Journal of Umm Al-Qura University for Applied Science 6 (2020) 21-24

Journal of Umm Al-Qura University for Applied Science

journal homepage: https://uqu.edu.sa/en/jas/87823

Effect of Fast Neutron Irradiation on Optical Properties of Lead Borate Glass

Y. A. El-Gammam [a].

[a] *Department of physics, Common first year deanship, Umm al-Qura University.*

ARTICLE INFO

Article History:
Submission date: 6/9/2019
Accepted date: 5/12/2019

Keywords:
Fast neutron irradiation, Lead borate glass, optical properties, samarium oxide.

ABSTRACT

Lead borate glass samples in the system $50B_2O_3$-$45PbO$-$5Al_2O_3$-$(100-x)$ Sm_2O_3, where x = 0, 0.42, 0.85, 1.7, 2.5 and 4.1 mole%, were prepared using the normal melt quench technique. The effect of fast neutron irradiation on optical properties of the prepared glasses was examined by measuring their optical density. The compositional dependence of the optical density, were measured and then were used to calculate and discuss some optical parameters such as: absorption coefficient (α), direct and indirect optical energy gap (E_{ogd} and E_{ogind}), Urbach's energy (E_u), Fermi energy (E_f), and steepness parameter (S). From the calculated optical parameters, it was found that E_f and E_u increase while E_{ogd} and E_{ogind} decrease with increasing neutron irradiation dose. Furthermore, the dependence of aforementioned parameters on the samarium oxide (Sm_2O_3) concentration has been interpreted on the light of band structure transition theory due to Sm^{+3} ions.

1. Introduction

Recently, interest in radiation effects on glass, generally, has been renewed as glass and used in different technology applications. Rare-earth doped glasses have been paid much more attention because of their high potential use for optical applications such as fibers, amplifiers, lasers and sensors [1]. They are also candidates for developing LED devices [2].

B_2O_3, which forms a network structure related to the silicates, creates a glass with higher melting point and greater ability to withstand temperature changes. For these reasons, their higher chemical durability and mechanical strength, borate glasses are often used as a host for Lanthanides ions. However, the emissive properties of Ln ions in this host suffer due to large phonon vibrational energy (~1300 cm^{-1}) [3].

Al_2O_3 has received significant consideration as the most likely matrix composition due to its high solubility of rare-earth ions [4].

Radiation creates a variety of defects in glass, which may be either permanent or temporary [5]. The effect of irradiation on glass is believed to depend on the type and energy of the irradiation, glass composition and sample parameters [6].

Neutron irradiation affects the structure of the glass matrix, resulting in changes in the optical, mechanical, chemical resistance and electrical properties [5–10]. Neutrons being uncharged interact with mater quite differently than the charged particles or the electromagnetic radiation. As neutrons pass through matter, they lose energy by a series of collisions, in scattering or capture events. In scattering process, a neutron collides with a nucleus but because the nucleus is incredibly small, the probability of a collision is low. The most dominant type of collisions is elastic scattering. In this type, a neutron collides with a nucleus and imparts a portion of its energy to the target nucleus. During this elastic scattering, no gamma radiation is given off by the nucleus. This recoil nucleus can cause excitation and ionization events. In the case of inelastic scattering type, the neutron is absorbed by the target nucleus, with a gamma ray and a less energetic neutron emitted from the target. After a neutron has lost a significant portion of its kinetic energy through the scattering events, it may be absorbed by a target nucleus in a capture event. The result of this event is that the new atom has its mass number increased by one, and as such will undergo one of many possible nuclear events. The result is often the emission of ionizing radiations, which result in the production of defects in the material via electron and hole productions [11]. Although neutrons are not directly ionizing radiation, they often produce secondary events that produce various forms of ionizing radiation i.e. radiation damage is not due to neutrons but is mainly from gamma radiation.

When ionizing radiation, such as gamma radiation, impinges on the glass electrons, they are initially excited from the valence band if the incident energy is greater than the band gap. The excess energy is converted to kinetic energy and as these electrons travel through the material, they will either recombine the positively charged holes, becoming trapped to form color centers, or produce a secondary electron cascade by knock-on collision with other bound electrons. Additional bound electrons are ionized by the secondary electrons through Coulomb interactions. The secondaries lose approximately 20 eV for each ionization. Finally, when the electrons energy becomes too low to ionize other electrons, they will either be trapped or recombine with holes. Therefore, in amorphous materials, radiation gives rise to optical absorption bands. These bands are associated with radiation-induced intrinsic and extrinsic defects. Vacancies and self-interstitials cause intrinsic defects. These defects can be introduced by ionization, atomic displacement mechanisms or via the activation of the preexisting defects [12]. Extrinsic defects are related to impurities such as alkali, alkaline earth and transition metals in the glass because they increase radiation- induced defects [13]. Materials which have such defects absorb photons at particular wavelengths, result in a modified absorption spectrum of the materials. The difference between the absorption spectra before and after irradiation is an important characteristic and is called the induced absorption spectrum.

The purpose of this work is to study the optical absorption spectrum of prepared lead borate glasses doped with samarium oxide before and after fast neutrons irradiation, to investigate induced transitions and to get information about the band structure and energy gap of this glass.

2. Experimental procedure

2.1. Preparation of glass samples

Glasses with the molar composition $(B_2O_3)_{50}$ $(PbO)_{45}$ $(Al_2O_3)_5$ $(Sm_2O_3)_x$,where x = 0, 0.42, 0.85, 1.7, 2.5 and 4.1, were prepared using the normal melt quench technique from AR grade chemicals of B_2O_3, PbO, Al_2O_3 and Sm_2O_3 . The composition of the glass samples is shown in Table 1. The chemical patches of every composition were mixed in porcelain crucibles, and then heated at 950°c for two hours under normal atmospheric conditions. The melt was stirred from time to time to promote complete mixing and finally poured into preheated molds made of stainless steel of radius 1.3 cm. All samples were properly annealed at 350°c in a muffle furnace to eliminate mechanical and thermal stresses. The samples were highly polished using alpha

* **Corresponding Author**
Department of physics, Common first year deanship, Umm al-Qura University.
E-mail address: yaahmed@uqu.edu.sa (Y. A. El-Gammam).

alumina polishing suspension to obtain optical flatness. The thickness of each sample was measured with micrometer.

The amorphous nature of these glasses was examined using Philips (X'pert MPD) diffractometer while applying the Bragg-Brentano para-focusing technique. Highly monochromated Cu-radiation (wavelength λ= 1.54051Å) was used. The step scan mode was applied in the 2θ-range (4-157.4612°). The step size (Δ2θ= 0.04°) and the counting time was 10 sec. for each reading. The corresponding accessible maximum scattering vector magnitude, K, was 8.0 Å-1. The air scattering was avoided by a suitable applied arrangement of XRD system. The receiving and divergence slits were properly chosen in both small and large 2θ-ranges, in order to improve the qualities of the data collected as it possibly could. The X-ray diffraction spectra of four samples (with x = 0, 0.42, 1.7 and 4.1) showed the diffused bands characteristic of the x-ray diffraction pattern of amorphous materials; the spectra did not show any sharp peaks and confirms that the glass samples are amorphous in nature.

Table 1. Composition of the glass samples

Sample no.	Glass composition (mol %)			
	PbO	B_2O_3	Al_2O_3	Sm_2O_3
Base	45	50	5	-
Sm1	45	50	5	0.42
Sm2	45	50	5	0.85
Sm3	45	50	5	1.7
Sm4	45	50	5	2.5
Sm5	45	50	5	4.1

2.2. UV-visible absorption measurements

The Optical properties of highly polished samples were measured at room temperature before and after each neutron irradiation dose using a UV/VIS spectrophotometer type JASCO, Corp., V–500, Japan, in the wavelength range 190–1100 nm.

2.3. Fast neutron irradiation

Prepared glass samples were irradiated with neutron beam from an Am–Be neutron source of 5 Ci activity, which has a neutron yield of $1.1x10^7$ n s^{-1}. Three irradiation dose of 3.229 $x10^{10}$, 5.045 $x10^{10}$ and $1.7x10^{11}$ n cm^{-2} were used.

3. Results and discussion

The measured UV-visible absorption spectra of the studied glasses are shown in Figure 1. From this figure, optical absorption spectra can be divided into three particular regions. The first region is the weak absorption tail, which originates from defects and impurities in the glass structure. The second region, found in the middle, exhibits exponential absorption edge that is strongly related to the structural randomness of the glass. The last region is the high absorption region that determines the optical energy gap. Study of these regions is a useful method for the investigation of optically induced transitions and for getting information about the band structure and energy gap of materials.

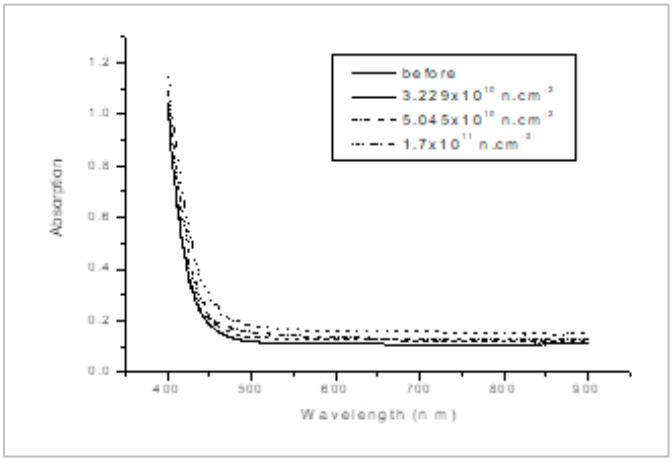


Fig. 1. UV–VIS spectra of sample free from Sm_2O_3 before and after neutron irradiation for 3 doses.

3.1. Glass Fermi energy

It is known that, the imaginary refractive index, *k*, can be represented by Fermi-Dirac distribution function [14]:

$$k = \frac{1}{1 + e^{\left(\frac{E_F - E}{K_B T}\right)}}, \quad (1)$$

where *E* is the energy of the incident photon, *T* is the temperature in Kelvin, E_B is Boltzmann constant and E_F is the Fermi energy. The Fermi energy is defined as the highest occupied energy level when electron configuration is in its ground state. Equation (1) can be written as

$$K_B T \ln(-1) = E_F - E \quad (2)$$

Linear fitting of the last equation is used to determine the glass Fermi energy and presented in Table 2. The calculated fermi energies reveal that E_F increases with increasing neutron irradiation dose.

3.2. Optical band energies

The optical absorption of an optical medium can be quantified in terms of optical density (O.D.), which is sometimes called *absorbance*, *A*. In terms of absorption, *I*, *absorbance* is defined as:

$$A = -\log 10 (I / Io), \quad (3)$$

and according to Beer's law, it can be write:

$$I = I_o e^{-\alpha x}, \quad (4)$$

Where α is the absorption coefficient and can be obtained from the relation

$$\alpha = 2.303 (A / x), \quad (5)$$

where *I* and I_o are optical intensities at thickness *x* and *x* = 0 respectively.

The optical absorption coefficient changes rapidly for photon energies comparable to that of the band gap, E_g [15].

According to Mott and Davis [14], the absorption of light by amorphous solid depends on the photon energy *E* of the incident photon and on the optical gap of the material. It is found that [16] this behavior may be represented by an equation of the form:

$$\alpha E = B (E - E_g)^r \quad (6)$$

where α is the absorption coefficient of the glass material, B is a constant and *r* is an index which assumes the values 1/2, 3/2, 2 and 3 depending on the nature of the electronic transition responsible for the absorption. In the present case *r* is taken equal to 1/2, for allowed direct transition and equal to 2, for allowed indirect transition [17]. The direct optical band gap energy, E_{ogd}, can be obtained by plotting $(\alpha E)^2$ versus the photon energy *E*. The indirect optical band gap energy, E_{ogind}, can be obtained by plotting $(\alpha E)^{1/2}$ versus the photon energy *E* extrapolating the linear portion of the curve to intersect the energy axis. The obtained optical band gap energies for the studied glasses are listed in Table 2. As Shawn in Table (2), one can notice a small decrease in E_{ogd} and E_{ogind} with increasing neutron irradiation dose.

Table 2. Calculated optical parameters of studied glasses doped with different concentrations of Sm_2O_3 irradiated with different neutron doses.

Sample no.	Dose (n.cm^{-2})	E_F (eV)	E_{ogd} (eV)	E_{ogind} (eV)	E_u	*S*
Base	0	5.186	3.293	2.963	0.182	0.142
	$3.229x10^{10}$	5.219	3.225	2.769	0.201	0.128
	$5.045x10^{10}$	5.245	3.219	2.765	0.215	0.120
	$1.7x10^{11}$	5.312	3.153	2.754	0.247	0.105
Sm1	0	5.413	3.223	2.793	0.266	0.097
	$3.229x10^{10}$	5.521	3.159	2.691	0.232	0.111
	$5.045x10^{10}$	5.497	3.175	2.782	0.241	0.107
	$1.7x10^{11}$	5.572	3.091	2.742	0.263	0.098
Sm2	0	5.844	3.187	2.682	0.285	0.091
	$3.229x10^{10}$	5.913	3.149	2.583	0.301	0.086
	$5.045x10^{10}$	5.902	3.112	2.597	0.316	0.082
	$1.7x10^{11}$	6.153	3.045	2.542	0.328	0.079
Sm3	0	6.362	3.193	2.671	0.331	0.078
	$3.229x10^{10}$	6.883	3.091	2.543	0.358	0.072
	$5.045x10^{10}$	7.594	3.093	2.573	0.451	0.057
	$1.7x10^{11}$	7.465	3.066	2.510	0.413	0.063
Sm4	0	6. 272	3.180	2.869	0.312	0.083
	$3.229x10^{10}$	6.299	3.132	2.767	0.354	0.073
	$5.045x10^{10}$	6.382	3.111	2.752	0.371	0.070
	$1.7x10^{11}$	6.571	3.073	2.739	0.405	0.064
Sm5	0	6.123	3.284	2.892	0.22	0.118
	$3.229x10^{10}$	6.153	3.251	2.821	0.263	0.098
	$5.045x10^{10}$	6.234	3.258	2.745	0.243	0.106
	$1.7x10^{11}$	6.417	3.198	2.768	0.301	0.086

3.3. Urbach energy and Steepness parameter

In the exponential region (the middle region) of the absorption dependence on the photon energy curve, the absorption coefficient, α , is given by the relation:

$$\alpha = C \exp(E/\Delta E), \quad (7)$$

where C is a constant, E is the energy of the incident photon and ΔE characterizes the slope of the exponential edge (Urbach's energy, E_u) region and it is the width of the band tails of the localized states. The existence of the long tails of the localized states is attributed to the amorphous nature of the material. To calculate this width, ΔE, of the energy tail, a model proposed by Urbach (1953) can be used:

$$\ln(\alpha) = \ln(C) + (E / \Delta E),$$

$$\text{or} \quad \ln(\alpha) = \ln(C) + (E / Eu), \quad (8)$$

Thus, E_u can be obtained from the linear plot of ln(α) as a function of photon energy. The steepness parameter, S, which characterizes the broadening of the optical absorption edge due to electron-photon or excitation-photon interaction at room temperature, T = 300 °K can be written as [17]:

$$S = K_B T / E_u, \quad (9)$$

The calculated values of E_u and S are listed in table (2). These values reveal that E_u increases, while S decreases with increasing neutron fluence.

3.4. Neutron irradiation effect

From the above results and discussion, it is clear that, the successive neutron irradiation doses caused changes in all optical parameters listed in Table (2). These changes can be attributed to the compositional changes in the glass matrix result from the collision of energetic neutrons with atoms dissipating their energy through the solid. This collisions cause displacement of atoms from their normal positions [18]. The neutron irradiation may also cause densified structural changes in glass or compact state which may refer to some bond angles becoming smaller, change in density and refractive index, and induced color centers. Induced color centers are responsible for induced absorption bands. However, this decrease in the optical band gap may be due to the fact that, in neutron irradiation, the electrons leave their normal positions and move through the glass network [19] that results in redistribution of the electrons in the glass matrix. The increase of Urbach's energy indicates an enhancement of the conduction and valence level electrons to the forbidden energy gap and may causes an increase in the conductivity of the glass due to neutron irradiation.

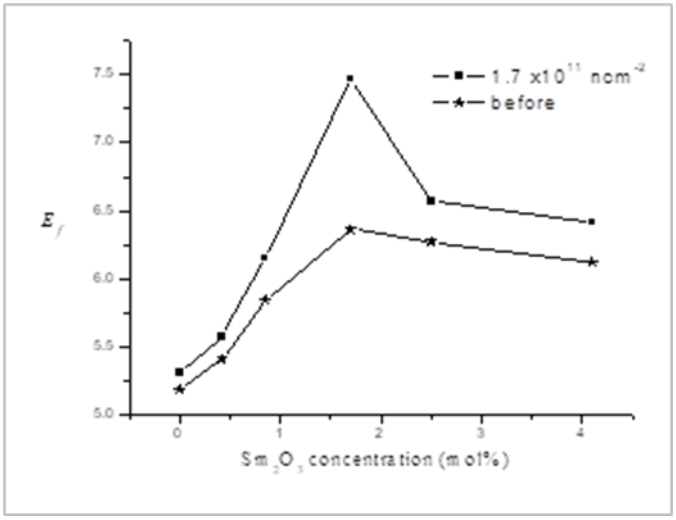
3.5. Sm_2O_3 concentration effect

From Table (2) it may be noticed that E_{ogd}, E_{ogind} and S decrease with increasing Sm_2O_3 content for the first three samples, then tend to increase with increasing Sm_2O_3 concentration in the other three samples. In contrast, E_F and E_u increase with increasing Sm_2O_3 concentration for the first three samples then tend to decrease with increasing Sm_2O_3 concentration in the other three samples. Figure 2 illustrates the change of E_f with Sm_2O_3 concentration before and after irradiation with 1.7×10^{11} (n.cm^{-2}) dose. These changes can be attributed to the fact that, when an oxide of a multivalent metal is dissolved in a glass, equilibrium is established between the different valence states of the metal. In case of samarium, the 3+ charge state is much more stable than the 2+ charge state [20]. As mentioned above, radiation damage, is not mainly due to the neutrons but due to gamma radiation that is responsible for most of it. Eugenia Malchukova *et al.* [21] suggested that gamma radiation is effective for reducing Sm^{3+} to Sm^{2+} ions. Sm^{2+}/Sm^{3+} ratio estimation demonstrates strong influence of both irradiation dose and dopant content on reduction of Sm^{3+}. In some studies, [21–23] it has been observed that increasing Sm_2O_3 content reveals interesting behavior with the value of 2–3 wt% concentration.

4. Conclusion

From the above study, it is clear that neutron irradiation has considerable effect on the investigated optical parameters of the studied glasses. It was found that the values of E_f and E_u increase while E_{ogd}, E_{ogind} and S decrease with increasing neutron irradiation dose. These changes may be attributed to the structural changes and redistribution of the electrons taking place in the glass matrix due to the collision of energetic neutrons. In addition, increasing Sm_2O_3 concentration affects the optical parameters for the glasses with low samarium content, an opposite trend takes place for the glasses doped with high content of Sm_2O_3 .

Fig. 2. The variation of E_f (eV) with Sm_2O_3 concentration before and after 1.7×10^{11} n.cm^{-2} dose.



References

[1] M. Nogami, T. Hagiwara, G. Kawamura, E. Ghaith, T. Hayakawa, Redox equilibrium of samarium ions doped in Al_2O_3–SiO_2 glasses. *J. Lumin.*, **2007**, *124*, 291–296. https://doi.org/10.1557/JMR.2002.0304

[2] C. Zhu, X. Liang, Y. Yang, G. Chen, Luminescence properties of Tb doped and Tm/Tb/Sm co-doped glasses for LED applications. *J. Lumin.*, **2010**, *130*, 74–77. https://doi.org/10.1016/j.jlumin.2009.07.023

[3] Y. Dwivedi, A. Bahadur, Spectroscopic study of Sm:Ce ions co-doped in barium fluoroborate glass. *Journal of Non-Crystalline Solids*, **2010**, *356*, 1650–1654. https://doi.org/10.1016/j.jnoncrysol.2010.06.013

[4] K. Arai, H. Namikawa, K. Kumata, T. Honda, Y. Ishii, T. Handa, Aluminum or phosphorus co-doping effects on the fluorescence and structural properties of neodymium-doped silica glass. *J. Appl. Phys.*, **1986**, *59*, 3430. https://doi.org/10.1063/1.336810

[5] N.A. El-Alaily, R.M. Mohamed, Effect of irradiation on some optical properties and density of lithium borate glass. *Mater. Sci. Eng. B.*, **2003**, *98*, 193-203. https://doi.org/10.1016/S0921-5107(02)00587-1

[6] M. Rajaram, E.J. Friebele, Effects of radiation on the properties of low thermal expansion coefficient materials: A review. *J. Non-Cryst. Solids*, **1989**, *108*, 1-17. https://doi.org/10.1016/0022-3093(89)90327-X

[7] H.A. El-Batal, H. Farouk, F.M. Ez-Eldin, Electric and dielectric properties of some gamma-irradiated cabal glasses. *Radiat. Phys. Chem.*, **1996**, *47*, 811-814. https://doi.org/10.1016/0969-806X(95)00168-W

[8] H.A. El-Batal, F.A. Khalifa, M.A. Azooz, Gamma ray interaction, crystallization and infrared absorption spectra of some glasses and glass-ceramics from the system $Li_2O.B_2O_3.Al_2O_3$, *Ind. J. Pure Appl. Phys.*, **2001**, *39*, 565-573. http://nopr.niscair.res.in/handle/123456789/26685

[9] Z.A. El-Hadi, Gamma Ray Interaction with Some High-Lead Glasses Containing Chromium Ions. *J. Solid State Chem.*, **2002**, *163*, 351-363. https://doi.org/10.1006/jssc.2001.9290

[10] M.I. Abd El-Ati, A.A. Higazy, Electrical conductivity and optical properties of gamma-irradiated niobium phosphate glasses. *J. Mater. Sci.*, **2000**, *35*, 6175-6180. https://doi.org/10.1023/A:1026768925365

[11] A.K. Sandhu, Surinder Singh, O. P. *Pandey / Materials Chemistry and Physics*, **2009**, *115*, 783–788.

[12] A. Agrawal, M. Tomazawa, Correlation of silica glass properties with the infrared spectra. *J. Non-Cryst. Solids*, **1997**, *209*, 166-174. https://doi.org/10.1016/S0022-3093(96)00542-X

[13] E.J. Friebele, M.E. Gingerich, K.J. Long, Appl. Opt. 21 (1982) 547.

[14] N.F. Mott, E.A. Davis, Electronic Processes in Noncrystalline Materials, Clarendon, Oxford, **1971**.

[15] S.R. Elliott, in: R.W. Cahn, P. Haasen, E.J. Kramer (Eds.), Materials Science and Technology: Glasses and Amorphous Materials, vol. 9, **1991**, p. 420, Published jointly by VCH, Weinheim Germany, and New York, USA.

[16] S. Hasegawa, S. Yazaki, T. Shimizuol, Effects of annealing on gap states in amorphous Si films. *Solid State Commun*., **1978**, *26*, 407-410. https://doi.org/10.1016/0038-1098(78)90515-X

[17] T. C Sabari Girisun and S. Dhanuskodi, Linear and nonlinear optical properties of tris thiourea zinc sulphate single crystals. *Crst. Res. Technol*., **2009**, *44*, 1297-1302. https://doi.org/10.1002/crat.200900351

[18] W. Primak, L.H. Fuchs, R. Day, Effects of Nuclear Reactor Exposure on Some Properties of Vitreous Silica and Quartz. *J. Am. Ceram. Soc.*, **1955**, *38*, 135-139. https://doi.org/10.1111/j.1151-2916.1955.tb14916.x

[19] S. Singh, A. K. Sandhu, S. Prasher, O. P. Pandey, Effect of neutron irradiation on etching, optical and structural properties of microscopic glass slide used as a solid state nuclear track detector. *Radiation Measurements*, 2007, *42*, 1328 – 1331. https://doi.org/10.1016/j.radmeas.2007.02.057

[20] A. Osvet, S. Emelianova, R. Weissmann, V. I. Arbuzov, A. Winnacker. Spectral hole burning in Sm^{2+}-doped alkaliborate glasses and Tb^{3+}-doped silicate and borate glasses. *J. Lumin.*, 2000, *86*, 323-332. https://doi.org/10.1016/S0022-2313(00)00176-9

[21] E. Malchukova, B. Boizot, D. Ghaleb, G. Petite. Optical properties of pristine and γ-irradiated Sm doped borosilicate glasses. *Nuclear Instruments and Methods in Physics Research A*, 2005, *537*, 411–414. https://doi.org/10.1016/j.nima.2004.08.054

[22] E. Malchukova, B. Boizot, G. Petite, D. Ghaleb, Optical properties and valence state of Sm ions in aluminoborosilicate glass under β-irradiation. *J. Non-Crystalline Solids*, 2007, *353*, 2397–2402. https://doi.org/10.1016/j.jnoncrysol.2007.04.003

[23] N. Yaru, L. Chunhua, Z. Yan, Z. Qitu, X. Zhngzi. Study on Optical Properties and Structure of Sm_2O_3 Doped Boron-Aluminosilicate Glass. *J. Rare Earths*, 2007, *25*, 94-98. https://doi.org/10.1016/S1002-0721(07)60532-8