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Optical Materials 19 (2002) 189-194

OPTICAL Materials

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$Li_2B_4O_7$ glasses doped with Cr, Co, Eu and Dy

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Abstract

Absorption and emission spectra of Cr, Co, Eu and Dy ions in $Li_2B_4O_7$ glasses melted in oxygen and hydrogen were measured for valency states analysis. It was stated that the presence of Cr^{6+} ion is limited by composition of the starting mixture and atmosphere of the melting and that this ion arises as $Cr^{6+}O^-$ complex. Independently of the above factors in all the glasses there were present Cr^{3+} ions. Under γ-irradiation Cr^{6+}–O^- complex of $3d^0$ configuration can be disintegrated giving additional absorption band of Cr^{3+} and may be Cr^{4+} and higher valency centers. Corresponding photoluminescence is centered at about 430 nm. Absorption of $Li_2B_4O_7$:Co glasses obtained in oxygen atmosphere reveals Co^{2+} and Co^{3+} ions which does not give any emission in the UV–VIS and near-infrared region of luminescence spectrum. The content and optical characteristics of Eu^{2+} and Eu^{3+}-doped $Li_2B_4O_7$ glasses are dependent of the growth atmosphere. © 2001 Published by Elsevier Science B.V.

1. Introduction

In the last four decades a great effort has been devoted to the study of glasses containing transition metal and rare-earth impurities [1–5]. Glasses as laser hosts have advantages such as mass production at low cost and form fibers more easily than single crystals. The emission properties in the glasses are characterized by broader emission spectra, a radiation lifetime with a non-exponential decay law, and a peculiar temperature dependence of the quantum efficiency [6].

Lithium tetraborate ($Li_2B_4O_7$) is a congruently melting compound with a melting point 917 °C. Single crystals of this material are used as substrates for surface acoustic wave (SAW) devices. The material has cuts with temperature stability of acoustic wave velocity and relatively high electromechanical coupling coefficient for SAW. Polycrystals of $Li_2B_4O_7$ with some dopants also find applications in thermoluminescent personal dosimeters [7,8].

Owing to small ionic radii of lithium and boron it is impossible to introduce dopants into $Li_2B_4O_7$ single crystals at high levels. Relatively high viscosity of molten lithium tetraborate, like other borates, is a source of serious problems during single crystal growth of this material. On the other hand this viscosity allows to obtain the material in a form of glass containing much higher amounts of dopants than in the case of single crystals.

One of the most investigated impurity ions also in glasses is chromium, and the large number of review articles and papers testifies to the high level of interest in this field [4,5,9], even in connection with the development of lasers. Also cobalt ion is very intensively investigated for its possible application for laser nonlinear absorbers [10]. Europium and dysprosium-doped glasses exhibit wide

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0925-3467/01/$ - see front matter
PII: S0925-3467(01)00218-X

application in gamma dosimetry and as scintillators.

In this paper we point out the possibility of easily hosting impurity ions: Cr, Co, Eu, Dy in a $Li_2B_4O_7$ glassy matrix. The purpose of this work is also to investigate possible valency states of Cr, Co, Eu and Dy ions in $Li_2B_4O_7$ glasses.

2. Experimental procedure

2.1. Glass preparation

The synthesis of lithium tetraborate was carried out from lithium carbonate Li_2CO_3, and boric oxide H_3BO_3 (Merck, extra pure) in platinum crucibles in air. After reaction of starting materials at 950 °C the obtained compound was overheated to 1150 °C to remove traces of water and carbon dioxide, which were present in the melt. Because of B_2O_3 losses, due to evaporation, 1 mol% surplus of H_3BO_3 was added to the starting composition. Cr_2O_3 was dissolved in lithium tetraborate at the level of 0.15 mol%. After rapid cooling below 550 °C the melt formed glass which did not show any tendency to crystallize. Prolonged heating of obtained glass at temperatures higher than 600 °C led to its crystallization and subsequent formation of polycrystalline material.

The addition of chromium oxide, Cr_2O_3, caused green coloration of the glass. The addition of cobalt oxide, Co_2O_3, caused blue coloration. The glasses were obtained in oxidizing atmosphere.

Almost completely transparent $Li_2B_4O_7$ glasses doped with Eu, Dy were obtained in oxidizing and reducing atmosphere of hydrogen.

The following $Li_2B_4O_7$ glasses were obtained: doped with Cr (0.13 and 2.5 wt%), Co^{2+} (10 wt%) and Eu, Dy (2 wt%, 2 wt%).

2.2. Absorption and photoluminescence measurements

The samples were polished to the thickness of about 1 mm. They were irradiated by gamma photons immediately after growth process. The ^{60}Co gamma source with a power of 1.5 Gy/s was used. Optical transmission was measured before and after γ treatment using LAMBDA-900 Perkin–Elmer spectrophotometer in UV–VIS range and FT–IR-1725 in the IR range. Additional absorption was calculated according to the formula:

$$\Delta K(\lambda) = (1/d)\ln(T_1/T_2), \tag{1}$$

where K is the absorption, λ is the wavelength, d is the sample thickness and T_1 and T_2 are transmissions of the sample before and after a treatment, respectively.

Photoluminescence (PL) was recorded using Perkin–Elmer spectrofluorimeter from 200–900 nm and He–Ne laser excitation of 630 nm.

3. Results

3.1. Absorption and the additional absorption measurements

Figs. 1–6 shows absorption spectra of representative samples obtained at 300 K.

In the case of pure $Li_2B_4O_7$ glass (Fig. 1, curve 1) the range of transparency originate at 190 nm (fundamental absorption edge – FAE) and ends at about 2700 nm (lattice absorption). Curve 2 shows absorption of this glass after γ-irradiation with a dose of 5×10^4 Gy.

In the 0.15 wt% chromium-doped $Li_2B_4O_7$ glass (Fig. 2(a) and (b), curve 1) we observe Cr^{3+} and Cr^{6+} ion spectra. FAE of the glass is equal to 245 nm and lattice absorption originate at 2700 nm.

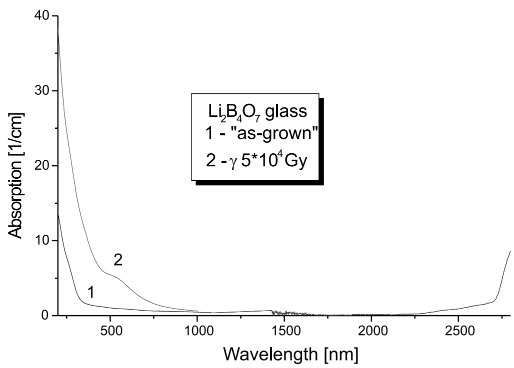

Fig. 1. Absorption of $Li_2B_4O_7$ glass before (1) and after (2) γ-irradiation with a dose of 5×10^4 Gy.

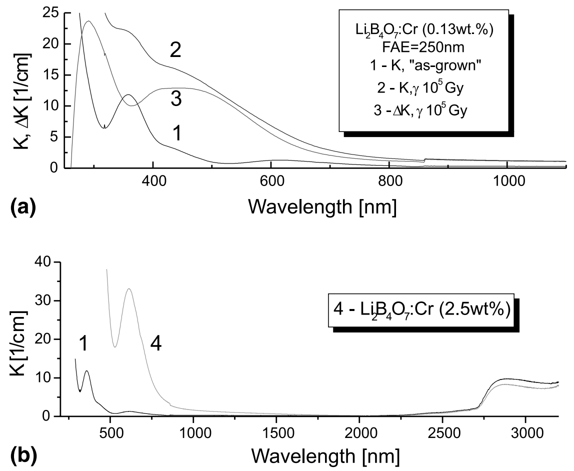

Fig. 2. Absorption before (1) and after γ-irradiation (2) and additional absorption (3) of $Li_2B_4O_7$:Cr (0.15 wt%) glass, and absorption of $Li_2B_4O_7$:Cr (2.5 wt%) glass (4).

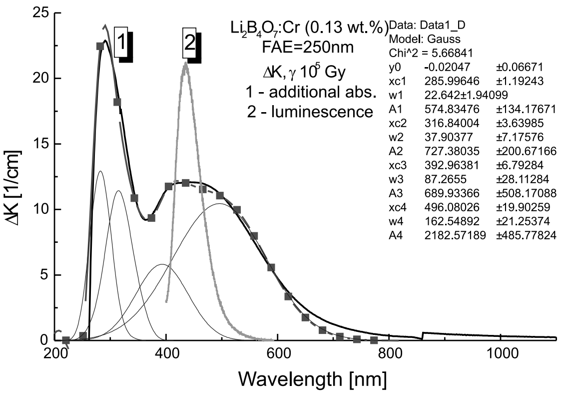

Fig. 3. Gauss distribution of the additional absorption in γ 10^5 Gy irradiated $Li_2B_4O_7$:Cr (0.13 wt%) glass (1) and photoluminescence of the glass (2) excited with 260 nm.

The Cr^{3+} ion has two absorption bands centered at about 430 and 614 nm due to d–d transition: the former was attributed to the spin-allowed but purity forbidden $^4A_2$–$^4T_1$ transition and the latter to the spin-allowed but parity-forbidden $^4A_2$–$^4T_2$ transition. The Cr^{6+} ion has strong absorption band centered at 358 nm and a weak one at 318 nm. It seems that these bands refer to Cr^{6+}–O^- complex of $3d^0$ configuration rather than to Cr^{6+} ion [5]. Curve 2 shows absorption of the glass after 10^5 Gy γ-rays while curve 3 the additional ab-

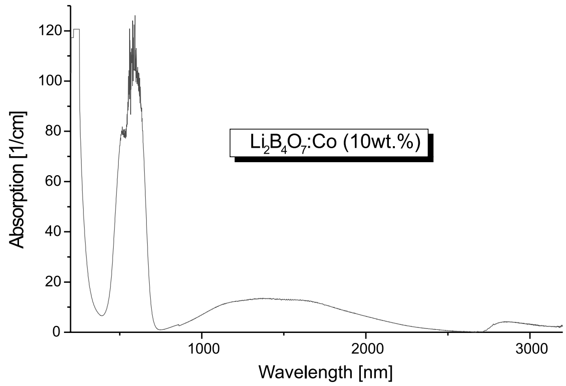

Fig. 4. Absorption spectrum of $Li_2B_4O_7$:Co (10 wt%) glass.

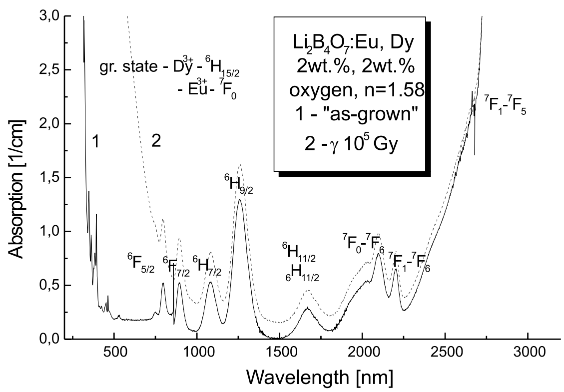

Fig. 5. The absorption of $Li_2B_4O_7$:Eu, Dy (2 wt%, 2 wt%) glass obtained in oxygen atmosphere at 300 K before (1) and after (2) γ-irradiation with a dose of 10^5 Gy.

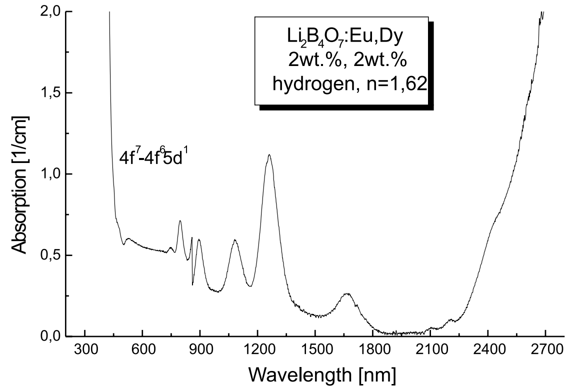

Fig. 6. Absorption of $Li_2B_4O_7$:Eu, Dy (2 wt%, 2 wt%) glass obtained in hydrogen atmosphere.

sorption. There are at least two bands seen in the additional absorption centered at about 297 and 450 nm. Curve 4 in Fig. 2(b) shows the absorption of highly doped with Cr (2.5 wt%) $Li_2B_4O_7$ glass. One can see that in the case of high doping only 614 nm band due to $^4A_2$–$^4T_2$ transition in Cr^{3+} ions is present.

Detailed analysis using the fitting with Gauss curves has shown that there are at least four bands in the additional absorption centered at about 285, 316, 392 and 496 nm (Fig. 3) which are responsible for 297 and 450 nm additional absorptions. Three of them seem to correspond to previously described color centers in $Li_2B_4O_7$ glasses. Fourth, at about 392 nm, seems to be responsible for 430 nm emission observed after 260 nm excitation. This broad-band 450 nm additional absorption may be due to $^4A_2$–$^4T_2$, $^4T_1$ transitions in Cr^{3+} and/or $^3A_2$–$^3T_2$, $^3T_1$–$^3T_2$ transitions in Cr^{4+} [10]. Parameters of the fitting are listed in a table inside the figure.

Fig. 4 shows the absorptions in $Li_2B_4O_7$ glass doped with 10 wt% of Co. As one can see strong absorption bands are observed in visible and infrared parts of the absorption spectrum. The main features of spectrum consist of a double band in the IR region (800–2500 nm) and a triple band in the visible region (400–750 nm). The latter absorption band is responsible for blue color of the sample. We notice also the strong absorption in the far IR, and in the UV region (not indicated in

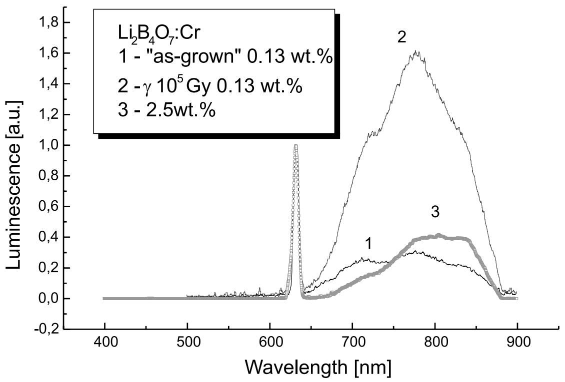

Fig. 7. PL of $Li_2B_4O_7$:Cr glasses excited by 630 nm He–Ne laser: 0.13 wt% Cr "as-grown" (1), 0.13 wt% Cr γ-irradiated with a dose of 10^5 Gy and 2.5 wt% Cr (3).

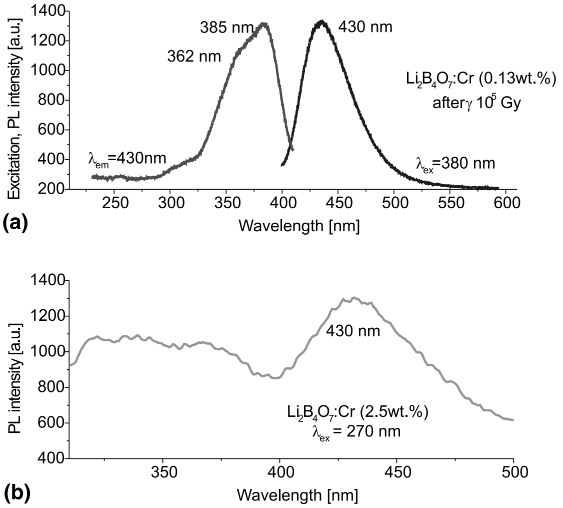

Fig. 8. Excitation–emission spectra of $Li_2B_4O_7$:Cr (0.13 wt%) glass after γ-exposure with a dose of 10^5 Gy (a) and emission from $Li_2B_4O_7$:Cr (2.5 wt%) glass (b) under 270 nm excitation.

figure). All these absorption bands, due to their mixed structure seem to be transitions in Co^{2+}–Co^{3+} mixed system [11].

Fig. 5 presents the absorption (1) from two ground states: Dy^{3+}–$^6H_{15/2}$ and Eu^{3+}–$^7F_0$ of $Li_2B_4O_7$:Eu, Dy (2 wt%, 2 wt%) glass. As one can see FAE in this case is equal to 270 nm. Refraction coefficient is equal to 1.58. Curve 2 shows the absorption after γ-irradiation with a dose of 10^5 Gy. Fig. 6 shows the absorption of Dy^{3+} from $^6H_{15/2}$ ground state and Eu^{2+} transitions $4f^7$–$4f^6 5d^1$ [12]. FAE is equal to about 355 nm and refraction coefficient 1.62.

3.2. Photoluminescence measurements

Fig. 7 presents photoluminescence of $Li_2B_4O_7$:Cr glasses excited with 630 nm He–Ne laser. As one can see γ-irradiation leads to the increase in Cr^{3+} PL intensity.

Fig. 8 shows excitation–emission spectra of $Li_2B_4O_7$: Cr (0.13 wt%) glass after γ-exposure with a dose of 10^5 Gy (a) and emission from $Li_2B_4O_7$:Cr (2.5 wt%) glass (b) under 270 nm excitation. As one can see emission at 430 nm is due to excitation at 362 and 385 nm. This same type of emission is observed also in the case of high doping of the glass with Cr (Fig. 8(b)).

The emission from $Li_2B_4O_7$:Co (10 wt%) glass was not observed up to 1700 nm. It may be due to fact that usual emission bands of Co^{2+} ions arises over 2.2 μm. Moreover, emission in the visible range of emission spectrum may be quenched by non-radiative transitions between Co^{3+} and Co^{2+} ions [11]. The shape of the emission spectrum from $Li_2B_4O_7$:Eu, Dy (2 wt%, 2 wt%) glass strongly depend on the type of growth atmosphere. Fig. 9 shows characteristic emissions for the two basic cases of the obtained glasses: oxidizing (a) and reducing (b) atmospheres [12].

4. Discussion

As one can see in Fig. 1 the absorption spectrum of pure $Li_2B_4O_7$ glass shows a transmission range larger than that of other glasses [1]. The relevant feature of the glass, as it takes place also in the case of other glasses, is its high susceptibility to γ-irradiation. Wide, almost non-structural additional absorption in the UV–VIS and NIR of the absorption spectrum (190–1000 nm) is seen with weakly distinguished bands centered at about: 250, 360 and 530 nm.

As one can see from Fig. 2 some changes under γ-radiation may be a positive one. Our experimental data cannot be interpreted in terms of Cr^{3+} alone, but have to be analyzed in view of the coexistence of Cr ions of different valences. Low

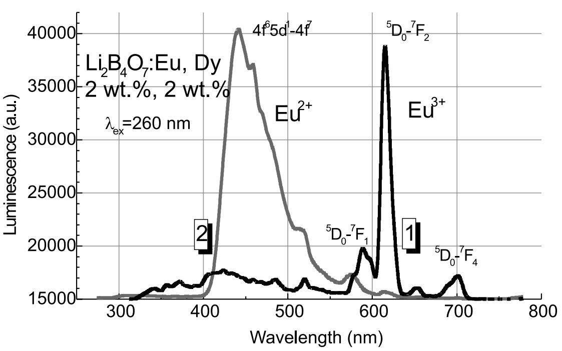

Fig. 9. Emission spectra of $Li_2B_4O_7$:Eu, Dy (2 wt%, 2 wt%) glasses obtained in oxidizing (1) and reducing (2) atmosphere.

chromium-doped $Li_2B_4O_7$ glass shows presence of Cr^{3+} and Cr^{6+} ions. The former exists tetrahedrally coordinated while the latter octahedrally coordinated. The former gives well-known emission, which is clearly seen in Fig. 7 for $\lambda_{ex} = 630$ nm of He–Ne laser. The latter does not give emission because $Cr^{6+}O^-$ complex of $3d^0$ configuration seem to be responsible for the 318 and 358 nm absorption. But under γ-irradiation with a dose of 10^5 Gy$Cr^{6+}O^-$ complex disintegrates giving additional absorption connected with the above mentioned, specific for $Li_2B_4O_7$ color centers and 392 nm band which may be attributed to $^3A_2$–$^3T_2$, $^3T_1$–$^3T_2$ transitions in Cr^{4+} and/or $^4A_2$–$^4T_2$, $^4T_1$ transitions in Cr^{3+} (Fig. 3). Emission spectrum of the gamma irradiated glass reveal an increase in PL intensity of Cr^{3+} ions (Fig. 7), while excitation–emission spectra presented in Fig. 8(a) suggest presence of other luminescence center. It was previously reported that the Cr^{4+} ion exists in aluminate-based glasses [13]. The mechanism of forming Cr^{4+} ions was discussed in detail in [5] based on point defects in the glasses. It was stated that Cr^{4+} is observed only in glasses in which oxygen excess defects such as super oxide ion radicals and peroxy linkages are observed. It is possible that in our case Cr^{6+} O^- complex disintegrates simultaneously to Cr^{4+}, Cr^{3+} or higher valency states of Cr. But it demands more and detailed investigations.

Highly doped with chromium $Li_2B_4O_7$ glasses show presence only $^4A_2$–$^4T_2$ absorption band (Fig. 2(b)) although 430 nm emission is also observed (Fig. 8(b)). Analyzing low and high doping in case of $Li_2B_4O_7$ glass one can state that there exists compositional dependence of the valency states of Cr ions in the glasses. In [5] it was stated that the contents of Cr^{3+} and Cr^{6+} vary systematically with basicity in the silicate and borate glasses.

As one can see from Fig. 4 high doping (10 wt%) of $Li_2B_4O_7$ glasses with cobalt is possible. Wide absorption bands seen in the visible as well as IR parts of the absorption spectrum suggest presence of both Co^{2+} and Co^{3+} ions which can interchange excitation energy not giving any emission [11].

Europium [12] and dysprosium co-doping characterizes dependency of Eu valence on growth atmosphere. As one can see in Fig. 5 absorption of $Li_2B_4O_7$:Eu, Dy glass obtained in oxidizing atmosphere shows many transitions from ground state of $Dy^{3+}(^6H_{15/2})$ and ground state of $Eu^{3+}(^7F_0)$ to higher states. Gamma irradiation does not change a valence of the impurities, but leads to strong additional absorption in the range 270–1000 nm. In case of $Li_2B_4O_7$:Eu, Dy glass obtained in reducing atmosphere of hydrogen (Fig. 6) well-known transitions of Dy^{3+} ions are seen in the absorption spectrum and the new one $4f^7$–$4f^6 5d^1$ of Eu^{2+} ions. Emission of both types of Eu ions is clearly seen in Fig. 9. As it follows from emission measurements both types of Eu ions exist in both types of the obtained glasses, but one of them dominates giving characteristic emission.

5. Conclusions

It was shown that in case of $Li_2B_4O_7$ glasses high doping with transition metal and rare-earth element impurities is possible. Obtained compounds are of good optical quality, giving clear luminescence especially for Cr^{3+} and Eu^{3+} and Eu^{2+} ions.

It was stated that the presence of Cr^{6+} ion is limited by composition of the starting mixture and atmosphere of the melting (oxidizing). Independently on the above factors in all the glasses there were present Cr^{3+} ions. Under γ-irradiation $Cr^{6+}O_4$ complex of $3d^0$ configuration can be disintegrated giving additional absorption band of Cr^{3+} and may be Cr^{4+} and higher valence ions. Photoluminescence of the latter center is centered at about 430 nm. γ-irradiation leads to arising of strong additional absorption in the range of 190–1000 nm with weakly distinguished bands peaked at about: 250, 360 and 530 nm.

Absorption of $Li_2B_4O_7$:Co glasses obtained in oxygen atmosphere reveals Co^{2+} and Co^{3+} ions which does not give any emission in the UV–VIS and near-infrared region of luminescence spectrum.

The content and optical characteristics of Eu^{2+} and Eu^{3+}-doped $Li_2B_4O_7$ glasses are dependent of the growth atmosphere.

Acknowledgements

The author would like to thank Mrs A. Majchrowski from Institute of Physics MUT, Warsaw and Mariusz Czuba from Institute of Optoelectronics MUT, Warsaw for glasses to investigations and luminescence measurements.

References

[1] H.L. Smith, A. Cohen, J. Phys. Chem. Glasses 4 (1963) 173.
[2] P.C. Schultz, J. Am. Ceram. Soc. 57 (1974) 307.
[3] A. Lempicki, L. Andrews, S.J. Nettel, B.C. McCollum, E.I. Solomon, Phys. Rev. Lett. 44 (1980) 1234.
[4] M. Casalboni, V. Ciafardonne, G. Giuli, B. Izzi, E. Paris, P. Prosposito, J. Phys.: Condens. Matter 8 (1996) 9059.
[5] T. Murata, M. Torisaka, H. Takebe, K. Morinaga, J. Non-Cryst. Solids 220 (1997) 139.
[6] M. Yamaga, B. Henderson, K.P. O'Donnell, Y. Gao, Phys. Rev. B 44 (1991) 4853.
[7] A. Majchrowski, in: Proc. SPIE 2373 (1995) 98–101; Józef_mija, Antoni Rogalski, Jerzy Zieli_ski (Eds.), Solid State Crystals: Materials Science and Applications.
[8] F. Rasheed, K.P. O'Donnell, B. Henderson, D. Hollis, J. Phys.: Condens. Matter 3 (1991) 3825.
[9] Laser Rangefinders, JANE's Armour and Artilery Upgrades, Eleventh Edition 1998–99, Jane's Information Group Ltd., Couldson, Surrey UK, 1998.
[10] N.A. Kulagin, W.A. Sandulenko, Fiz. Tw. Tela 31 (1) (1989) 243.
[11] M. Grinberg, S.M. Kaczmarek, T. Tsuboi, Phys. Rev. B, 2000, in the print.
[12] W. Chen, J.O. Malm, V. Zwiller, Y. Huang, S. Liu, R. Wallenberg, J.O. Bovin, L. Samuelson, Phys. Rev. B 61 (16) (2000) 11021.
[13] X. Wu, S. Huang, U. Hommerich, W.M. Yen, B.G. Aitken, M. Newhouse, Chem. Phys. Lett. 233 (1995) 28.