Adıyaman University Journal of Science
https://dergipark.org.tr/en/pub/adyujsci
DergiPark AKADEMİK
ISSN 2147-1630
e-ISSN 2146-586X

Synthesis and Optical, Thermal, Structural Investigation of Zinc-Borate Glasses Containing V_2O_5

Gökhan KILIÇ[1,*]

[1]*Eskisehir Osmangazi University, Faculty of Science and Letters, Department of Physics, TR-26040 Eskisehir, Turkey*
gkilic@ogu.edu.tr, ORCID: 0000-0002-6762-6898

Received: 22.01.2020 **Accepted:** 27.02.2020 **Published:** 25.06.2020

Abstract

Vanadium pentaoxide (V_2O_5) doped zinc borate (ZnB) oxide glasses that could be used in fiber optic cable cores in optoelectronics, in laser crystals in solar energy systems have been synthesized successfully. Structural characters of synthesized glasses were determined with differential scanning calorimeter (DSC) and Fourier-Transform infrared spectroscopy (FTIR). Glass transition (T_g), crystallization (T_c) and melting temperatures (T_m), and thermal stabilities (ΔT) of the glasses were determined and also their association with the change in V_2O_5 was explained. Structural units of boron and zinc that form the structure were determined according to FTIR data. As a result, it was determined that boron formed the glass matrix with BO_3, BO_4 and boroxol ring structural units; on the other hand, zinc contributed to the glass matrix with tetrahedral ZnO_4 and octahedral ZnO_6 structural units, and vanadium usually had modifier role in the structure with its VO_4 and VO_5 structural units. V_2O_5's presence in the structure with increasing amount changes thermal, structural and physical properties. Among the properties that significantly change, the most important one is optical properties. Indirect optical band gaps, Urbach energies, refractive index values of these synthesized samples were determined, and quite clear shifts towards red region were observed in the transmittance and absorption spectra. Optical band gap decreased to 1.24 eV from 2.55 eV with increasing amount of V_2O_5; on the other hand,

* Corresponding Author DOI: 10.37094/adyujsci.678938

Urbach energy was determined to increase to 0.630 eV from 0.246 eV. Densities, molar volumes of these synthesized glasses were also examined and commented on.

Keywords: ZnO; B_2O_3; V_2O_5; Zinc-Borate glass; FTIR.

V_2O_5 İçeren Çinko-Borat Camların Sentezi ve Optik, Termal, Yapısal İncelenmeleri

Öz

Optoelektronikte fiber optik kablo korlarında, laser kristallerinde ve güneş enerji sistemlerinde kullanılabilecek vanadium pentaoksit (V_2O_5) katkılı çinko borat (ZnB) oksit camlar başarıyla sentezlenmiştir. Sentezlenen camlara ait yapısal karakterler diferansiyel taramalı kalorimetre (DSC) ve Fourier dönüşümlü kızılötesi spektroskopisi (FTIR) ile belirlenmiştir. Camsı geçiş (T_g), kristallenme (T_c), erime sıcaklıkları (T_m) ve termal kararlılıklar (ΔT) belirlenerek V_2O_5 değişimiyle ilgisi açıklanmıştır. FTIR verilerine göre yapıyı oluşturan bor ve çinkonun yapısal birimleri belirlenmiştir. Borun cam matrisini BO_3, BO_4 ve boroksol halka yapısal birimleriyle oluşturduğu, çinkonun ise cam matrisine tetrahedral ZnO_4 ve oktahedral ZnO_6 yapısal birimleri ile katkıda bulunduğu, vanadyumun yapıda çoğunlukla VO_4 ve VO_5 yapısal birimleriyle yer alarak düzenleyici görev üstlendiği belirlenmiştir. V_2O_5 katkısının artması yapının termal, yapısal ve fiziksel özelliklerini değiştirmektedir. Belirgin biçimde değiştirdiği özelliklerin başında optik özellikler gelmektedir. Sentezlenen numunelere ait indirekt optik bant aralığı, Urbach enerjisi, kırılma indisi değerleri belirlenmiş, geçirgenlik ve absorpsiyon spektrumlarında kırmızı dalgaboyuna kaymalar net bir şekilde gözlenmiştir. Optik bant aralığı V_2O_5 artışıyla 2.55 eV dan 1.24 eV'a azalmış, buna karşılık Urbach enerjisi 0.246 eV'dan 0.630 eV'a arttığı belirlenmiştir. Ayrıca, sentezlenen numunelere ait yoğunluk, molar hacim incelenmiş ve yorumlanmıştır.

Anahtar Kelimeler: ZnO; B_2O_3; V_2O_5; Çinko-Borat cam; FTIR.

1. Introduction

Glass, an amorphous material, has an important place in respect to technology and science. Besides silicon dioxide (SiO_2), phosphorus pentoxide (P_2O_5), boron oxide (B_2O_3), and vanadium pentoxide (V_2O_5) are being used in the synthesis of glasses the most. Among these, B_2O_3 is known to be the best glass former [1, 2]. Borate glasses in which B_2O_3 establishes the glass network are very important optical materials due to their low melting points, high transmittance properties and high thermal stabilities [3]. They are frequently being used in the making of dielectric materials and used as isolation materials. Though they are being used as dielectric materials, the inclusion

of transition metal ions in the borate glass network leads to the achievement of semiconductor character or these glasses. Transition metals are nowadays being extensively used in glass science due to their presence in two or more valance states that alters the structural and optical characters [4-10].

It is possible to find examination studies performed on binary zinc-borate structures among transition metal doped borate glasses and also ternary structures and structures having more components in the literature [11-22]. Except for glass systems, it is possible to find zinc-borate ceramic structures, as well [23].

Zinc-borate glasses are being used in plasma screens and panels for high quality and performance [24, 25]. Zinc-borate glasses are promising materials for a large field including television panels and computer monitors. They are preferred due to having high voltage resistance in providing rapid surge in dielectric layers and being highly transparent. Since zinc borate glasses that do not contain lead possess all the aforementioned qualities, they are shown to be appropriate materials for applications that are in question [26].

Studies on vanadium due to their interesting optical, electrical and magnetic properties have significantly increased recently. Though studies on transition metal doped glasses can be found in the literature frequently [27-37], there are still components, compositions and properties that have not yet been studied. Glasses containing vanadium, which is a transition metal, show semiconducting properties since they contain V^{4+}, V^{5+} valance states [38-45]. Vanadium doped glasses are known to be n-type semiconductors for low V^{4+}/V^{5+} ratio [46]. Glasses with vanadium content have a wide range of use from the production of solid-state devices to memory and optical switching, devices like electrical threshold, and in the formation of fiber optics [47, 48]. Therefore, they are materials with potential for most electronic and optoelectronic applications [49]. In the literature, some characteristics of glasses having different compositions as a result of combining zinc-borate glass systems with V_2O_5 have been elaborated [50, 51].

In this study, ZnO-B_2O_3-V_2O_5 glasses doped with V_2O_5 and containing high ratio of ZnO, so they can find a use in optoelectronics were synthesized successfully. Compared borate glasses that are sensitive to humidity, these synthesized glasses are resistant to air, water; therefore, they are considered to be important since boron is able to find use in respect to technological applications. Structural and thermal properties of these synthesized glasses were examined in a detailed way and discussed. Characterization of this structure considered to become a potential material that could be used in fiber cable cores in optoelectronics, in laser settings and, also in solar energy systems was revealed.

2. Materials and Methods

2.1. Sample preparation

ZnO-B_2O_3 glass samples containing V_2O_5 were synthesized from chemicals having 99.5% purity (Alfa Aesar) according to $(100\text{-}x)(0.6ZnO\text{-}0.4B_2O_3)$. $(x)(V_2O_5)$ (x = 1, 2, 3, 4) composition. The method that was used in the synthesis of the glasses was melt-quenching method. Chemicals were weighed on an analytical scale having accuracy of 0.00001g, and then weighed chemicals were mechanically mixed for approximately 10 min and made uniform.

Prepared powder mixture was left in a porcelain crucible for 60 minutes in a Nabertherm LHT 02/17 LB brand high temperature furnace that was previously heated to 1100 °C for reaction to take place. At the end of the process, molten glass samples were shaped cylindrically in a steel mold and annealed for 60 minutes at 400 °C.

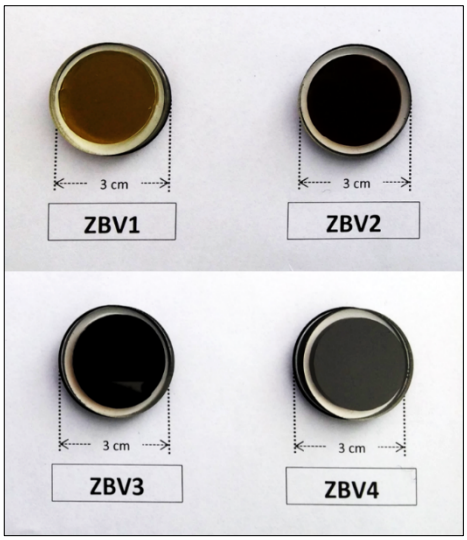

Figure 1: Synthesized ZnO-B_2O_3-V_2O_5 glass samples

Glass samples synthesized by this way (Fig. 1) were sliced with a Metkon brand Micracut 152 model cutting device with diamond disc for optical measurements having a diameter of 2.5 cm and a thickness of 2 mm; both surfaces of the cut samples were polished with a Metkon brand Forcipol 102 model polishing device. Some of the samples were grounded with a Retsch RM200 brand grinder to study their thermal and structural properties.

2.2. Characterization

Densities of glasses were determined with the principle of Archimedes. Samples were first weighed in the air with a KERN brand ABT 100-5m model analytical scale having an accuracy of 0.00001g, and then weighed again in immersion fluid. Ultra-pure water was selected as

immersion fluid. By using the measurements taken in the air and in the immersion fluid, densities of the samples were calculated with the below equation [52]:

$$D = \frac{W_a}{W_a - W_l} \cdot \rho_o \quad (1)$$

In this equation, W_a is the weight of the sample in the air, W_l is the weight of the sample in the fluid and ρ_o is the density of immersion fluid (ρ_o = 0.998272 g.cm^{-3}) at 20 °C. Molar volumes (V_m) of glass samples were calculated with the following equation:

$$V_m = \frac{\sum x_i M_i}{D} \quad (2)$$

Here, x_i is the mole ratio of the *i.*th component, M_i is the molecular weight.

Transmittance and absorption spectra of the glasses were determined with Analytik Jena SPECORD 210 UV-Vis Spectrophotometer with steps of 1 nm. In addition, in order to determine the uniformity of the sample, transmittance spectra were determined with scanning attachment of the device by using 1.5 cm piece of the surface. Absorption spectra were used to calculate optical band gaps and Urbach energies of the synthesized samples.

Refractive index due to optical band gap was calculated with the following empirical relation [53]:

$$\frac{(n^2 - 1)}{(n^2 + 2)} = 1 - \sqrt{\frac{E_0}{20}} \quad (3)$$

n, is the refractive index of the samples, E_0 is optical band gap.

In order to determine the structural properties, powdered forms of the samples were used and their FTIR spectra were obtained. FTIR analyses were performed at room temperature within the wavenumber range of 400-1400 cm^{-1} by using diamond ATR with a resolution of 4 cm^{-1}. Origin 2018 program was used to determine hidden bands in the spectrum.

Netzsch STA 449F3 simultaneous thermogravimetric analyze device was used in the determination of thermal properties. DSC measurements were made with approximately 50 mg of powdered sample between the range of room temperature and 1000 °C with increments of 1 °C. Glass transition, crystallization and melting temperatures were calculated from the obtained

graphs with ONSET method (Fig. 3). In addition, thermal stabilities (ΔT) belonging to glasses were calculated with the following equation:

$$\Delta T = T_c - T_g \tag{4}$$

Here T_c is the first crystallization temperature, T_g is glass transition temperature.

3. Results and Discussion

3.1. Density and molar volume

Sample densities and molar volume values calculated with the help of Eqn. (1) are given in Table 1. In addition, sample codes and ratio of components within the glass can also be seen. As you can see in Fig. 2, density values of the samples decreased regularly from 3.392 g.cm^{-3} to 3.329 g.cm^{-3} with increasing amount of V_2O_5. On the other hand, molar volume values increased from 22.910 cm^3.mol^{-1} to 24.289 cm^3.mol^{-1} almost linearly. V_2O_5's being a more complex molecule led to volume increase, in addition, since masses of shifting vanadium and zinc were close to each other, it resulted in decrease in the molar volume. Similar impact can also be found in the literature [54].

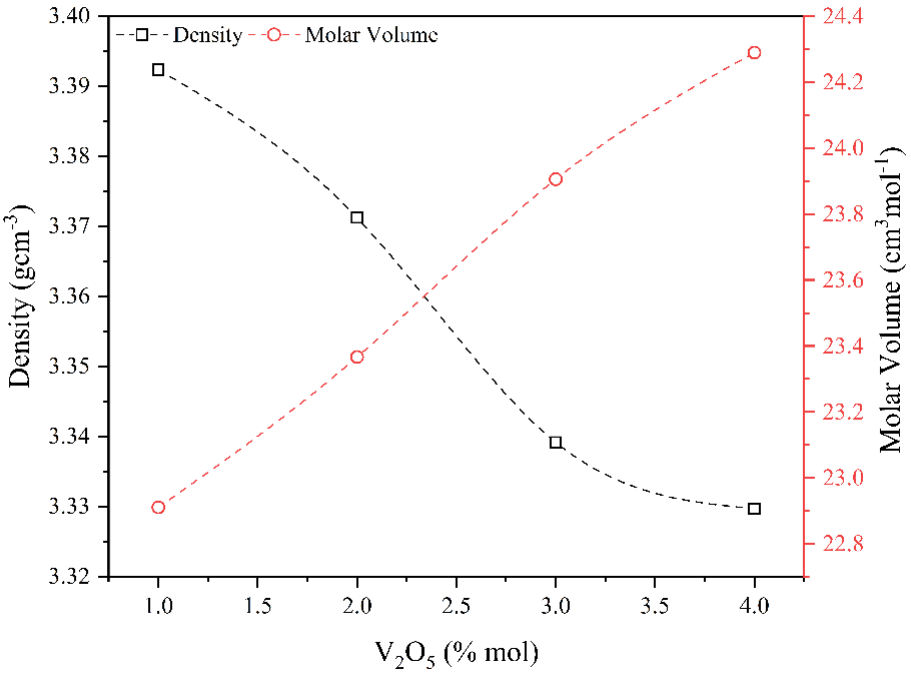

Figure 2: Change in density and molar volume values according to V_2O_5 concentration

Table 1: Sample codes, % compositions and calculated density and molar volume values of synthesized samples

Sample Code	ZnO mol %	B_2O_3 mol %	V_2O_5 mol %	Density $g.cm^{-3}$ (±0.001)	Molar volume $cm^3.mol^{-1}$ (±0.005)
ZBV1	59.40	39.60	1.00	3.392	22.910
ZBV2	58.80	39.20	2.00	3.371	23.366
ZBV3	58.20	38.80	3.00	3.339	23.906
ZBV4	57.60	38.40	4.00	3.329	24.289

3.2. Thermal properties

DSC thermograms belonging to synthesized ZBV glass samples are given in Fig. 3, and their glass transition temperatures, crystallization and melting temperatures are given in Table 2. As it can be seen in DSC thermograms, curves belonging to 4 samples are almost identical in respect to their shapes. 3 ambiguous exothermic peaks in the shape of shoulders are followed by 1 endothermic peak. Glass transition temperatures can be seen within the range of 530-550 °C and glass transition temperature has decreased with increasing amount of V_2O_5. First crystallization temperature was around 740 °C; the range of 818-833 °C was the region of second crystallization temperature. When we have reviewed the literature, we can see that various crystalline phases are mentioned between glassy transition temperature and melting temperature in similar systems [55]. These are $Zn_3B_2O_6$ crystalline phase around 680 °C and $Zn_3V_2O_8$ crystalline phase around 700 °C. In Nb_2O_5 doped zinc-borate glasses, $ZnNb_2O_6$ crystalline phase containing Nb is found around 740 °C.

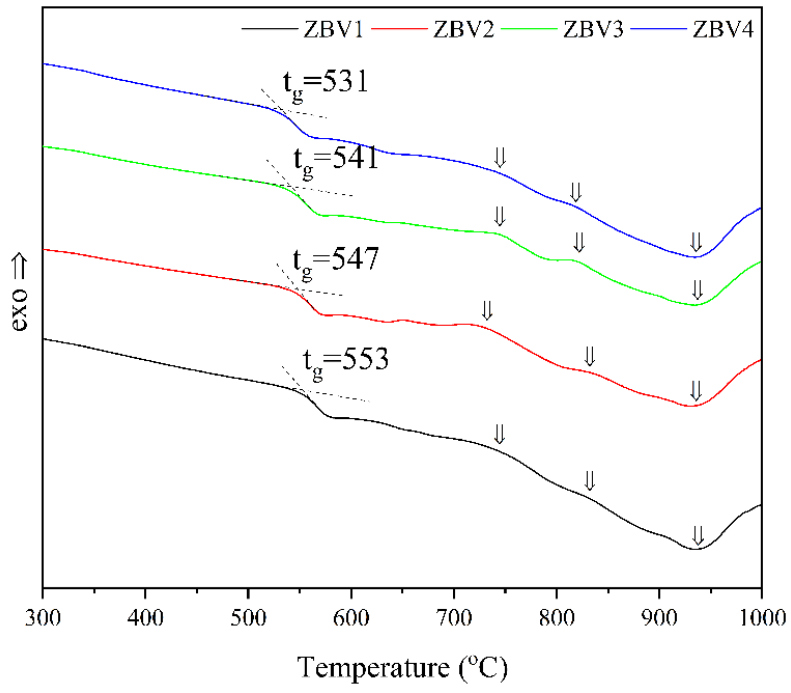

Figure 3: DSC thermograms belonging to samples

In the light of all these data, we estimate that the peak that we have observed in the proximity of 740 °C belong to $Zn_3V_2O_8$ and ZnV_2O_6 crystalline phases in the glasses that we have synthesized. The second crystallization temperature decreased with increasing amount of V_2O_5. Melting temperatures belonging to were almost the same and around 935 °C. Decrease in glass transition temperatures and crystallization temperatures remaining almost the same with increasing amount of V_2O_5 naturally resulted in increase in the thermal stability (ΔT). Glassy transition temperatures are reported to increase in tellurium and silicon-based glasses with the addition of Nb_2O_5, V_2O_5 in increasing amounts. Decrease in glass transition temperatures of the samples in this study with increasing concentration of V_2O_5 can be explained with bond enthalpy. While B-O bond enthalpy was 809 kJmol^{-1}, V-O bond enthalpy was lower (637 kJmol^{-1}). Substituting O-B-O bonds with weaker O-V-O connections lowers activation energy for structural reorganizations. Accordingly, glass transition temperature decreases with increasing V_2O_5.

Table 2: Glass transition, crystallization, melting temperatures and thermal stabilities of synthesized ZBV glasses

Sample Code	T_g (°C)(±1)	T_{c1} (°C)(±1)	T_{c2} (°C)(±1)	T_m (°C)(±1)	ΔT (°C)(±1.2)
ZBV1	553	743	833	935	190
ZBV2	547	730	831	933	183
ZBV3	541	743	820	935	202
ZBV4	531	743	818	935	212

3.3. Structural examination

FTIR spectra are given all together in Fig. 4. In addition, basic structural units of boron and vanadium and their corresponding localizations in our synthesized glasses are also given within this figure. In Fig. 5, deconvolutions of FTIR spectra belonging to samples are given. FTIR spectra were examined in three basic regions.

The first region is the 400-800 cm^{-1} region. In this region, vibrations belonging to various connections can be seen. The second region is between 800-1200 cm^{-1} and mostly vibrations belonging to BO_4 structural units of boron are observed in this region. The third region is the region around 1200-1500 cm^{-1} and mostly various vibrations corresponding to BO_3 structural unit of boron can be seen in these regions. Except for boron that forms the glass network, vibrations corresponding to various states of zinc and vanadium found in the glass can also be observed within these regions (Table 3).

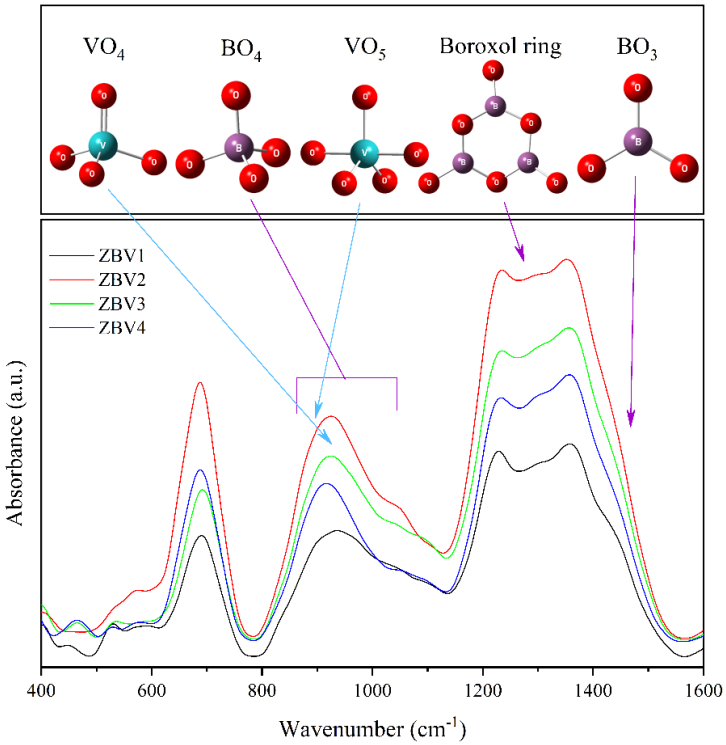

Figure 4: 400-1600 cm^{-1} region FTIR spectra and localizations of structural units belonging to ZBV samples

One or more intensive peaks can be seen in all regions. Bands found between 449-464 cm^{-1} within the first regions are known to belong to the vibrations in the ZnO_4 unit. Apart from this, O-V angular vibration is reported to correspond to 526-534 cm^{-1}, Zn-O stretching vibration correspond to 575-595 cm^{-1}, and B-O-B connection vibration correspond to the bands within 676-730 cm^{-1}. The most intense peak in this region belongs to the band around 680 cm^{-1} and shows the abundance of B-O-B connections within the structure.

Bands belonging to B-O stretching vibrations belonging to BO_4 unit in the second region are found within the ranges of 873-886 cm^{-1}, 930-939 cm^{-1}, 1042-1055 cm^{-1}. It is also known in V_2O_5 containing structures that the presence of bands belonging to the vibrations of VO_5 and VO_4 structural units are also found within the regions of 873-886 cm^{-1} and 930-939 cm^{-1} where B-O stretching vibrations have been encountered. Intensity of bands belonging to B-O vibration is known to decrease with increasing concentration of V_2O_5 in penta- and diborate groups within the range of 1103-1114 cm^{-1}; however, the intensity of the band belonging to B-O vibration in meta- and orthoborate groups increases within the range of 1222-1231 cm^{-1} found in the third region.

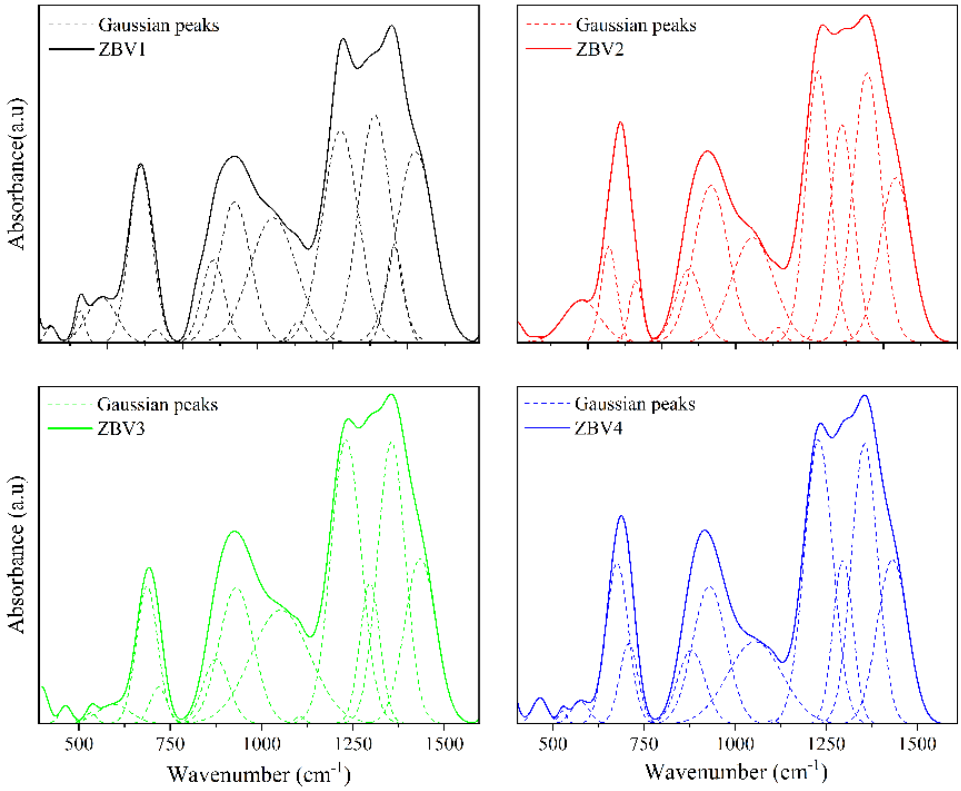

Figure 5: Deconvolution of FTIR spectra belonging to ZBV samples. Straight lines show the FTIR spectra belonging to samples and dashed lines show the Gaussian bands obtained from deconvolution

Table 3: Bands belonging to ZBV samples and corresponding vibrations

ZBV1 (cm^{-1})	ZBV2 (cm^{-1})	ZBV3 (cm^{-1})	ZBV4 (cm^{-1})	Vibrations	References
449	458	464	464	Zn-O vibration in ZnO_4 structure	[56]
527	-	534	526	O-V angular deformation vibration	[57]
584	582	595	575	Zn-O stretching vibration	[58]
688	693	686	676	B-O-B connection vibration	[59]
729	730	718	708	B-O-B connection vibration	[60]
882	873	876	880	➢ B-O stretching vib. in BO_4 unit ➢ Stretching vib. of VO_5	[59]
939	933	931	930	➢ B-O stretching vibration in BO_4 unit ➢ Stretching vib. of VO_2 in VO_4 unit	[59]
1042	1046	1052	1055	Vibration belonging to tetrahedral BO_4 unit	[61]
1110	1114	1104	1103	B-O vibration in penta- and di- borate groups	[59]
1222	1223	1231	1229	B-O vibration in meta- and ortho- borate groups	[59]
1313	1287	1297	1296	B-O vibration in boroxol ring	[58]
1365	1355	1356	1356	➢ B-O-B connection vibration ➢ Zn-O-B connection vibration	[10] [59]
1421	1433	1435	1432	NBO B-O- stretching vibration in BO_3 unit	[62]

In the third region, it was observed that bands belonging to boroxol ring and BO_3 structure of boron was prominently found; nevertheless, bands belonging to B-O-B and Zn-O-B vibrations

were also present. Bands within the range of 1287-1365 cm^{-1} belong to B-O in the boroxol ring, bands in the 1421-1435 cm^{-1} regions belong to B-O- vibrations found in the BO_3 unit having non-bridging oxygen (NBO). Although the band around 1355 cm^{-1} is known to belong to B-O-B connection vibration, it was reported in some studies that it corresponded to Zn-B-O connection vibration in similar structures.

3.4. Optical properties

Transmittance spectra obtained with scanning 1.5 cm piece of the surface belonging to the synthesized glassed are given in Fig. 6 and transmittance and absorption spectra obtained from a single point of the samples are given in Fig. 7. Transmittance spectra obtained from surface scanning spectrophotometer were obtained from 16 different regions with intervals of 1 mm each. When compared with the transmittance curves found in these spectra, which were used to determine the uniformity of the samples, transmittance was seen to be similar in spectrum of every sample. This proves that a significant aggregation or bubble was not present and the samples had uniform distribution.

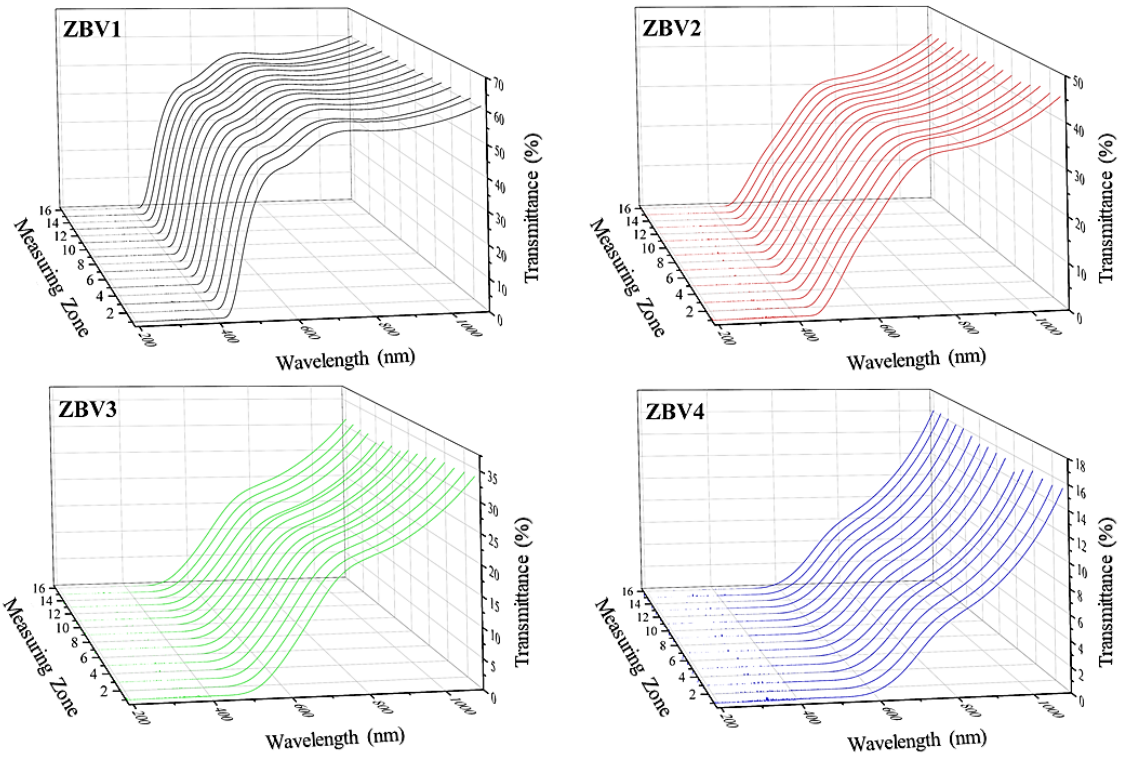

Figure 6: Transmittance spectra obtained by scanning approximately 1.5 cm regions of the samples

In Fig. 7, in which data obtained from a single point were evaluated collectively, absorption edges of spectra belonging to transmittance and absorption were observed to shift towards red (long wavelength) with increasing concentration of V_2O_5. Spectra shifted towards long

wavelength for approximately for 25 nm each. Transmittance value decreased significantly. Switching oxygen bond in the glass network and change in the number of non-bridging oxygen (NBO) in the network also changes absorption properties [54]. Shifting of the absorption edge towards long wavelength with increasing amount of V_2O_5 and also decrease in optical band gaps might be explained with this change.

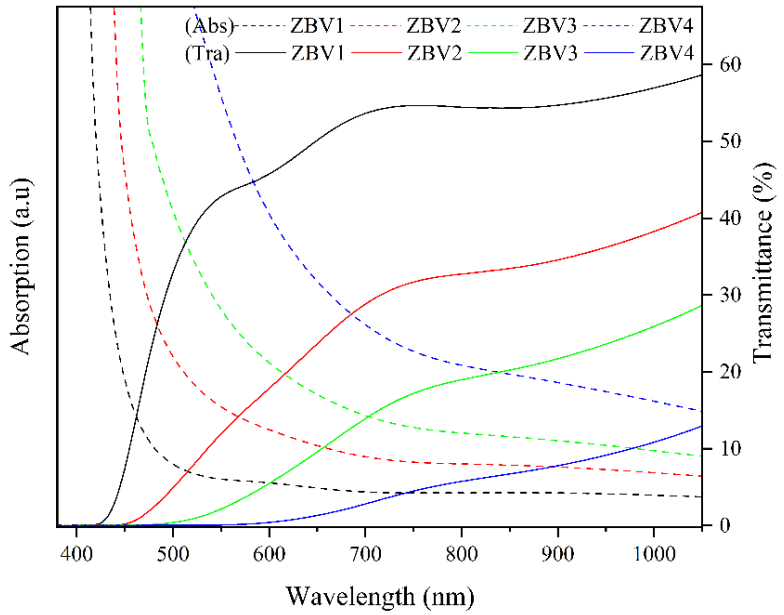

Figure 7: Absorption-transmittance spectra of ZBV samples against wavelength

Optical band gaps of synthesized glass samples were calculated by using absorption spectrum for indirect transitions. Absorption coefficient is given according to Lambert – Beer – Bouguer Law [63].

$$\alpha = 0.202\left(\frac{A}{d}\right) \tag{5}$$

Here, A is the absorbance, d is the thickness of the sample. Photon energies belonging to wavelengths corresponding to linear part of the absorption spectrum were calculated with the help of the following equation [63]:

$$E = h\upsilon \tag{6}$$

Moreover, $(\alpha h\upsilon)^{1/2} \sim h\upsilon$ graphics were plotted for indirect transitions for each sample. In these equations, α is the absorption coefficient, h is the Planck constant, υ is photon frequency and in addition, $h\upsilon$ is the photon energy.

From the value of this line passing through the linear part of this plotted Tauc curve (Fig. 8) corresponding to $(\alpha h\upsilon)^{1/2} = 0$ optical band gap belonging to the sample is found. Optical band gaps of V_2O_5 doped glasses varied between 2.55 eV and 1.24 eV. Increase in V_2O_5 regularly reduced the optical band gap.

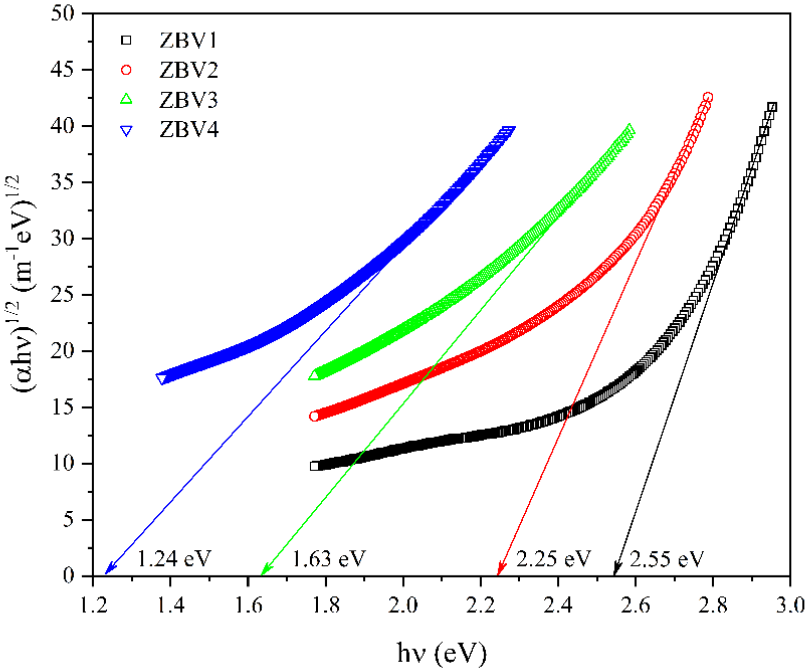

Figure 8: Tauc Plots belonging to ZBV samples

With the curve of the absorption edge in the semi-logarithmic plot (Fig. 9),

$$\Delta E = \left[\frac{d(ln\alpha)}{d(h\upsilon)}\right]^{-1} \tag{7}$$

Urbach Energies were calculated [63]. Fitting values of lines plotted from the straight part of the absorption edge were $R^2 > 0.99$. Here, ΔE is named as Urbach energy, α is absorption coefficient and $h\upsilon$ as photon energy.

A stable increase was observed in Urbach energies due to increase in V_2O_5 concentration. Urbach energy was calculated between the range of 0.246 eV and 0.630 eV. Urbach energy belonging to non-doped, pure 60% ZnO-40% B_2O_3 glass was calculated within the range of 0.17 eV [54]. This result is in line with the values that have been obtained in this study. Low Urbach energy value shows us that the structure of the synthesize glass structure is uniform and stable. Increase in V_2O_5 concentration in the glass network shows that the structure has become irregular and unstable [64].

Table 4: Optical band gap, Urbach energies and refractive indices of synthesized ZBV glasses

Sample Code	Optical band gap (eV)	Urbach energies (eV)	Refractive index
ZBV1	2.55	0.246	2.530
ZBV2	2.25	0.346	2.635
ZBV3	1.63	0.630	2.917
ZBV4	1.24	0.630	3.170

Refractive index is an important data for materials that are considered to be used in optoelectronics. Refractive indices were determined with the help of Eqn. (3) using optical band gaps data within the region corresponding to the absorption edge. Refractive indices of the samples were calculated within the range of 2.530-3.170. As it can be seen in Table 4, refractive index increased in direct proportion to increase in V_2O_5.

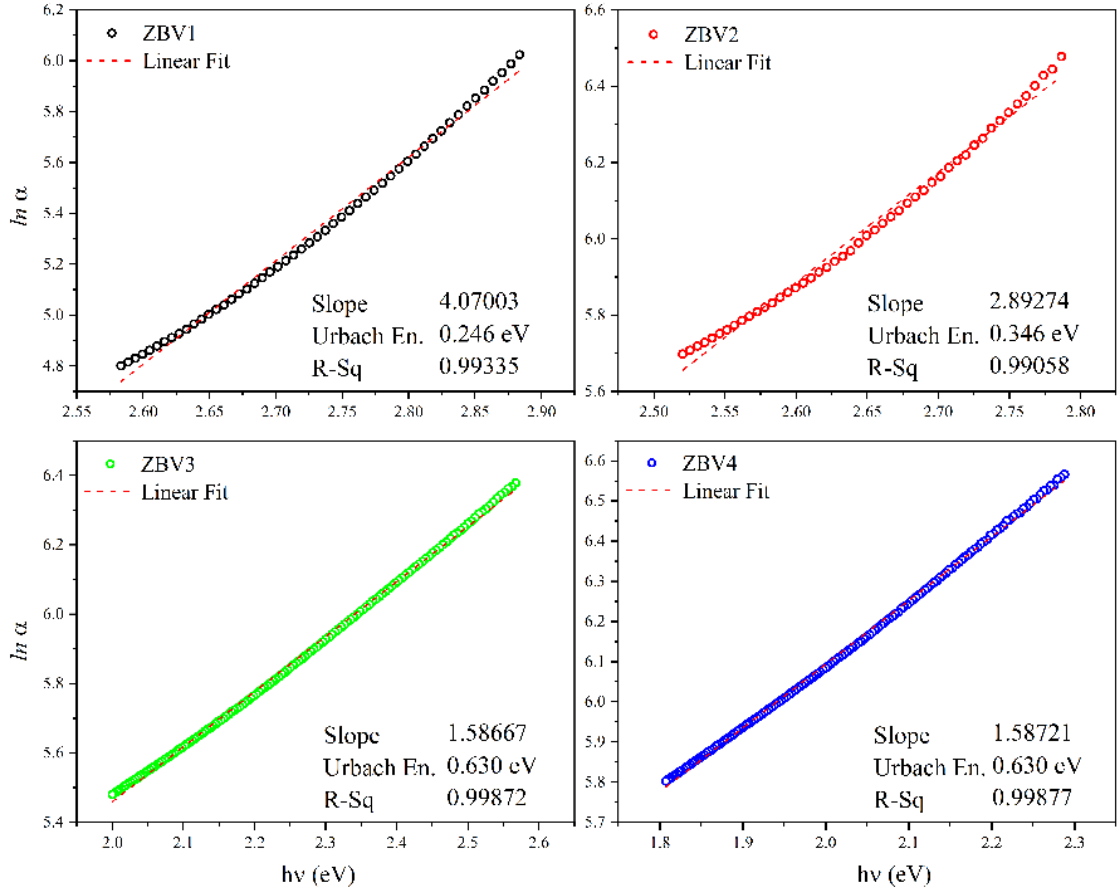

Figure 9: Urbach Energies, slopes, and R^2 fitting values of ZBV samples

4. Conclusions

Ternary zinc borate oxide glass samples doped with different ratios of V_2O_5 were synthesized successfully. Physical, structural, thermal, and optical characterization of these

synthesized samples were performed. Structural units were determined with FTIR. B_2O_3 was found to be present in the glass network in the structure of the boroxol ring, planar BO_3, tetrahedral BO_4. ZnO, acting as the organizer with its low concentration in the structures in which it is found, was determined to be present in the samples of this study in tetrahedral ZnO_4 and octahedral ZnO_6 structural units; and it was concluded that it might be present in the glass network as a glass former. Vanadium is present in the glass network with VO_4 and VO_5 structural unit. Increase in VO_5 shifted the absorption edge significantly towards the red region and correspondingly decrease optical band gap to 1.24 eV from 2.55 eV and as expected, led to increase in Urbach energy. Increase in Urbach energy proves that V_2O_5 renders the structure nonuniform and unstable. As a result of thermal characterization, V_2O_5 increase was found to decrease glass transition temperature to 531 °C from 553 °C. While density decreased with increasing amount of V_2O_5, molar volume values demonstrated increase, as well. Similar to molar volume, refractive index also increased. High refractive indices increasing to 3.170 from 2.530 showed that synthesized glasses are potential materials that could be used in optical system requiring high refractive index. These glasses, considered to find application in many fields of optoelectronics also have the property of being novel materials for solar energy systems due to their semiconducting properties.

References

[1] Kılıç, G., *Değişik bileşimli camların hazırlanması, fiziksel ve optik özelliklerinin incelenmesi*. PhD Thesis, Eskişehir Osmangazi University, Eskişehir, Turkey, 2006.

[2] Rao, R.B., Veeraiah, N., *Study on some physical properties of Li_2O-MO-B_2O_3: V_2O_5 glasses*, Physica B: Condensed Matter, 348, 256-271, 2004.

[3] El-Batal, H.A.R., Ezz-El-Din, F.M., *Interaction of γ-rays with Some Alkali Alkaline Earth Borate Glasses Containing Chromium*, Journal of the American Ceramic Society, 76, 523, 1993.

[4] Abdel-Baki, M., El-Diasty, F., *Role of oxygen on the optical properties of borate glass doped with ZnO*, Journal of Solid State Chemistry, 184, 2762-2769, 2011.

[5] El-Falaky, G.E., Gaafar, M.S., Abd El-Aal, N.S., *Ultrasonic relaxation in Zinc-Borate glasses*, Current Applied Physics, 12, 589-596, 2012.

[6] Sumalatha, B., Omkaram, I., Rao, T.R., Raju, Ch. L., *Alkaline earth zinc borate glasses doped with Cu^{2+} ions studied by EPR, optical and IR techniques*, Journal of Non-Crystalline Solids, 357, 3143-3152, 2011.

[7] Kumar, R.R., Bhatnagar, A.K., Rao, J.L., *EPR of vanadyl ions in alkali lead borate glasses*, Materials Letters, 57, 178-182, 2002.

[8] Rada, M., Rada, S., Pascuta, P., Culea, E., *Structural properties of molybdenum-lead-borate glasses*, Spectrochimica Acta A, 77, 832-837, 2010.

[9] Rao, T.R., Reddy, Ch.V., Krishna, Ch.R., Thampy, U.S.U., Raju, R.R., Rao, S., Ravikumar, R.V.S.S.N., *Correlation between physical and structural properties of Co^{2+} doped mixed alkali zinc borate glasses*, Journal of Non-Crystalline Solids, 357, 3373-3380, 2011.

[10] Singh, G.P., Kaur, S., Kaur, P., Kumar, S., Singh, D.P., *Structural and optical properties of WO_3-ZnO-PbO-B_2O_3 glasses*, Physica B: Condensed Matter, 406, 1890-1893, 2011.

[11] He, F., Wang, J., Deng, D., *Effect of Bi_2O_3 on structure and wetting studies of Bi_2O_3-ZnO-B_2O_3 glasses*, Journal of Alloys and Compounds, 509, 6332-6336, 2011.

[12] Lian, Z., Wang, J., Lv, Y., Wang, S., *The reduction of Eu^{3+} to Eu^{2+} in air and luminescence properties of Eu^{2+} activated ZnO-B_2O_3-P_2O_5 glasses*, Journal of Alloys and Compounds, 430, 257-261, 2007.

[13] Saritha, D., Markandeya, Y., Salagram, M., Vithal, M., *Effect of Bi_2O_3 on physical, optical and structural studies of ZnO-Bi_2O_3-B_2O_3 glasses*, Journal of Non-Crystalline Solids, 354, 5573-5579, 2008.

[14] Li, S., Chen, P., Li, Y., *Structural and physical properties in the system ZnO-B_2O_3-P_2O_5-R_nO_m*, Physica B: Condensed Matter, 405, 4845-4850, 2010.

[15] Aleksandrov, L., Komatsu, Iordanova, R., Dimitriev, Y., *Structure study of MoO_3-ZnO-B_2O_3 glasses by Raman spectroscopy and formation of $ZnMoO_4$ nanocrystals*, Optical Materials, 33, 839-845, 2011.

[16] Lakshminarayana, G., Buddhudu, S., *Spectral analysis of Sm^{3+} and Dy^{3+}: B_2O_3-ZnO-PbO glasses*, Physica B: Condensed Matter, 373, 100-106, 2006.

[17] Singh, H., Singh, K., Gerward, L., Singh, K., *ZnO-PbO-B_2O_3 glasses as gamma-ray shielding materials*, Nuclear Instruments and Methods in Physics Research B, 207, 257-262, 2003.

[18] Thulasiramudu, A., Buddhudu, S., *Optical characterization of Sm^{3+} and Dy^{3+}: ZnO-PbO- B_2O_3 glasses*, Spectrochimica Acta A, 67, 802-807, 2007.

[19] Mosner, P., Vosejpkova, K., Koudelka, L., Montagne, L., Revel, B., *Structure and properties of ZnO-B_2O_3-P_2O_5-TeO_2 glasses*, Materials Chemistry and Physics, 124, 732-737, 2010.

[20] Wu, J., Xie, C., Hu, J., Zeng, D., Wang, A., *Microstructure and electrical characteristics of ZnO-B_2O_3-PbO-V_2O_5-MnO_2 ceramics prepared from ZnO nanopowders*, Journal of the European Ceramic Society, 24, 3635-3641, 2004.

[21] Bale, S., Rahman. S., *Electrical conductivity studies of Bi_2O_3-Li_2O-ZnO-B_2O_3 glasses*, Materials Research Bulletin, 47, 1153-1157, 2012.

[22] Ji, L.N., Li, J.B., Liang, J.K., Sun, B.J., Liu, Y.H., *Phase relations and flux research for ZnO crystal growth in the ZnO-B_2O_3-P_2O_5 system*, Journal of Alloys and Compounds, 459, 481-486, 2008.

[23] Hu, Y., Wei, D., Fu, Q., Zhao, J., Zhou, D., *Preparation and microwave dielectric properties of $3ZnO{\cdot}B_2O_3$ ceramics with low sintering temperature*, Journal of the European Ceramic Society, 32, 521-524, 2012.

[24] Raju, G.N., Reddy, M.S., Sudhakar, K.S.V., *Spectroscopic properties of copper ions in ZnO-ZnF_2-B_2O_3 glasses*, Optical Materials, 29, 1467-1474, 2007.

[25] Kim, D.N., Lee, J.Y., Huh, J.S., *Thermal and electrical properties of BaO-B_2O_3-ZnO glasses*, Journal of Non-Crystalline Solids, 306, 70-75, 2002.

[26] Masuda, H., Kimura, R., Sakamoto, N., *Properties and Structure of Glasses in the System BaO-B_2O_3-ZnO*, Journal of the Japan Institute of Metals, 63, 284, 1999.

[27] Kundu, V., Dhiman, R.L., Goyal, D.R., Maan, A.S., *Physical and electrical properties of semiconducting Fe_2O_3-V_2O_5-B_2O_3 glasses*, Journal of Optoelectronics and Advanced Materials, 2(7), 428-432, 2008.

[28] Saritha, D., Markandeya, Y., Salagram, M., Vithal, M., *Effect of Bi_2O_3 on physical, optical and structural studies of ZnO-Bi_2O_3-B_2O_3 glasses*, Journal of Non-Crystalline Solids, 354, 5573-5579, 2008.

[29] Toderaş, M., Filip, S., Ardelean, I., *Structural study of the Fe_2O_3-B_2O_3-BaO glass system by FTIR spectroscopy*, Journal of Optoelectronics and Advanced Materials, 3(8), 1121-1123, 2006.

[30] Schwarz, J., Ticha, H., *Some optical properties of BaO-PbO-B_2O_3 glasses,* Journal of Optoelectronics and Advanced Materials, 5(1), 69-74, 2003.

[31] Nagaraja, N., Sankarappa, T., Kumar, M.P., *Electrical conductivity studies in single and mixed alkali doped cobalt–borate glasses*, Journal of Non-Crystalline Solids, 354, 1503-1508, 2008.

[32] Chaudhry, M.A., Altaf, M., *Optical absorption studies of sodium cadmium phosphate glasses*, Materials Letters, 34, 213-216, 1998.

[33] Al-Hajry, A., Al-Shahran, A., El-Desoky, M.M., *Structural and other physical properties of barium vanadate glasses*, Materials Chemistry and Physics, 95, 300-306, 2006.

[34] Sharma, B.I., Robi, P.S., Srinivasan, A., *Microhardness of ternary vanadium pentoxide glasses*, Materials Letters, 57, 3504-3507, 2003.

[35] Ghosh, A., Bhattacharya, S., Ghosh, A., *Optical and other structural properties of some zinc vanadate semiconducting glasses*, Journal of Alloys and Compounds, 490, 480-483, 2010.

[36] Tawaki, D.M., Adlan, M.J.B., Abdullah, M.J., *DC electrical conductivity of semiconducting cobalt–phosphate glasses*, Journal of Non-Crystalline Solids, 357, 2152-2155, 2011.

[37] Mandal, S., Ghosh, A., *Electrical properties of lead vanadate glasses*, Physical Review B: Condensed Matter and Materials Physics, 49, 3131, 1994.

[38] Rao, R.B., Veeraiah, N., *Study on some physical properties of Li_2O-MO-B_2O_3: V_2O_5 glasses*, Physica B: Condensed Matter, 348, 256-271, 2004.

[39] Mott, N.F., *Conduction in glasses containing transition metal ions*, Journal of Non-Crystalline Solids, 1, 1-17, 1968.

[40] Austin, G., Mott, N.F., *Polarons in crystalline and non-crystalline materials*, Advances in Physics, 18, 41-102, 1969.

[41] Sen, S., Ghosh, A., *Structure and other physical properties of magnesium vanadate glasses*, Journal of Non-Crystalline Solids, 258, 29-33, 1999.

[42] Moustafa, Y.M., El-Damrawi, G., Meikhail, M.S., *Effect of Vanadium oxide on the structure and properties of lithium borate glasses*, Mans Science Bulletin C, 20, 71, 1993.

[43] El-Damrawi, G., Moustafa, Y.M., Meikhail, M.S., *Phase separation and NMR studies on sodium boro-silicate glasses containing V_2O_5*, Mans Science Bulletin C, 20, 83, 1993.

[44] Singh, K., Ratnam, J.S., *Electrical conductivity of the Li_2O-B_2O_3 system with V_2O_5*, Solid State Ionics, 31, 221-226, 1988.

[45] Mekki, A., Khattak, G.D., Holland, D., Chinkhota, M., Wenger, L.E., *Structure and magnetic properties of vanadium–sodium silicate glasses*, Journal of Non-Crystalline Solids, 318, 193-201, 2003.

[46] Ebendorff-Heidepriem, H., Riziotis, C., Taylor, E.R., *Novel photosensitive glasses*, Glass Science and Technology, 75, 54, 2002.

[47] Ghosh, A., *Transport properties of vanadium germanate glassy semiconductors*, Physical Review B: Condensed Matter and Materials Physics, 42, 5665, 1990.

[48] Sudarsan, V., Kulshreshtha, S.K., *Study of structural aspects of V_2O_5–P_2O_5–B_2O_3 glasses*, Journal of Non-Crystalline Solids, 258, 20-28, 1999.

[49] Ezz-Eldin, F.M., *Radiation effects on some physical and thermal properties of V_2O_5–P_2O_5 glasses,* Nuclear Instruments and Methods in Physics Research B, 159, 166-175, 1999.

[50] Sindhu, S., Sanghi, S., Agarwal, A., Kishore, N., Seth, V.P., *Effect of V_2O_5 on structure and electrical properties of zinc borate glasses*, Journal of Alloys and Compounds, 428, 206-213, 2007.

[51] Li, H., Lin, H., Chen, W., Luo, L., *IR and Raman investigation on the structure of (100-x)[0.33B_2O_3–0.67ZnO]–xV_2O_5 glasses*, Journal of Non-Crystalline Solids, 352, 3069-3073, 2006.

[52] Elkhoshkhany, N., El-Mallawany, R., Syala, E., *Mechanical and thermal properties of TeO_2–Bi_2O_3–V_2O_5–Na_2O–TiO_2 glass system*, Ceramics International, 42(16), 19218–19224, 2016.

[53] Dimitrov, V., Sakka, S., *Linear and nonlinear optical properties of simple oxides. II*, Journal of Applied Physics, 79, 1741-1745, 1996.

[54] Altaf, M., Chaudhry, M.A., Zahid, M., *Study of optical band gap of zinc-borate glasses*, Journal of Research (Science), 14(2), 253-259, 2003.

[55] Kaur, A., Khanna, A., Sathe, V.G., Gonzalez, F., Ortiz, B., *Optical, thermal, and structural properties of Nb_2O_5-TeO_2 and WO_3-TeO_2 glasses*, Phase Transitions, 86(6), 598-619, 2013.

[56] Mohamed, N.B., Yahya, A.K., Deni, M.S.M., Mohamed, S.N., Halimah, M.K., Sidek, H.A.A., *Effects of concurrent TeO_2 reduction and ZnO addition on elastic and structural properties of (90−x)TeO_2–10Nb_2O_5–(x)ZnO glass*, Journal of Non-Crystalline Solids, 356, 1626–1630, 2010.

[57] Laila, S., Supardan, S.N., Yahya, A.K., *Effect of ZnO addition and concurrent reduction of V_2O_5 on network formation and elastic properties of lead vanadate (55−x)V_2O_5–45PbO–(x)ZnO glass system,* Journal of Non-Crystalline Solids, 367, 14–22, 2013.

[58] Pascuta, P., Vladescu, A., Borodi, G., Culea, E., Tetean, R., *Structural and magnetic properties of zinc ferrite incorporated in amorphous matrix*, Ceramics International, 37, 3343–3349, 2011.

[59] Arora, S., Kundu, V., Goyal, D.R., Maan, A.S., *Effect of stepwise replacement of LiF by ZnO on structural and optical properties of LiF. B_2O_3 glasses*, Turkish Journal of Physics, 37, 229–236, 2013.

[60] Agarwal, A., Sheoran, A., Sanghi, S., Bhatnagar, V., Gupta, S.K., Arora, M., *Structural investigation and electron paramagnetic resonance of vanadyl doped alkali niobium borate glasses*, Spectrochimica Acta A, 75, 964–969, 2010.

[61] Jiao, Q., Yu, X., Xu, X., Zhou, D., Qiu, J., *Relationship between Eu^{3+} reduction and glass polymeric structure in Al_2O_3-modified borate glasses under air atmosphere*, Journal of Solid State Chemistry, 202, 65–69, 2013.

[62] Razali, W.A.W., Azman, K., Hashim, S., Alajerami, Y.S.M., Syamsyir, S.A., Mardhiah, A., Ridzwan, M.H.J., *Physical, Structural, and Luminescence Studies of Nd^{3+} Doped MgO–ZnO Borate Glass*, Optics and Spectroscopy, 115, 701–707, 2013.

[63] Kilic, G., Issever, U.G., Ilik, E., *Characterization of Er^{3+} doped ZnTeTa semiconducting oxide glass*, Journal of Materials Science: Materials in Electronics, 30(9), 8920-8930, 2019.

[64] Issever, U.G., Kilic, G., Peker, M., Ünaldi, T., Aybek, A.S., *Effect of low ratio V^{5+} doping on structural and optical properties of borotellurite semiconducting oxide glasses*, Journal of Materials Science: Materials in Electronics, 30 (16), 15156-15167, 2019.