-Xun Dai, Structure and spectroscopic properties of $Er^{3+}$/$Ce^{3+}$ co-doped $TeO_2$–$Bi_2O_3$–$TiO_2$ glasses modified with various $WO_3$ contents for 1.53 μm emission, Opto Elect. Lett. 9 (6) (2013) 461–464.
[12] W. Stambouli, H. Elhouichet, B. Gelloz, M. Férid, N. Koshida, Energy transfer induced $Eu^{3+}$ photoluminescence enhancement in tellurite glass, J. Lumin. 132 (2012) 205–209.
[13] W. Stambouli, H. Elhouichet, B. Gelloz, M. Férid, Optical and spectroscopic properties of Eu-doped tellurite glasses and glass ceramics, J. Lumin. 138 (2013) 201–208.
[14] Z.G. Xia, J.F. Sun, H.Y. Du, D.M. Chen, J.Y. Sun, Luminescence properties of double-perovskite $Sr_2Ca_{1-2x}Eu_xNa_xMoO_6$ red-emitting phosphors prepared by the citric acid-assisted sol-gel method, J. Mater. Sci. 45 (2010) 1553–1559.
[15] G.J. Gao, N. Da, S. Reibstein, L. Wondraczek, Enhanced photoluminescence from mixed-valence Eu-doped nanocrystalline silicate glass ceramics, Opt. Exp. 18 (S4) (2010) A575–A583.
[16] Z.G. Xia, S. Jin, J.Y. Sun, H.Y. Du, P. Du, L.B. Liao, Facile morphology-controlled synthesis and luminescence properties of $BaMoO_4$:$Eu^{3+}$ microparticles and micro-rods obtained by a molten-salt reaction route, J. Nanosci. Nanotechnol. 11 (2011) 9612–9630.
[17] Z.G. Xia, J.Q. Zhuang, L.B. Liao, Novel red-emitting $Ba_2Tb(BO_3)_2Cl$:Eu phosphor with efficient energy transfer for potential application in white light-emitting diodes, Inorg. Chem (51) (2012) 7202–7209.
[18] K. Maheshvaran, K. Marimuthu, Optical studies on $Eu^{3+}$ doped boro-tellurite glasses, AIP Conf. Proc. 1447 (2012) 549–550.
[19] Yin Yu, Feng Song, Chengguo Ming, Jun Zhang, Fengxiao Wang, Photo-luminescence properties of $Tm^{3+}$/$Tb^{3+}$/$Eu^{3+}$ tri-doped phosphate glass and glass ceramics for white-light-emitting diodes, Appl. Opt. 52 (23) (2013) 5606–5610.
[20] F. Wang, L.F. Shen, B.J. Chen, E.Y.B. Pun, H. Lin, Broadband fluorescence emission of $Eu^{3+}$ doped germanotellurite glasses for fiber-based irradiation light sources, Opt. Mater. Exp. 3 (11) (2013) 1931–1943.
[21] W.S. Zhang, H.J. Seo, Luminescence and structure of a novel red-emitting phosphor $Eu^{3+}$-doped tellurate garnet $Li_3Y_3Te_2O_{12}$, J. Alloys Compd. 553 (2013) 183–187.
[22] V.V. Atuchin, A.S. Aleksandrovsky, O.D. Chimitova, T.A. Gavrilova, A.S. Krylov, M.S. Molokeev, A.S. Oreshonkov, B.G. Bazarov, J.G. Bazarova, Synthesis and spectroscopic properties of monoclinic α-$Eu_2(MoO_4)_3$, J. Phys. Chem. C 118 (28) (2014) 15404–15411.
[23] L.A. Solovyov, A.M. Astachov, M.S. Molokeev, A.D. Vasiliev, Powder diffraction crystal structure analysis using derivative difference minimization: example of the potassium salt of 1-(tetrazol-5-yl)-2-nitroguanidine, Acta Crystallogr. B 61 (2005) 435–442.
[24] V.V. Atuchin, T.A. Gavrilova, V.G. Kesler, M.S. Molokeev, K.S. Aleksandrov, Low-temperature synthesis and structural properties of ferroelectric $K_3WO_3F_3$ elpasolite, Chem. Phys. Lett. 493 (2010) 83–86.
[25] T.H. Keil, Theory of the urbach rule, Phys. Rev. 144 (1966) 582–585.
[26] D.T. Sviridov, R.K. Sviridova, Yu.F. Smirnov, Optical Spectra of Transition Metal Ions in Crystals, Nauka, Moscow, 1978 (in Russian).