Effect of NiO and Light Intensity on Dielectric Constant of SiO_2-B_2O_3-Bi_2O_3-Na_2CO_3 Glass Based on Silica Gel of Natural Sands

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Abstract. The use of silica in various fields is significantly increasing. One common application is silica based functional glass which has naturally show specific dielectric, optical, and magnetic properties. Many studies have been performing to explore the influence of dopant, composition, and other processing parameters as well as employing various characterization. In the previous work, we report the use of silica from silica sands. To reduce the melting temperature, we used silica sol-gel beside the utilization of some oxides such as B_2O_3, Na_2CO_3, and Bi_3O_3. We also used NiO as dopant explore the glass properties. We have prepared a series of sample with the composition of $50SiO_2$-$25B_2O_3$-(6.5-x) $Bi_3O_{3-18.5}$ Na_2CO_3-xNiO (x = 0, 1, 2, 3 and 4 wt%). After weighting process, the composition was blended, then heated to 450 ^{o}C for 120 minutes and then raised at 950 ^{o}C for 60 minutes in the crucible. Then samples of glass separated from the crucible and in the characterization of the structure using the DTA, XRD, SEM-EDAX and FTIR and measuring dielectric constant using a capacitance meter. The increase of NiO dopant resulted in increasing the dielectric constant of glass. On the other hand, the dielectric constant gradually decreases with the increase of light intensity. One can be noted that the applied intensity give rise to the step-like decrease of the dielectric constant. Whereas, the increasing magnetic field indicate the increase of dielectric constant.

Keywords: NiO, light intensity, dielectric constant, borosilicate glass, natural sand

1. Introduction
One of the abundant natural resources of Indonesia is silica. Silica can be obtained from many resources, such as silica sands, pyrophyllite, bauxite, and from many parts of plants. The content of silica of natural sand of Tuban district east java is approximately 50.1% [1]. The huge amount of silica source needs to be developed for many kinds of application. The use of silica for daily life is

becoming diverse. The common use of silica is for producing architectural glass. Recently, glass can be fabricated to more functional materials. Some examples of modern silica application are smart glass, solar glass, electro-optic devices, optic-fibers, absorbing x-rays [2] and even absorbing gamma rays which have a very high energy [3].Silica glass can fabricate by solely use of silica without any material. But it is not practical due to very high temperatures, i.e., 1760-1870 $^{\circ}$C for synthesis. One way to lower the melting point of silica is the modifying to a smaller size and feed the raw silica as an amorphous form. To fit the desired silica, the sol-gel method can be implemented. In the other hand, the addition of another oxide can also give the lower melting point of silica.

The addition of metal on the structure of the glass will affect the optical, electrical and magnetic properties [4]. Silica glass dipped in a solution of $Ni(NO_2)_3.6H_2O$ (0.5 M) with a relatively high heat treatment between 760-850 K produces a rise the field polarization of the glass up to of 500 V/cm [5]. NiO can also be said to have good optical properties, in the form of the film has an energy of optical band gap of 3.58 eV [6]. Ni is expected to be a good candidate fo absorbing of electromagnetic waves properties reaching at 12-18 GHz [7]. Nickel also has potential to provide optical properties, electrical, and magnetic of glass materials.

So far in Indonesia has not been found the study of glass with multi-functional properties, namely optical glass that has the properties, dielectric and magnetic, comprehensively. Hence in the research of silica glass added NiO show to provide high optical, dielectric and magnetic properties. The addition oxide such as B2O3 [8]. add optical properties of glass, B_2O_3 [9], and Na_2CO_3 are mostly to reduce the melting point as well as to improve the optical or dielectric properties of the glass.

2. Experimental Methods

2.1 Materials and Instrumentation
The instrument is the balance of Digital HF-3000 (0.019), Furnace Brother XD-1700M, Hot Plate, Beaker, Burret, Mortar, and Pestle. The materials of synthesis SiO_2 are HCl 32%, 5M HCl, and 5M NaOH. The raw material of glass based on the natural sand beach of SiO_2 Bancar, B_2O_3 Merck 100169, B2O3 Merck 101862, and Na_2CO_3 NiO Merck 106723.

2.2 Preparation of SiO_2
Silica sand from the beach of Tuban Bancar washed six times using aquades, then crushed up to 100 mesh. It already soaked with 32% HCl for 12 hours and rinsed using aquades up to a pH 7 hence dried.

2.3 Sol-Gel Method
Sixty grams of silica sand and 1920 mL NaOH [5 M] was stirred by magnetic stirrer using 600 rpm at 140 °C until no the moisture content. Added water as much as 1920 mL stirring for 3 hours then keep under ambient temperature. The filtrate was separated by decantation, then followed by stirring using a magnetic stirrer at 600 rpm while titrated up to 5M HCl that is showing pH 7. The gel was formed then dried for 24 hours at 125 °C. The obtained sample then was characterized by using XRF to obtain the purity of silica.

2.4 Synthesis of Glass 50SiO_2-25B_2O_3-(6.5-x)B2O3-18.5Na_2CO_3-xNiO
The glass of $50SiO_2-25B_2O_3-(6.5-x)$ $B_2O_3-18.5$ $Na_2CO_{3-x}NiO$ with x = 0, 1, 2, 3, and 4 wt% were mixed until homogeneous and followed by heated using Furnace Brother XD-1700M at 450 °C for 2 hours and rinsed again up to 950 °C for 1 hour in a ceramics crucible. Then cooled to room temperature. The sample was separated from the crucible and characterized by DTA, XRD, SEM-EDX and capacitance meter.

3. Result and Discussion

3.1 Silica Sol-Gel

The elemental composition of silica powder was characterized by XRF ass shown in Table 1. It is showed the composition of silica sand before and after via sol-gel process. The purity of silica increase from 88.1% to 95.5%. The results of the sol-gel method are able to reduce some of the impurities contained in the silica sand, such as K, Ca, Ti and Fe. These elements are remain in the sol-gel because the element or in the form of its compounds are insoluble completely with NaOH and HCl.

Table 1. Elemental composition of silica

Element	before Sol-gel (%)	after Sol-gel (%)
Si	88.1	95.5
K	4.36	0.00
Ca	2.76	1.2
Ti	1.37	0.44
Fe	2.97	1.92

3.2 The Influence NiO on Structure of SiO_2-B_2O_3-$B2O3$-Na_2CO_3 Glass

In this study, the structure of the $50SiO_2$-$25B_2O_3$-$(6.5-x)$ Bi_3O_3-18.5 $Na_2CO_{3-x}NiO$ glass have been showed by DTA, and XRD diffraction pattern, and FTIR. Previously the samples of glass have been characterized by SEM-EDX to obtain the composition contained therein. Table 2 presents the composition of the prepared glass from EDX analysis.

3.2.1 DTA Pattern of $50SiO_2$- $25B_2O_3$- $(6.5-x)Bi_3O_3$- $18.5Na_2CO_3$- $xNiO$ Glass.

The typical DTA pattern of the $50SiO_2$ -$25B_2O_3$-$(6.5-x)$ $B2O3$-18.5 $Na_2CO_{3-x}NiO$ glass is shown in Figure 1. The pattern of DTA can be seen from the range of temperature between 0-1000 °C. Changing patterns of heat flow and baseline. This alteration is showed by the transition temperature of glass [2].
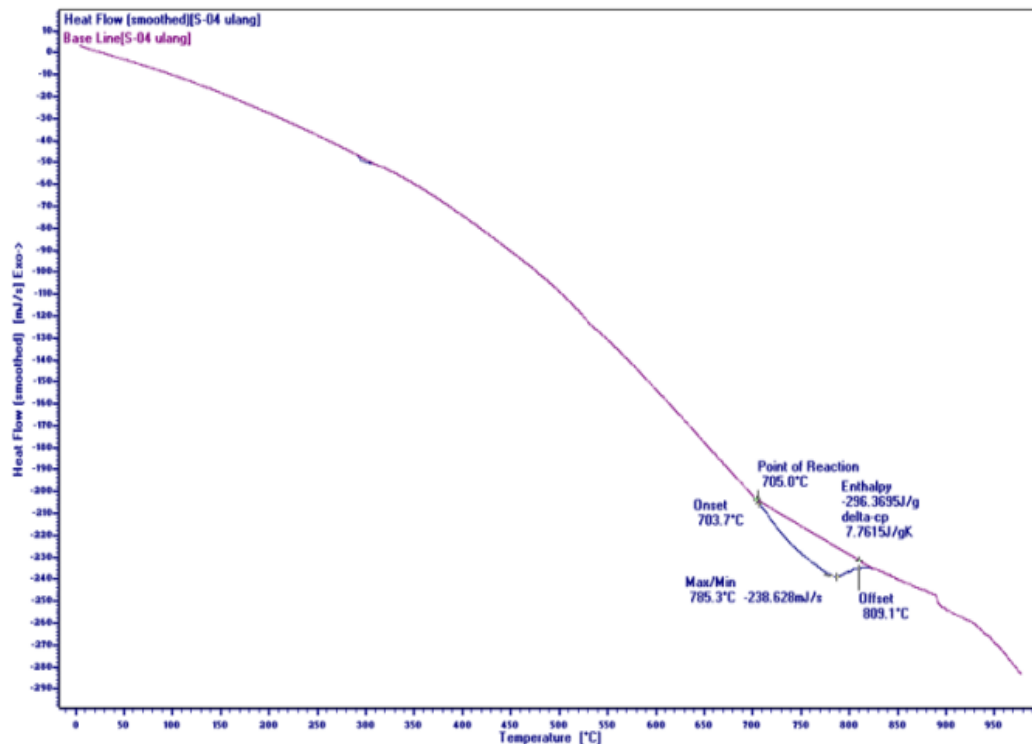
Figure 1. The Pattern DTA of $50SiO_2$- $25B_2O_3$- $(6.5-x)Bi_3O_3$- $18.5Na_2CO_3$- xNiO x=3 wt%
Glass

It is obtained that occurrence of an endothermic process is at 705-809.1 ^{o}C. This temperature is also indicated the onset of melting B_2O_3 and Na_2CO_3 with a maximum at 785.3 ^{o}C.

3.2.2 Diffraction Patterns of Glass. The Diffraction patterns of $50SiO_2$-$25B_2O_3$-$(6.5-x)$ Bi_3O_3-18.5 Na_2CO_{3-x}NiO Glass with x = 0, 1, 2, 3, 4 wt% which has normalized shown in Figure 2.
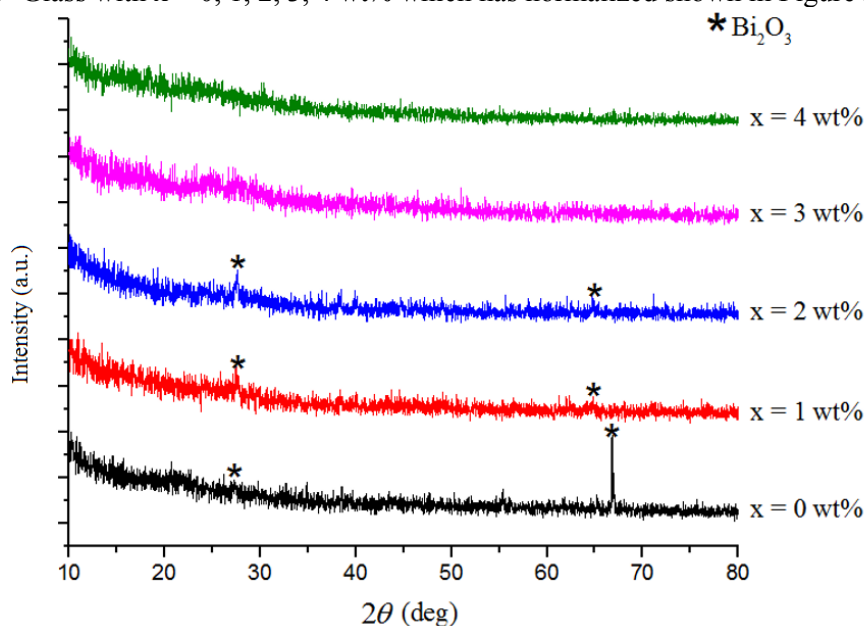
Figure 2. Diffraction Patterns of $50SiO_2$- $25B_2O_3$- $(6.5-x)Bi_3O_3$- $18.5Na_2CO_3$- xNiO
Glass with x = 0, 1, 2, 3, 4 wt%

It looks that the samples are amorphous. For sample with x = 0 wt%, x = 1 wt%, and x = 2 wt%, there is a weak peak which indicates a few crystalline of B_2O_3phase. The higher of NiO induced in the sample, the glassy phase tend to higher purity. Samples with higher content of NiO provide the homogeneity of the compositional diffusion to maintain in forming an amorphous phase. It looks that increase of NiO reduce the crystallinity of $50SiO_2$-$25B_2O_3$-$(6.5-x)$ Bi_3O_3-6, $5Na_2CO_{3-x}$NiO glass. These conform with the SEM results.

Table 2. Composition of $50SiO_2$- $25B_2O_3$- $(6.5-x)Bi_3O_3$- $18.5Na_2CO_3$- xNiO Glass

Element	Composition (at%)					Element	EDX Result (at%)				
	S0	**S1**	**S2**	**S3**	**S4**		**S0**	**S1**	**S2**	**S3**	**S4**
SiO₂	60.34	60.34	60.34	60.34	60.34	**Si**	33.61	21.20	24.13	28.34	25.25
B₂O₃	26.01	26.01	26.01	26.01	26.01	**B**	-	-	-	-	-
B2O3	1.01	0.85	0.69	0.53	0.38	**Bi**	01.15	00.31	00.29	00.26	00.14
Na₂CO₃	12.64	12.64	12.64	12.64	12.64	**Na**	14.27	16.32	16.40	15.02	15.13
NiO	0.00	0.96	1.91	2.84	3.76	**Ni**	00.00	00.37	00.80	1.30	01.41
						O	56.92	61.79	58.38	55.09	58.07

3.2.3 Morphology of 50SiO$_2$-25B$_2$O$_3$-(6.5-x)B2O3-18.5Na$_2$CO$_{3-x}$NiO Glass by SEM. Based on morphology of 50SiO$_2$-25B$_2$O$_3$-(6.5-x)B$_2$O$_3$-18.5Na$_2$CO$_{3-x}$NiO glass which can be seen in Figure 3.
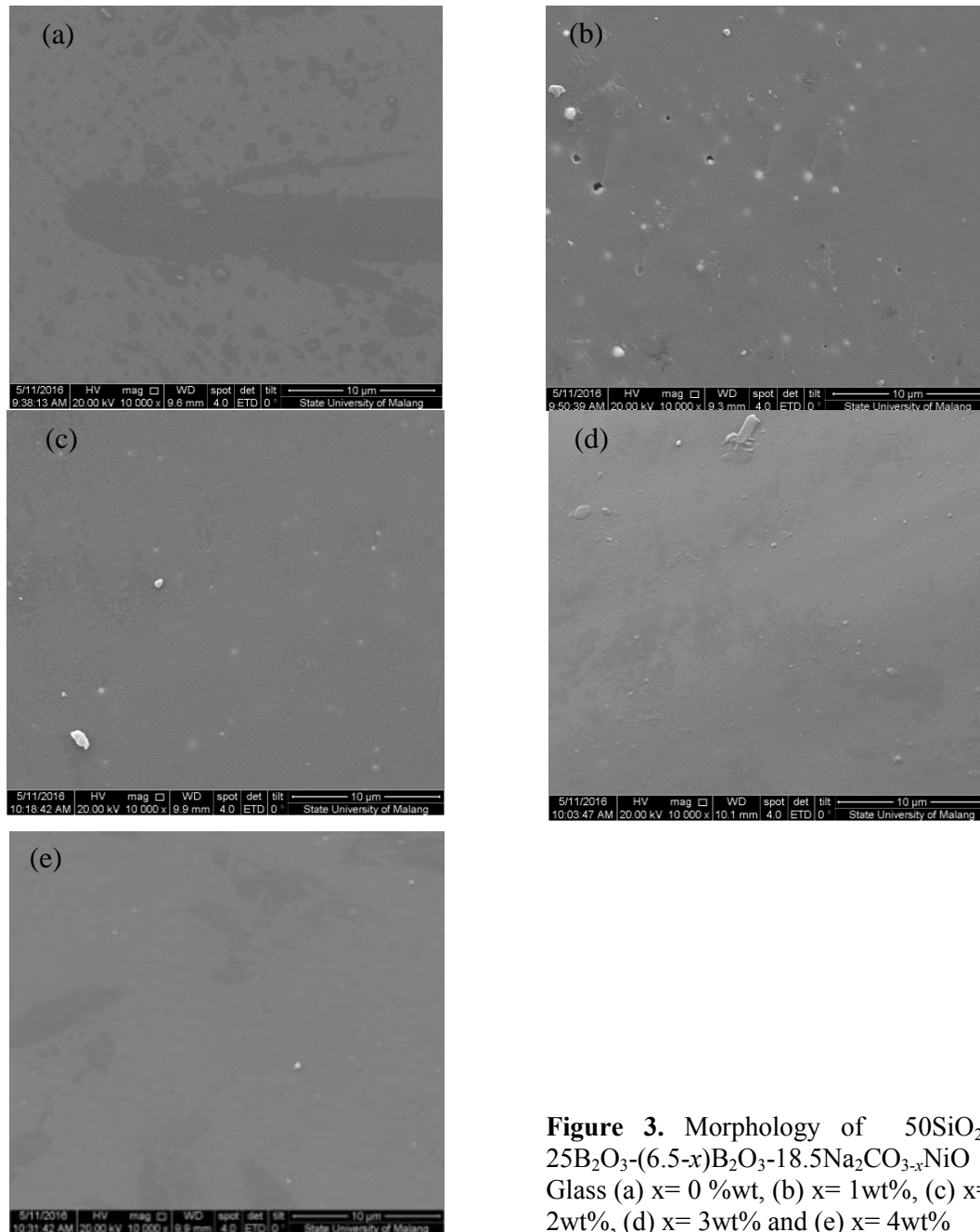
Figure 3. Morphology of 50SiO$_2$-25B$_2$O$_3$-(6.5-x)B$_2$O$_3$-18.5Na$_2$CO$_{3-x}$NiO Glass (a) x= 0 %wt, (b) x= 1wt%, (c) x= 2wt%, (d) x= 3wt% and (e) x= 4wt%

Figure 3 represents the morphology of 50SiO$_2$-25B$_2$O$_3$-(6.5-x) -18, 5Na$_2$CO$_3$-B$_2$O$_3$ xNiO glass.

The small white spots indicate a presence of B$_2$O$_3$ which is also revealed the existing of B$_2$O$_3$ phase from XRD histogram. It looks that the surface of the sample is relatively homogeneous, with increasing NiO doping give rise to reduce the white spots and porosity.

3.2.4 The Binding Vibration of 50SiO₂-25B₂O₃-(6.5-x)B₂O₃-18.5Na₂CO₃-xNiO Glass by FTIR. Bond vibration on $50SiO_2$-$25B_2O_3$-(6.5-x) B_2O_3-18.5 Na_2CO_3-xNiO glass at sample 0-4 can be seen in Figure 4. Bonding of silica group looks at wavenumbers between 950 – 1200 cm⁻¹ [10][11]. On the wave-number 950-1000 cm⁻¹ shows the variation of the antisymmetric stretching vibration on bonds from the bonds of O-Si-O tetrahedral SiO_4 units. It also appears of the wave-numbers of 1000-1200 cm⁻¹ showing te asymmetry strain of Si-O. With the rise in the concentration of NiO there is some change of FTIR patterns. The appearance of the Valley in the 1200-900 cm⁻¹ from a sample of ten 0-4 takes part at a wavelength of 1116, 1139, 1141, 1161, and 1172 cm⁻¹. This shows that the addition of NiO, changing the structure of the network, marked with the location of the peaks are formed differently. These results is in contrast with previous research which shows that the addition of NiO did not change the structure of the functional groups of glass [12]. However, this research has been showed that the phase of NiO tended to form as crystalline, and the NiO is also bound with other oxides.
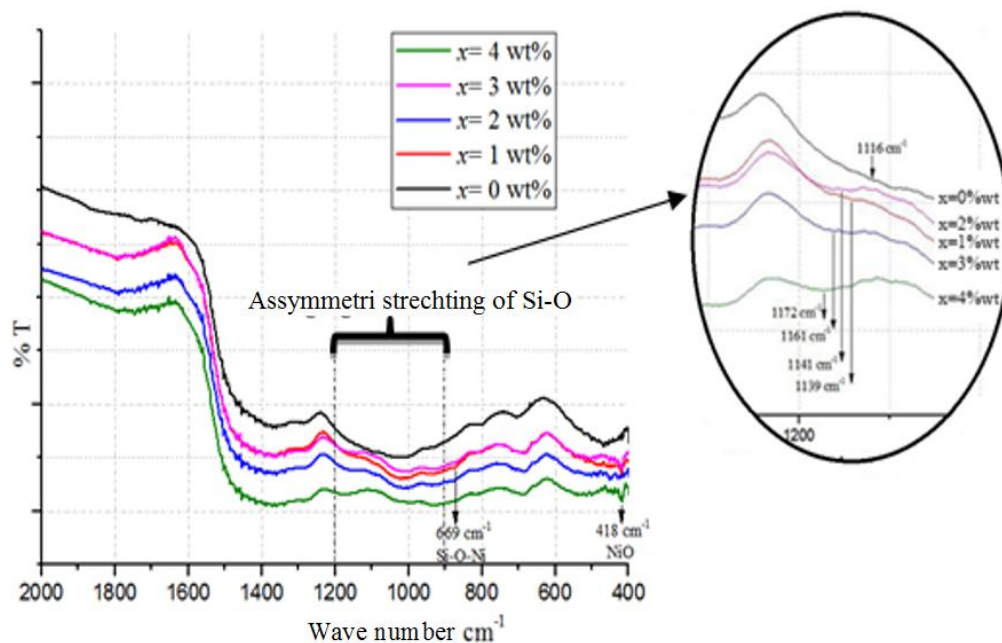

Figure 4. Vibration Peak of $50SiO_2$-$25B_2O_3$-(6.5-x)B_2O_3-18.5Na_2CO_3-xNiO Glass

Vibrational NiO bonds appear at 412, 418, 445, 449 cm⁻¹ and at 669 cm⁻¹ represent the bonds of Si-O-Ni. Based on Figure 4, some peaks have been showed the presence of Ni-O bond vibration on the wavenumber of 418 cm⁻¹. NiO is linked bonds crossed with silica [13].
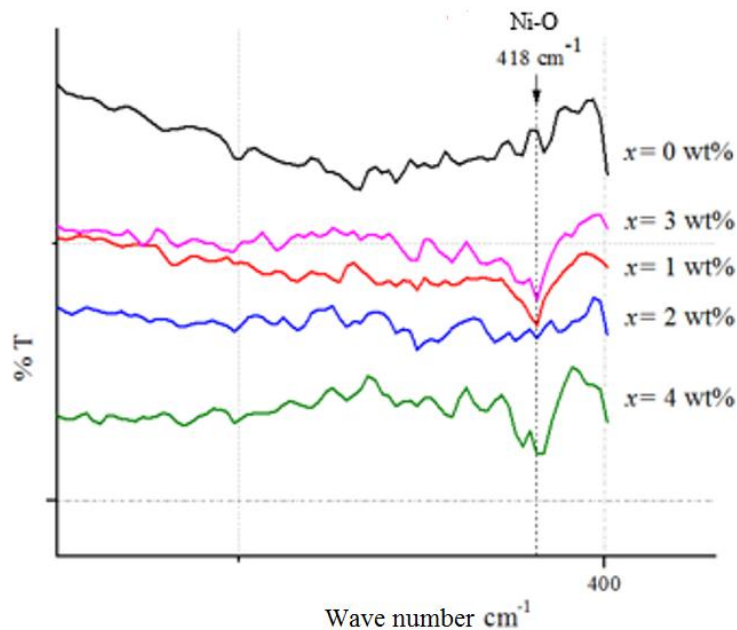
Figure 5. Binding Vibration of Bi-O-Bi on $50SiO_2$-$25B_2O_3$-$(6.5-x)B_2O_3$-$18.5Na_2CO_3$-xNiO Glass**.**

3.3 The Influence of NiO to the Dielectric of SiO_2-B_2O_3-B_2O_3-Na_2CO_3 Glass

The value of these measurements by capacitance meter is the capacitance. By using the Equation 1. knowable large dielectric constants whose results have been presented in the form of graphs in Fig 6. it shows the influence of the addition of NiO at the constant dielectric glass in dark circumstances or the intensity of zero. NiO with dielectric constants, look also increasing. The improvement of dielectric constant (ε) reached up to 12.68 x 10^3 which was calculated using the Equation (1).

$$\varepsilon_r = \frac{C.d}{\varepsilon_0.A}$$

(1)

The data were obtained from the measurement of electric capacitance (*C*) with respect to samples' surface area (*A*) and thickness (*d*). The results from the calculation for all samples show that the higher the addition of NiO, dielectric constants are also increased as depicted in Figure 6. This indicates that the Ni^{2+} ion has been modifying the glass sample. This modification cause defects in the glass chain which resulted in rising space charge polarization leading to a high dielectric constant.
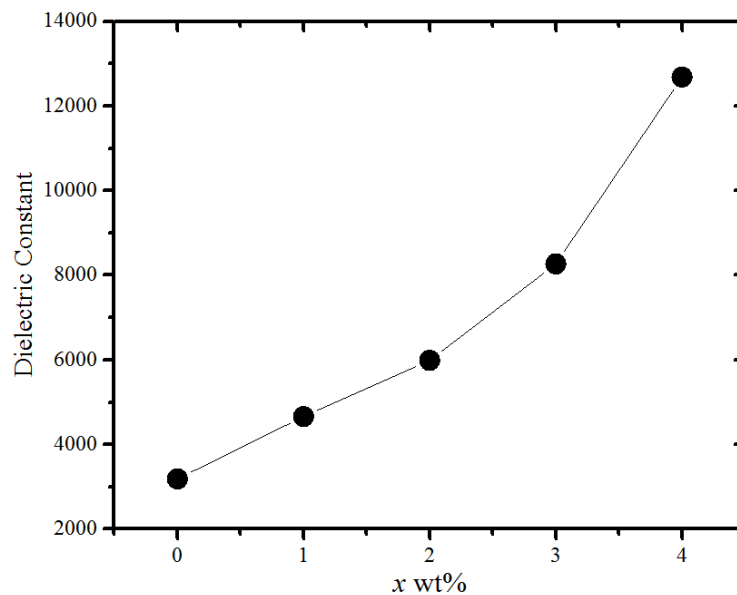
Figure 6. The influence of NiO on Dielectric Constant in the absence of Light Intensity

3.4 The Influencing intensity of light to dielectric of 50SiO₂- 25B₂O₃- (6.5-x)B₂O₃-18.5Na₂CO₃- xNiO Glass.

The influence of light intensity on the dielectric constant of $50SiO_2$-$25B_2O_3$-$(6.5-x)$ B_2O_3-18.5 Na_2CO_3-$xNiO$ glass has also been explored using a capacitance meter. Equipped with a lux meter to obtain the intensity of a light source of 100 W Philips 5d. The range of the Intensity used was from 0-2500 lux. Using Equation 1 the dielectric constant can also be obtained. The results of the dielectric constant calculation are presented in Figure 7. It can be seen from Figure 7 that for all samples are obviously showing that employing light intensity on the samples reduce the dielectric constant. This suggests the existence of an interaction between light and glass samples. The intensity of light on the sample may drive to the excitation of electrons within atoms. With the greater radius of the atom, the electron binding energy becomes weak, allowing for the electrons jump up to the excited state. The mechanism resulted in reducing the dielectric constant.
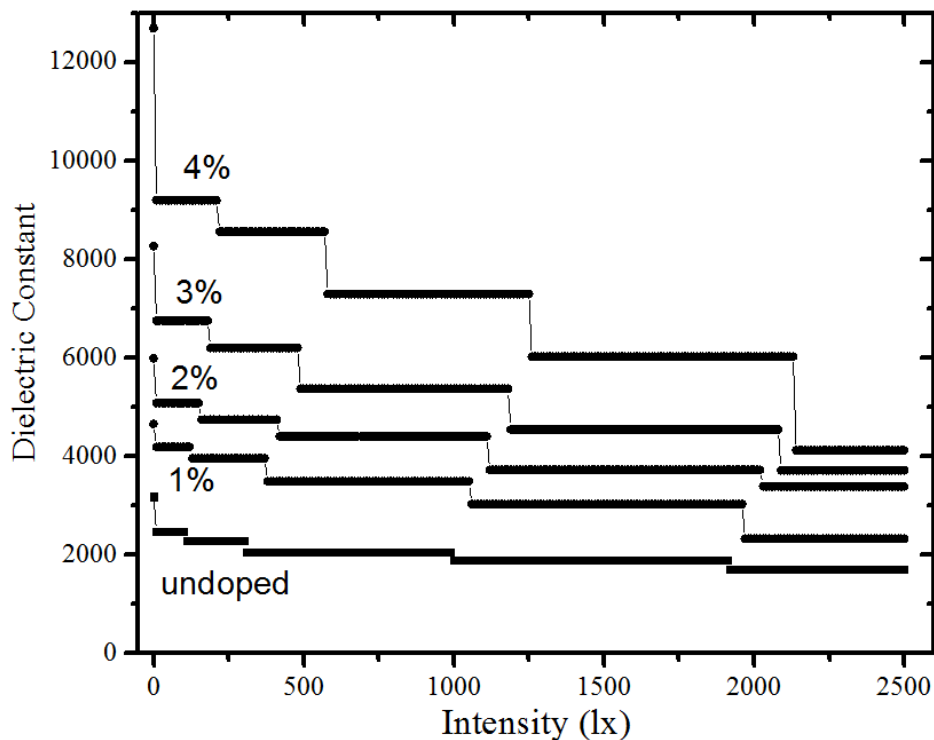
Figure 7. The influence of intensity on dielectric Constant

When we look closer in Figure 7, it is an interesting phenomenon observed. The reducing dielectric constant by the intensity of light is not a continuum. A step-like curve of the dielectric constant exists in all sample at a particular value of intensity. Following the description of excitation, the intensity of light represents the energy of photons of $E = nh\upsilon$ which is absorbed by the electrons to excite to the next outer energy levels. When this phenomenon related to the electronics polarization, the energy from the intensity of light is absorbed. The energy used for electrons to excite to occupy a higher energy level also quantized. This step-like features also shown by alumina doped orosilicate glass [14]

3.5 The Influencing magnetic field to dielectric 50SiO₂- 25B₂O₃- (6.5-x)B₂O₃-18.5Na₂CO₃- xNiO Glass

Influence of magnetic field against dielectric constant of glass 50SiO$_2$-25B$_2$O$_3$-(6.5-x) B$_2$O$_3$-18.5 Na$_2$CO$_3$-xNiO was measured using a capacitance meter. Using the same Equation 1 the dielectric constant of the glass can be obtained. Figure 8 is a graph of the results of calculation of dielectric constants. It can be seen that along with the rising of the magnetic field applied; the dielectric constant is also rising. This shows that the NiO was able to increase the magnetic field response of sample glass. On the experimental results also brings about the relationship between the external magnetic field is applied to the dielectric constant of the material with antiferromagnetic is linear [14].
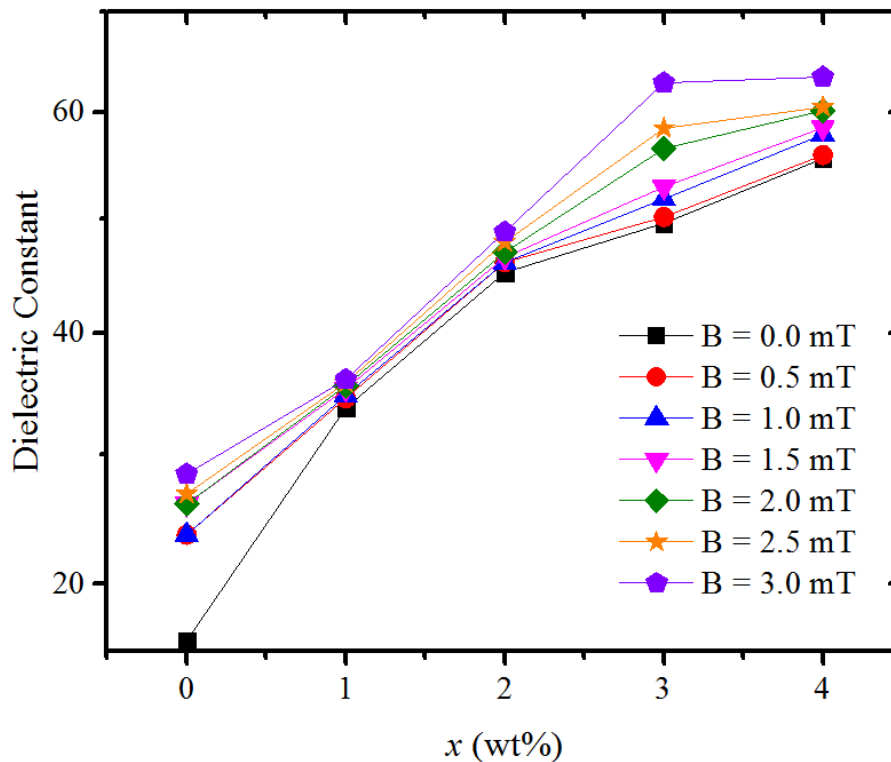
Figure 8. The influence of magnetic field on dielectric Glass

4. Conclusion

It can be concluded that the addition of NiO give rise to maintain the glassy structure of $50SiO_2$-$25B_2O_3$-$(6.5-x)$ B_2O_3-18.5 Na_2CO_3-$xNiO$, and modify the functional bonds. The increase of NiO in the glass increase the dielectric constant. However, in the presence of light intensity onto the samples, the dielectric constants decrease with a distinct step-like at a certain amount. On the other hand, the applied of a magnetic field was able to increase the dielectric constant of the glass.

5. References

[1]   Diantoro M, Yuwita P E, Olenka D and Nasikhudin 2014 Fabrication of $CuAl_{1-x}M_xO_2$ (M = Fe, Cr)/Ni film delafossite compounds using spin coating and their microstructure and dielectric constant *AIP Conf. Proc.* **1617** 170–4

[2]   C Gautam, Kumar D, Parkash, O and Singh, P 2013 Synthesis, IR, crystallization and dielectric study of $(Pb, Sr)TiO_3$ borosilicate glass–ceramics **36** 461–9

[3]   R K, S S and Pandey O.P 2012 FTIR structural investigation of gamma irradiated $BaO–Na_2O–B_2O_3–SiO_2$ glasses. *Phys B Condens MatterPhys B Condens Matter* **407** 4765–4769

[4]   Moustafa F A, Fayad A M, Ezz-Eldin F M and El-Kashif I 2013 Effect of gamma radiation on ultraviolet, visible and infrared studies of NiO, Cr_2O_3 and Fe_2O_3-doped alkali borate glasses *J. Non-Cryst. Solids* **376** 18–25

[5]   Macalik B, Suszynska M, Rysiakiewicz-Pasek E, Krawczyk L, Morawska-Kowal T and Okal J 2005 Spectroscopic and dielectric characteristics of nickel-doped porous silica glasses *Opt. Appl.* **35** 761

[6]   Patil P S and Kadam L D 2002 Preparation and characterization of spray pyrolyzed nickel oxide (NiO) thin films *Appl. Surf. Sci.* **199** 211–221

[7]   Yan S J, Xu C Y, Jiang J T, Liu D B, Wang Z Y, Tang J and Zhen L 2014 Strong dual-frequency electromagnetic absorption in Ku-band of C@ FeNi 3 core/shell structured microchains with negative permeability *J. Magn. Magn. Mater.* **349** 159–164

[8]   He F, He Z, Xie J, Li Y and others 2014 IR and Raman Spectra Properties of Bi_2O_3-ZnO-B_2O_3-BaO Quaternary Glass System *Am. J. Anal. Chem.* **5** 1142

[9]   Singh L P, Agarwal S K, Bhattacharyya S K, Sharma U and Ahalawat S 2011 Preparation of silica nanoparticles and its beneficial role in cementitious materials *Nanomater. Nanotechnol.* **1** 9

[10]   Suresh B, Reddy M S, Reddy A S S, Gandhi Y, Kumar V R and Veeraiah N 2015 Spectroscopic features of Ni^{2+} ion in PbO–Bi_2O_3–SiO_2 glass system *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **141** 263–271

[11]   X G, H M, M L, J Y and Li, B 2012 Facile synthesis route to NiO–SiO_2 intercalated clay with ordered porous structure: Intra gallery interfacially controlled functionalization using nickel–ammonia complex for deep desulfurization **148** 25–33

[12]   Yao R, Liao S, Chen X, Tang G, Wang G and Zheng F 2016 Effects of ZnO and NiO on material properties of microwave absorptive glass-ceramic tile derived from iron ore tailings *Ceram. Int.* **42** 8179–8189

[13]   Twej W A 2013 Spectral analysis of electronic transitions for low doping concentration of nickel ions in silica matrices at different phases *J. Non-Cryst. Solids* **382** 45–51

[14]   Lu Y P, Ji C X, Sun Y L, Fang Y, Zhang L, Han Z D, Qian B, Jiang X F and Zhou W P 2016 Magnetic, dielectric and magnetoelectric properties of polycrystalline $Nb_2Co_4O_9$ *J. Alloys Compd.* **679** 213–217