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Negative induced absorption and negative index of refraction for iron doped potash–alumina–borate glasses subjected to thermal-radiation treatment

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Abstract

This work experimentally revealed, that ^{60}Co-gamma-irradiation of potash-alumina-borate glasses doped with 1 and 2 mass% of iron oxide to the dose of 1.7 MR in the temperature range of 150–300 °C induced differential optical density changes within $-6 \leq \Delta D \leq 0$ in the wave length range of 300–350 nm, which is characteristic for meta-material. Calculations have shown that variation of optical refraction index within $-0.05 \leq \Delta n_\omega \leq 0.05$ due to microstructure transformation causes changes in the differential absorption index of the glass $-0.5 < \Delta \alpha_\omega < 0.55$.

1 Introduction

The potash alumina-borate (PAB) glass containing iron ions (Fe^{2+}, Fe^{3+}) are widely used in magneto-optics, spectroscopy and dosimetry of ionizing radiation. The prospects of their application in various branches of science and technical applications, including computer technologies, have motivated us to modify microstructure of PAB glasses so as to obtain optical metamaterial properties.
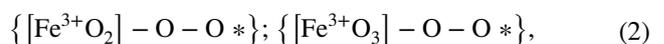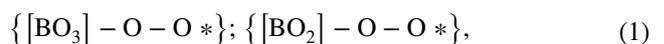
PAB glass consists of three oxides B_2O_3–Al_2O_3–K_2O with different valence of cations and oxygen positions. Therefore, adding ambivalent transition metal oxides over stoichiometry provided variable ion ratio, which resulted in particular non-linear optical properties of the glasses [1, 2].

We will consider some most characteristic operations where the questions of nanostructure potash alumina-borate glasses, activated by ions (Fe^{3+}, Cr^{3+}, Cu^{2+} and Cu^{1+}) the transition elements, and also silver ions are raised. The authors of [1] used X-ray diffraction to show formation of $[Al_4B_2O_9 \cdot Cr^{3+}]$ nanocrystals in PAB-glasses doped by Cr^{3+} ions and studied optical and luminescent properties. Such glasses turned out similar to ruby crystals and can be used as fiber amplifiers in information transmission systems. Non-linear and optical properties of PAB-glasses with CuCl and CuBr nanocrystals with a characteristic spectrum at wavelength of 532 nm were studied in [2].

Different experimental approach was done in [3], where irradiation of silicate glasses containing silver with 5–50 keV electrons to doses from 20 to 50 mC/cm^2 caused the modification of near-surface nano-layers < 20 nm, where the gradient optical wave guide with increase in the refraction index $\Delta n = 0.01$–0.04. The mechanisms resulting in these nanoeffects are a rupture of a few hundred chemical bonds by each keV electron, formation of a volume negative charge where positive metal ions migrate. This can be used for devices of photonics, integrated optics and nanoplasmonics [3].

Earlier we showed, that melting and processing alkaline borate glass without and with Fe_2O_3 additives in ^{60}Co γ-radiation source resulted in generation of new peroxide radical-like paramagnetic centers [4]:

$$\left\{ [BO_3] - O - O * \right\}; \left\{ [BO_2] - O - O * \right\}, \tag{1}$$

$$\left\{ [Fe^{3+}O_2] - O - O * \right\}; \left\{ [Fe^{3+}O_3] - O - O * \right\}, \tag{2}$$

where (1) for pure glass, and (2) for glass with Fe_2O_3 additive. Analysis of EPR spectra allowed us to estimate the size of nanoparticles within 46–51 nm. So thermal radiation treatment of PAB-glasses with iron oxides provided creation of magnetic nanoparticles and can be considered as a new glass nanotechnology.

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Then we studied another composition of PAB-55 glass with Fe_2O_3 additives from 0.1 to 1.5 mass% over 100% stoichiometry, which were subjected to heat treatment at 673 ± 2 K in the ^{60}Co gamma-source of 26 Gy/s at INP AS RUz [5]. Optical absorption spectra measured before irradiation (but after the same heat treatment at 673 K) and after irradiation to doses of 10^3, 10^4, 10^5, 10^6 and $5 \cdot 10^7$ Gy revealed the negative optical density relative to non-irradiated sample at $\lambda_{max} = 530$ nm within wide spectral range of 340–700 nm. So we obtained the glass which has become self-transparent after thermoradiation processing in certain conditions (temperature, dose and dose rate). Cluster like and radical-like nanoparticles are formed in the volume and also on the surface of oxide glasses. Changing the size, form and structure, it is possible to operate magneto optical characteristics (the induced paramagnetic and optical centers).

The physical model of self-organization of nanostructures is suggested in [6, 7]. Besides synthesis of metamaterials, alternative possible way to obtain them is self-organization of multielement disordered matrix under simultaneous influence of heating and ionizing irradiation, which is called the dynamic non-linear effect [8].

P.W. Levy [9] studied the kinetics of coloring of glass, presented the radiation induced absorption as superposition of several individual absorption bands, in the form of Gaussian for each color center $\alpha(E)$ in the glasses as coefficient of absorption of photons with energy E:

$$\alpha(E) = \alpha_m \exp\left[\frac{4\ln 2}{\Delta E_{1/2}} \times (E - E_0)^2\right], \tag{3}$$

where α_m is the absorption coefficient at the maximum of Gaussian curve; $\Delta E_{1/2}$ is the width at half-height maximum. But the formula does not take into account the refraction index characterizing individual material. Dexter [10] studied light absorption by atoms in ionic crystals and improved Smakula's formula for the concentration of F_n color centers in alkali halide crystals

$$N_i \cdot f = 0.87 \times 10^{17}\left[\frac{n}{(n^2+2)^2}\right] \cdot \Delta E_{1/2} \cdot \alpha_m,$$
$$\alpha_m = (2.303/d) \cdot D, \tag{4}$$

where f is the oscillator force, n is the optical refraction index at the wavelength, D is the optical density, d is the sample thickness in cm. But this one can not be used directly for multicomponent oxide glasses. Therefore, we will use differential absorption and dispersion analysis of such glasses.

The purpose of this work is to study "meta"—like optical properties related with microstructural transformations at thermal radiation treatment of multicomponent oxide

glasses at higher concentration of iron oxide with the use of semi-empirical calculations of optical refraction index with dispersion effect.

Theoretical background Earlier we showed that it is possible to estimate the number of color centers N_i from optical spectra of borosilicate glasses prior and after gamma-irradiations [11, 12].

In the case of radiation induced absorption bands it is necessary to consider dispersion curves and their relation from (3) and (4): $\alpha_m = \alpha_m(E)$, $n = n(E)$, and so for changes of α_m and n we can write,

$$\left[\frac{d\alpha_m(E)}{dn(E)}\right] = \left[\frac{d\alpha_m(E)/dE}{dn(E)/dE}\right]. \tag{5}$$

Let's assume that

$$n(E) = n_0 + \delta n_E = n_0\left(1 + \frac{\delta n_E}{n_0}\right), \tag{6}$$

where n_0 is the constant refraction index, $\delta n_E/n_0$ is the relative refraction index taking into account dispersion. Replacing, for simplicity $\alpha_m(E) = \alpha_\omega$; $n_E = n_\omega$ for irradiated sample and considering (4) and (5) for derivative $[d\alpha_\omega/dn_\omega]$ we find:

$$[d\alpha_\omega/dn_\omega] = C \cdot [N/\Delta E_{1/2}]\{(d/dn_\omega)$$
$$\times [((n_0^2 + 2)/(n_0 + n_\omega)) + ((2n_0 + n_\omega)/(n_0 + n_\omega))]\}. \tag{7}$$

For simplicity we will designate $(n_\omega/n_0) = n'_\omega$ after irradiation and finally obtain,

$$[d\alpha_\omega/dn'_\omega] = \Delta\alpha_\omega = [2/(1 + n'_\omega)]$$
$$- \left[(1 + (2/n_0^2))/(1 + n'_\omega)^2\right]$$
$$- \left[(2n'_\omega)/(n_0(1 + n'_\omega)^2)\right]. \tag{8}$$

For metamaterial [8] it is possible to accept limits of change, in linear approximation $(6) - 0.05 \leq \Delta n_\omega \leq 0.05$ for doped PAB-glasses at the determined $n_0 = 1.46$ for 530 nm, and calculate according to $(8) - 0.5 < \Delta\alpha_\omega < 0.549$ (Fig. 1a).

Thus, due to the thermal-radiation effect on the iron-doped PAB glass, the negative value of absorption index caused by a negative value of optical refraction index. It means physically self-transparency under thermal radiation treatment. In the second approximation [5] differential equation is solved and results in dependence of Δn_ω on $\Delta\alpha_\omega$ becomes quadratic (parabolic) (Fig. 1b).

2 Objects of research and experimental results

We studied experimentally PAB-50 glass matrix with the composition ($50B_2O_3 25Al_2O_3 25K_2O$) in mol% both undoped and doped with 1–2 mass% Fe_2O_3. The samples

A

B
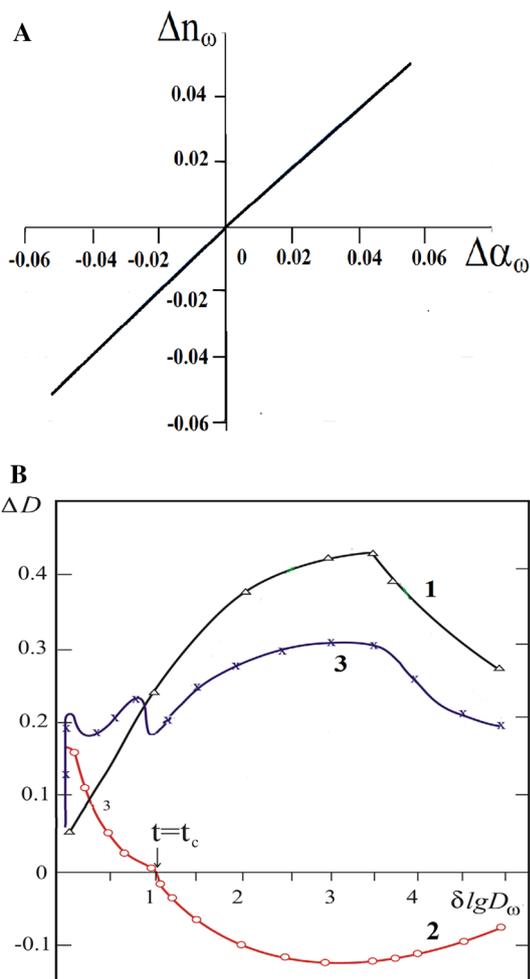
Fig. 1 **a** Dependence of refraction index change on the absorption index change at 530 nm (first linear approximation) of glass PAB-50 within 0.1–1 mass% Fe_2O_3. **b** Dependence of differential optical density at 530 nm on the irradiation dose logarithm ($\delta lg D_\omega$) of glass PAB-55 with 1.5 mass% Fe_2O_3: 1—calculated values of ΔD without thermal radiation induced optical band; 2—calculated by the Eq. [5] in parabolic approximation with thermal radiation induced optical band depending on gamma-dose and dose rate; 3—difference between curves 1 and 2

were irradiated in ^{60}Co gamma-source at the power dose of 2.36 Gy/s to the dose of 1.7×10^4 Gy in the range of irradiation temperatures 423–573 K with 50 K step, so as to thermally activate charge (electron or hole) trapped in various centers.

Figure 2 shows the absorption spectrum of undoped PAB-50 taken as a reference for obtaining differential absorption spectra of iron-doped samples (Figs. 4, 5).

Figure 2 demonstrates a narrow intensive band at 350 nm, which is attributed to electronic center at the radical-like nanostructure $[BO_3]^{e-}$ with the size ≤ 8.5 nm [5]. After gamma-irradiation the band at 350 nm grows and
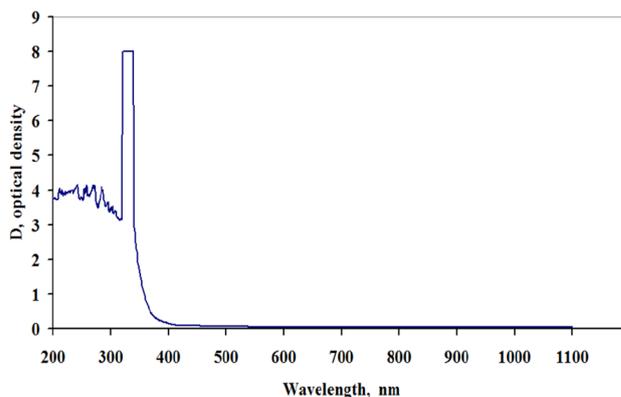

Fig. 2 Absorption spectrum of undoped PAB-50 prior to irradiation (reference value D_{ref})

additional band at 550 nm appears, because these centers transform into the above mentioned peroxide centers (1).

Figure 3 shows the absorption spectrum of the sample doped with 1 mass% Fe_2O_3 irradiated to the dose of 0.85×10^4 Gy at 300 K. Unlike Fig. 2, iron doping results in splitting the narrow intensive band at 350 nm, shift the absorption edge to 380 nm and appearing of the band at 420 nm attributed to $[Fe^{3+}O_6]$. This causes splitted negative difference absorption within 320–340 nm as seen in the inset.

Figures 4 and 5 show the differential absorption spectra of the samples doped to 1 and 2 mass% Fe_2O_3, respectively, after irradiation at the indicated temperatures. The particular feature occurs in the wavelength range of 300–350 nm, where the differential optical density becomes negative and changes in the range of $-5.7 \leq \Delta D_\lambda \leq 0$.

In the sample doped with 1 mass% Fe_2O_3 and irradiated at the elevated temperatures the absorption edge broadens and
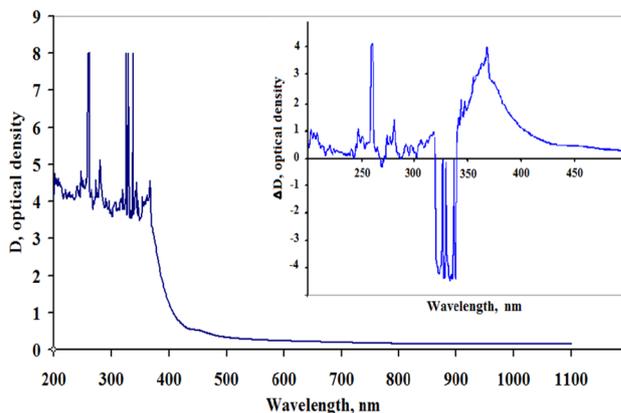
Fig. 3 Absorption spectra of PAB-50 doped with 1 mass% Fe_2O_3 irradiated to 0.85×10^4 Gy at 300 K ; inset - difference spectrum $\Delta D = D_{irr} - D_{ref}$
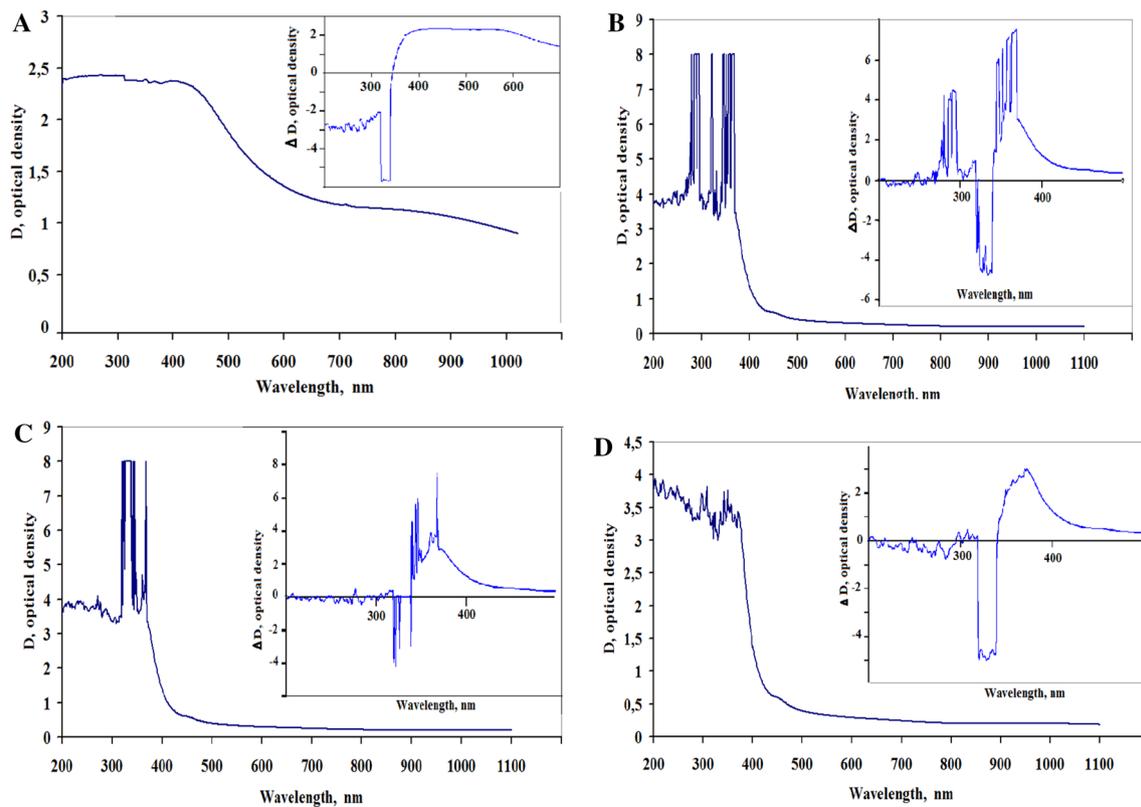
Fig. 4 a Absorption and differential spectra (inset) for PAB-50 glasses with 1 mass% Fe_2O_3 irradiated at 423 K. **b** Absorption and differential spectra (inset) for PAB-50 glasses with 1 mass% Fe_2O_3 additives irradiated at 473 K. **c** Absorption and differential spectra (inset) for PAB-50 glasses with Fe_2O_3 (1 mass%) additives irradiated at 523 K. **d** Absorption and differential spectra (inset) for PAB-50 glasses with Fe_2O_3 (1 mass%) additives irradiated at 573 K

moves to the long-wave side (Fig. 4) due to the absorption band of Fe^{3+} ion complexes at 440 nm, and also scattering in the visible range. Negative absorption in all UV range occurs only in Fig. 4a, d insets that means influence of gamma-irradiation on the glass matrix at 423 and 573 K.

At high doping level 2 mass% Fe_2O_3 the exchange interaction between neighboring iron complexes becomes stronger due to clustering, that results in higher absorption and scattering.

Indeed Fig. 5 demonstrates a significant (200 nm) red shift of the absorption edge to 580 nm. Such effect may be due to formation of sub-band on the bottom of the conductivity band by strongly interacted clusters of nanoparticles $[FeO]^x$ bound in the continuous chain. Figure 5a inset shows negative absorption in the whole absorption range from UV to NIR which was caused by thermal radiation treatment at 423 K. However irradiation at higher temperatures 473 and 523 K increases the optical density in the range of 300–580 nm and scattering below the edge (Fig. 5b, c). Spectra in Fig. 5b–d demonstrates intensive narrow resonances above the absorption edge. Both the scattering of visible photons and UV-absorption resonances characterize free (or quasi free) charge carriers in

highly doped glass. Interesting what with increase in irradiation temperature to 573 K the negative absorption in the UV decreases again due to compensation (see Fig. 5d). Most likely, this phenomenon is caused by ion–ion super-paramagnetic interactions (iron ions—the glass matrix) and electron–hole generation-recombination processes at the UV-absorption edge [13–15].

The switching effect in the UV- and visible ranges is caused by changing of coordination and valence of iron ions negative absorption means a "negative" response of multicomponent system to strong combine external influence (radiation + temperature) that is due to the negative refraction index at the interface of iron oxide nanocomplex with the complicate glass matrix which have different densities.

Therefore, if negative differential absorption $\Delta\alpha_\omega$ exists, as it is mentioned above, it is possible to connect with the negative index of refraction, then the nanoparticles formed at thermoradiation influences can be sign of "metamaterial": doped glass becomes self-transparent.
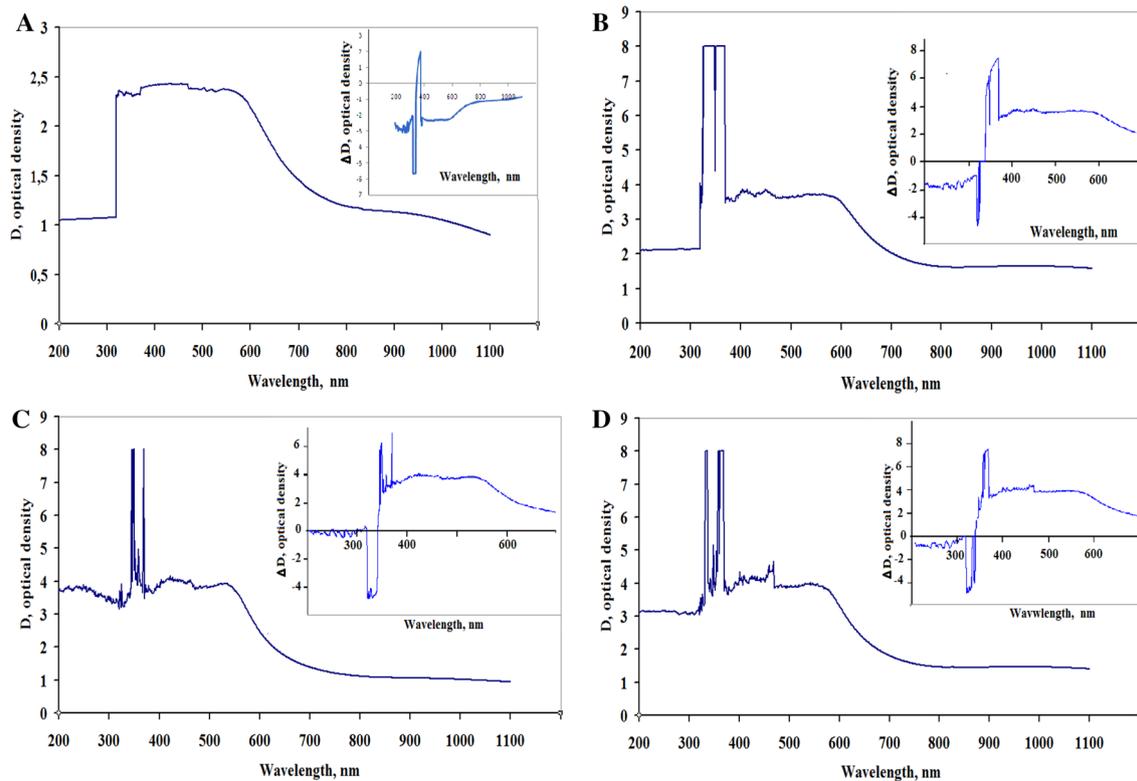
Fig. 5 a Absorption and differential spectra (inset) for PAB-50 glasses with 2 mass% Fe_2O_3 additives irradiated at 423 K. **b** Absorption and differential spectrums (inset) for PAB-50 glasses with 2 mass% Fe_2O_3 additives irradiated at 473 K. **c** Absorption and differ-ential spectra (inset) for PAB-50 glasses with Fe_2O_3 (2 mass%) additives irradiated at 523 K. **d** Absorption and differential spectrums (inset) for PAB-50 glasses with Fe_2O_3 (2 mass%) additives at 573 K

3 Conclusion

1. Comparison of results of thermoradiation effects in PAB-glass doped with iron oxide at ^{60}Co the γ-dose rate 26 Gy/s at the irradiation temperature 673 K with those at 2.36 Gy/s and irradiation temperatures 423–573 K has shown that under certain conditions of irradiation temperature and the iron concentration the glass becomes self-transparent in some optical window because of negative differential optical density.

2. Thermoradiation treatment of PAB-50 glass with additives of iron oxide (1–2 mass %) causes valent and coordination transition of iron ions in 4–6 oxygen ligand.

3. Theoretical model of differential absorption was suggested on the base of Levy and Dexter formulas and taking into account anomaly dispersion. It could explain the experimentally obtained negative differential optical absorption spectra, calculate the coefficient of optical absorption $\Delta\alpha$ and the refraction index Δn at strong external thermoradiation influences.

4. The suggested formula in the linear and parabolic approximations and experimental techniques of thermoradiation treatment and optical measurements can be applied for searching of non-linear optical metamaterial with trigger (switching) function, for creation of dynamic memory of the quantum computer.

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