The effect of Cr$_2$O$_3$ doping on structures and dielectric constants of SiO$_2$-Bi$_2$O$_3$-B$_2$O$_3$-Na$_2$CO$_3$ glass based on silica gel of natural sand

M Diantoro$^{1,2,*}$, M B Zaini$^1$, Z Muniroh$^1$, Nasikhudin$^{1,3}$ and AHidayat$^{1,2}$

$^1$Department of Physics, Faculty of Mathematics and Natural Sciences, State University of Malang, Jl. Semarang 5 Malang, Indonesia
$^2$Minerals and Advanced Materials Science Laboratory, State University of Malang, Jl. Semarang 5 Malang, Indonesia
$^3$Department of Physics, Faculty of Mathematics, Gadjah Mada University, Jl. Sekip Utara Bulaksumur 55281, Yogyakarta, Indonesia

*Corresponding email address: markus.diantoro.fmipa@um.ac.id

Abstract: One of the abundant natural resources along the coastal lines of Indonesia is silica sand. One of the beaches which has a lot of silica content is Bancar-Tuban beach. Silica can be used as a raw material of glass that has multiple properties in optic, dielectric, and other physical properties by introducing specific dopants. Some oxides have been used as dopant e.g. Al$_2$O$_3$, Fe$_3$O$_4$, and NiO. However, there has not been any comprehensive study discussing the multiple properties of natural silica-sand-based glass with Cr$_2$O$_3$ dopant so far. A series of samples have been prepared, which mean two solid steps to state melting technique. Cr$_2$O$_3$ was selected as a dopant due to its potential to control its color and to increase the dielectric constant of the glass. The synthesis of silica (SiO$_2$) sand from Bancar-Tuban beach was conducted through the sol-gel process. The composition varied as the addition of Cr$_2$O$_3$ on 50SiO$_2$-25B$_2$O$_3$-(6.5-x) Bi$_2$O$_3$-18.5Na$_2$CO$_3$-xCr$_2$O$_3$ (x = 0, 0.02, 0.04, 0.06 and 0.08mol), later called SBBN glass. The samples’ characterizations of the structure and morphology were conducted through the use of XRD, and SEM-EDX. The measurements were done by using a DC capacitance meter in order to investigate the dielectric properties of the sample, under the influence of light. It is shown that addition of Cr$_2$O$_3$ did not alter the crystal structure but changed the structure of the functional bond formation. It is also revealed that the dielectric constant increased along with the increasing of Cr$_2$O$_3$. An interesting result was that the dielectric constant of the glass was quantized decreasingly as the increase of light.

1. Introduction
It is known that one of the abundant natural resources along the coastal lines of Indonesia is silica sand. One of the beaches which has a lot of silica content is Bancar-Tuban beach. The content of silica in BancarTuban, which is also called as natural sand beach, is 80.7% [1]This potential needs to be developed considering the relatively simple method of silica manufactur. In science, the use of silica is
very diverse. One of silica utilizations is as the raw material of glass which exhibits multiple properties. The raw materials of typical glass consist of silica, soda ash, and limestone. Synthesis of pure-silica glass needs a relatively high temperature around 1760-1870°C. The use of high temperature for large scale production is not cost effectively, and needs more complicated equipment and technologies. Many efforts have been studied to lower the melting temperature, and to modify the glass properties itself. The addition of some oxides material such as Bi₂O₃, B₂O₃, and Na₂CO₃ has been used to reduce the melting temperature of silica. Another technique to lower the melting temperature is by reducing silica grains or by modifying in the form of amorphous. The sol-gel-method can be implemented to prepare silica down to nanometer size as well as in the form of amorphous[2].

Glass is one of the essential material in human life. Rapid technological developments have also initiated the development of glass, e.g. the glass for household application to glass for sensors. Glass ceramics can be applied in materials science and biotechnology [3].Glass is widely used as window and drinking glasses for centuries. Nowadays, glass is used as touch screens, mobile phone screens, LCD screens, laser materials, memory devices, photonic devices, glass windshields of cars and others. A super hydrophobic glass has generated a widespread interest because of its applications in solar panel lighting [2].In solid glass, there is no contribution from dipole orientation. There is a distortion in the infrared region and an electronic vibration in UV region. In between of those regions, there is no strong coupling. This region is called a window transparency of the glass [4].

It was resulted from our previous work that oxidic dopant can change the glass properties[1]. An interesting outcome also showed that the light intensity rose to an interesting and prominent dielectric constant. The use of oxides material as dopant e.g. Al₂O₃, Fe₂O₃, and NiO has been studied with specific change of dielectric properties. A comprehensive study reducing melting temperature by silica sol-gel and the use of CrO₃ dopant to modify the dielectric constant under visible light intensity has not been reported this yet so far. The use of Cr₂O₃ causes its stability in magneto-dielectric[5]. Chromium has a configuration of 3d⁵ 4s¹ in paramagnetic ion transition group [5]. It has several oxidation state as follows Cr³⁺, Cr⁴⁺, Cr⁵⁺, Cr⁶⁺. The most stable valence is Cr³⁺ and Cr⁴⁺[6]. Cr₂O₃ is one of the oxide studied intensively due to its wide band gap of 3.3 eV[7]. The aims of this work is to study the effect of Cr₂O₃ and to intensity of visible light on the dielectric constant of the SBBN glass.

2. Research Methods

2.1 Tools and materials
The raw materials used in this works were Bancar beach natural sands as the source of silica, B₂O₃ Merck 100169, Bi₂O₃ Merck 101862, Na₂CO₃ and Cr₂O₃ Merck 102483. Several tools and equipment utilized in this study were digital balance HF-3000 (0.019), Brother Furnace XD-1700M, magnetic stirrer hot plate, beaker glass, ceramic mortaranpestel. For characterization, we operated Pan Analytical XRF and XRD, DTA, FEI SEM-EDX, FTIR, DC electric capacitance, standard Philips 100 W lamps and optical system.

2.2 Procedures

2.2.1 Preparation of SiO₂. Silica sand collected from BancarTuban beach was washed six times with distilled water, and then ingrainned to 100 mesh. The fine grains sand that had been soaked with 32% HCl for 12 hours, then washed with distilled water to pH 7 and dried.

2.2.2 Sol-gel process. Sixty grams of silica sand and 1920 mL 5M NaOH was stirred by using a magnetic stirrer at a speed of 600 rpm and at 140°C until the water content was lost. 1920 mL of water was added while stirring for 3 hours and then, it was allowed to stand in order to precipitate. The filtrate was separated by sediment. The filtrate was stirred with a magnetic stirrer at a speed of 600 rpm while titrated with 5M HCl to pH 7. Then it formed a gel which was set aside to stand for up to 24
hours and dried at a temperature of 125°C. Furthermore, it was tested through the use of XRF to determine the percentage of purity of the silica.

2.2.3 Synthesis of SBBN glass.
The composition used in the synthesis is 50SiO$_2$-25B$_2$O$_3$-(6.5-x)Bi$_2$O$_3$-18.5Na$_2$CO$_3$-xCr$_2$O$_3$ SBBN with $x = 0, 0.02, 0.04, 0.06, 0.08$ mol were mixed until it became homogeneous and heated via Brother Furnace XD-1700M at a temperature of 450 °C for 2 hours and was raised up to 950 °C for 1 hour in ceramics crucible, and then cooled to room temperature. Samples were separated from the crucible and their characterization was tested by using DTA, XRD, FTIR, SEM-EDX and capacitance meter.

3. Results and Discussion

3.1 Synthesis of SiO$_2$ via sol-gel
Silica powders were tested by using XRF. Table 1 shows the composition and content of silica sand before and after the synthesis via the sol-gel process. The silica quartz sand has 88.1% purity before the sol-gel process and increases up to 95.5% after the process. Based on the results, the sol-gel method was able to reduce some of the impurities contained in the silica sand, such as K, Ca, Ti and Fe. The small amount of impurity elements was still contained in the sol-gel due to insoluble of the compounds inNaOH and HCl or may need longer time and also smaller size of particles.

| Element | Si (%) | Ca (%) | Ti (%) | Fe (%) |
|---------|--------|--------|--------|--------|
| before extraction | 88.1 | 2.76 | 1.37 | 2.97 |
| after extraction | 95.5 | 1.2 | 0.44 | 1.92 |

3.2 The results of the DTA analysis
The DTA observation curves of SiO$_2$-B$_2$O$_3$-Bi$_2$O$_3$-Na$_2$CO$_3$ glass samples without doping ($x=0$) is demonstrated in Figure 1. From the DTA curve, it can be seen that the melted sample (Tm) is observed at 943.3 °C which is much lower than pure SiO$_2$ itself.

![Figure 1. DTA Test Results of SBBNGlass without Cr$_2$O$_3$ doping.](image-url)
Regarding to Figure 2, in SBBN glass with Cr\textsubscript{2}O\textsubscript{3} 0.02 mol doping, there is a noticeable decrease in the DTA curve indicating the melting temperature of the sample glass. The optimum melting temperature increases at 949.2 °C. The introduction of 0.02 mol of Cr2O3 affects to rise the melting temperature of the glass as expected.

![Graph showing DTA Test Results of SiO\textsubscript{2}-B\textsubscript{2}O\textsubscript{3}-Na\textsubscript{2}CO\textsubscript{3}-Bi\textsubscript{2}O\textsubscript{3} Glass with 0.02 mol of Cr\textsubscript{2}O\textsubscript{3} doping.](image)

**Figure 2.** DTA Test Results of SiO\textsubscript{2}-B\textsubscript{2}O\textsubscript{3}-Na\textsubscript{2}CO\textsubscript{3}-Bi\textsubscript{2}O\textsubscript{3} Glass with 0.02 mol of Cr\textsubscript{2}O\textsubscript{3} doping.

### 3.3 Results of XRD structure analysis

Based on the Figure 3, the diffraction pattern of the Cr\textsubscript{2}O\textsubscript{3} sample doping of 0.02 mol, 0.04 mol, 0.06 mol and 0.08 mol indicates that the structure is in the glassy amorphous form (non-crystalline). The diffraction pattern shows only one weak peak at the 2θ position of about 27 degrees, illustrating the formation of a new phase of Bi\textsubscript{2}O\textsubscript{3}. One peak in the sample without doping at approximately 66 degrees (2θ position) is the culmination of boron oxide.

![Graph showing Comparison of XRD histograms of SBBN glass at various Cr\textsubscript{2}O\textsubscript{3} doping.](image)

**Figure 3.** Comparison of XRD histograms of SBBN glass at various Cr\textsubscript{2}O\textsubscript{3} doping.
3.4 FTIR Analysis Results
An FTIR transmittance spectra of undoped and 0.02% Cr₂O₃ doped glass is displayed in Figure 4. The sample of glass without Cr₂O₃ doping (x=0) showed the Si-O-Si bond stretching vibration at a wavelength of 667 cm⁻¹, the vibration of Si-O-Si asymmetric at 1033 cm⁻¹, BO₃ unit at 1283 cm⁻¹, and the bending vibration is at 763 cm⁻¹.

![Figure 4. FTIR spectra of SBBN glass with x=0 and x=0.02 mol doping.](image)

In samples with x= 0.02 mol Cr₂O₃ doping at wave number 447.49 cm⁻¹, there is a Cr-O bond. The wave numbers are 472.56 to 698.23 Si-O-Si asymmetric vibration bond and the wavenumber at 425 cm⁻¹ as O-Cr-O bond [8]. The sample has also seen the modes of CrO₄²⁻ vibration at wave numbers of 862.18 and 879.54 cm⁻¹. Figure 4 describes that in the sample without doping in the range of wave number 800 cm⁻¹ to 900 cm⁻¹, there is no peak detecting the presence of CrO₄²⁻ vibration. Also, in the range of wave number of 1300 cm⁻¹ to 1400 cm⁻¹, there is no visible strong peak as well as samples with 0.02 mol Cr₂O₃ doping which should exist as the wave numbers are the BO₃ bond. It can be said that the doping sample with 0.02 mol Cr₂O₃ which generated a new peak in the range of wave number of 1300 cm⁻¹ up to 1400 cm⁻¹ is a composite material.

3.5 Analysis of SEM microstructure
Based on Figure 5, morphology of the glass with a 100-time magnification did not show any differences between samples of glass without Cr₂O₃ doping, and with 0.02 mol doping. There was no grains that was very similar in the whole area under inspection. However, overall, it was looked like a homogeneous sample. A several tiny grains at Figure 5a) and 5b) was actually not intrinsic in the samples. From the results of SEM-EDX above, even smooth small white granules can be seen, and white grain was detected from the Bi₂O₃.
3.6 Effect of the intensity of the glass dielectric constant

The dielectric constant influenced by the intensity of the glass was measured by using a series of LCR meters equipped with the lux meter. The lux meter is designated to measure the intensity of the visible light engaged. The value obtained from this measurement was electric capacitance ($C$) with respect to samples’ surface area ($A$) and thickness ($d$). By using equation 1, the dielectric constant ($\kappa = \varepsilon / \varepsilon_0$) was presented in Figure 6. Figure 6 illustrates the effect of addition of Cr$_2$O$_3$ on the dielectric constant of 50SiO$_2$-25B$_2$O$_3$-(6.5-x)Bi$_2$O$_3$-18.5Na$_2$CO$_3$-xCr$_2$O$_3$ glass on the intensity ranged from 0 to 2500 Lux.

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

(1)

Figure 5. The result of SEM-EDX morphology SiO$_2$-B$_2$O$_3$-Bi$_2$O$_3$ Na$_2$CO$_3$ glass with Cr$_2$O$_3$ doping: a) x=0 mol and b) 0.02 mol.

Figure 6. Dielectric constant of SiO$_2$-B$_2$O$_3$-Bi$_2$O$_3$ Na$_2$CO$_3$ glass against Cr$_2$O$_3$ doping.
The addition of Cr$_2$O$_3$ doping significantly affected the dielectric constant. The greater the Cr$_2$O$_3$ were added, the greater the dielectric constant was. This was caused by a high dielectric constant in the Cr$_2$O$_3$ material, and since Cr$_2$O$_3$ has a centrosymmetric crystal structure\cite{9}, i.e. the high dielectric constant \cite{10}, so the addition of Cr$_2$O$_3$ doping into SiO$_2$-B$_2$O$_3$-Na$_2$CO$_3$-Bi$_2$O$_3$ glass resulted in the increase of dielectric constants. On the other hand, the intensity of light reduced the dielectric constant. The detail inferred dielectric constant measurement is shown in Figure 7.

![Figure 7](image)

**Figure 7.** Dielectric Constant of SiO$_2$-B$_2$O$_3$-Bi$_2$O$_3$ Na$_2$CO$_3$ Glass as a Function of Intensity of Light.

The influence of the visible light intensity on the dielectric constant of the glass is depicted in Figure 7. It is significantly seen that the dielectric constant is inversely proportional to the intensity of use. The greater the intensity of use, the smaller the dielectric constant. Another distinct feature of Figure 7 is the quantization phenomena of the dielectric constant. This is in contrast to the influence of the increase of the Cr$_2$O$_3$ dopant. The decrease of the dielectric constant by light intensity as well as the quantization effect can be described as the increased volume of the crystal originated from the quantized of electron excitation by light. This mechanism may cause to the binding energy of the crystal and the further distance between atoms so that the dielectric constant decreases and quantized.

4. **Conclusions**

Based on the analysis and discussion in the previous sections, it can be concluded as follows; the addition of Cr$_2$O$_3$ does not alter the crystal structure of SiO$_2$-B$_2$O$_3$-Bi$_2$O$_3$-Na$_2$CO$_3$ yet functionally creates bond formation of the glass. It remains as a glass which is shown by XRD diffraction pattern.
On the other hand, its change on the structure of bond formation is indicated by the results of FTIR. The addition of Cr$_2$O$_3$ generally increases the dielectric constant of the glass. The most interesting fact is that the employment of light intensity causes the decrease of dielectric constant with some features of quantization phenomena at a specific intensity.

5. References

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