Investigations of physical and structural properties of calcium alumino silicate glasses doped with samarium (III) oxides

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Abstract. We synthesized and investigated the physical and structural properties of calcium alumino-silicate glasses systems: (60-x)SiO$_2$–2.5Al$_2$O$_3$–10CaO–17Na$_2$O–10K$_2$O–0.5Sb$_2$O$_3$–xSm$_2$O$_3$. The samples were prepared using melt quenching method. Density was measured using Archimedess principle, and the physical properties such as the ion concentrations, interatomic distance, polaron radius, and field strength were calculated. The density, the calculated ion concentrations, and field strength increased while the interatomic distance and polaron radius decreased with increasing of Sm$_2$O$_3$ contents. The structure of the glasses was characterized using the Fourier transform infrared spectrometer. The FTIR result showed that the change in the network structures of these glasses depends on the concentration of Sm$_2$O$_3$.

1. Introduction
A light emitting diode (LED) is an electronic device that always uses for lighting and displaying application fields such as, waveguide laser, solid-state laser, mobile screen, computer monitor, etc. However, a traditional white light emitting diode (W-LED) is a low efficiency, many research groups have been studied the new W-LED that is a higher efficiency than its. Basically, the W-LED is produced by a combination of red, green, and blue LED. However, it found to be that the combination of RGB LED system leads to the low efficiency of white light emission due to the low efficiency of red emission [1]. Therefore, there were many research groups that developed the efficiency of red emission.

Glasses doped with rare earth oxides (RE) have been investigated in recent years to use as a new light emitting diode (LED) because they offer high transparency, homogeneity, easy formability in shape and size. Samarium oxide (Sm$_2$O$_3$) doped in glasses has been interested because of their robust luminescence in the visible region. Moreover, they prepossess orange-red fluorescence [2]. In addition, Ramteke et al. [3] have been reported the effect of Sm$^{3+}$ ions on structural and luminescence properties of lithium borate glasses. It was shown the addition of Sm$^{3+}$ led to changing of structural and luminescence properties in glasses. Furthermore, various research has been also reported the Sm$^{3+}$ ions adding in several host glasses such as borate, borophosphate, and phosphate glasses [4–6]. It was revealed that these glasses emit red color when doping Sm$^{3+}$.
Nowadays, the optical properties of doping Sm$_2$O$_3$ in silicate glass haven’t been investigated. Moreover, the effect of network glass structure on the optical properties has been interested in explanation of these properties. Thus, the aims of this research are investigations of the physical properties that effect on the optical properties such as polaron radius, interatomic distance, and field strength. Furthermore, the structural transformations of these glasses have been studied using the Fourier transform infrared spectroscopy technique.

2. Experimental details
2.1. Preparation of glass samples
The glasses in system (60-x)SiO$_2$–2.5Al$_2$O$_3$–10CaO–17Na$_2$O–10K$_2$O–0.5Sb$_2$O$_3$–xSm$_2$O$_3$ (where $x = 0, 0.1, 0.25, 0.5, 0.75,$ and $1$ in mol% respectively) were prepared using melt quenching method. For preparing glass samples, the high purity chemicals (SiO$_2$, Al$_2$O$_3$, CaO, Na$_2$CO$_3$, K$_2$CO$_3$, Sb$_2$O$_3$, and Sm$_2$O$_3$) were weighed using an electronic balance with accuracy of 0.0001 g. They were mixed thoroughly in ceramic crucibles. The mixed powders were melted in an electric furnace at 1250°C for 2.5 hours to ensure homogenously. Then, the melted glass was poured into the pre-heated rectangular stainless-steel molds, and then was immediately annealed at 500°C for 2 hours to reduce the thermal stress in the glass samples, they were naturally cooled down to room temperature. The prepared glasses were cut and polished using different silicon carbide grades to achieve a good optical surface. These glasses were measured thickness by using vernier caliper.

2.2. Physical properties
The density of glass samples is measured at room temperature by using Archimedess principle with the n-hexane as the immersion liquid. This measurement is repeated five times for accreting the value of the density. This result is used for calculating the molar volume for each sample from the expression: $V_m = \frac{M_g}{\rho}$. The ion concentrations ($N$), interatomic distance ($r_i$), polaron radius ($r_p$), and field strength ($F$) were also determined from the following equation [7, 8].

$$N = \frac{(\text{mol\% of RE})(N_A)\rho}{M_g}$$ (1)

$$r_i = \left[\frac{1}{N}\right]^{1/3}$$ (2)

$$r_p = \frac{1}{2}\left[\frac{\pi}{N}\right]^{1/3}$$ (3)

$$F = \frac{Z}{r_p^2}$$ (4)

Where $N_A$ is Avogadros number, $\rho$ is the density of glass samples, $M_g$ is molecular weight of glass samples, and $Z$ is atomic mass of RE ion.

2.3. Structural property
The structural property is studied using the Fourier transform infrared (FTIR) spectroscopy technique. The FTIR absorption spectra of glass samples are recorded on a thermo scientific Nicolet 6700 FTIR spectrometer in the 400–4000 cm$^{-1}$ region which uses the KBr method in the ratio 1:100 mg.
3. Results and discussion

3.1. Physical properties

The calculated physical parameters are shown in table 1. The density and molar volume of the glass samples was firstly discussed. These parameters increased with increasing the Sm$_2$O$_3$ contents.

| x mol% of Sm$_2$O$_3$ | ρ±0.0011 (g/cm$^3$) | $M_g$±0.0107 (cm$^3$/mol) | $N \times 10^{20}$ (ions/cm$^3$) | $r_i$ (nm) | $r_p$ (nm) | $F \times 10^{16}$ (cm$^{-2}$) |
|----------------------|-------------------|-----------------------------|--------------------------------|--------|--------|-----------------------------|
| 0.00                 | 2.6252            | 25.0098                     | –                             | –      | –      | –                           |
| 0.10                 | 2.6321            | 25.0406                     | 0.2405                        | 3.4644 | 1.3962 | 0.7714                      |
| 0.25                 | 2.6456            | 25.0766                     | 0.6043                        | 2.5482 | 1.0269 | 1.4257                      |
| 0.50                 | 2.6692            | 25.1252                     | 1.2194                        | 2.0166 | 0.8127 | 2.2767                      |
| 0.75                 | 2.6953            | 25.1500                     | 1.8469                        | 1.7559 | 0.7076 | 3.0026                      |
| 1.00                 | 2.7174            | 25.2105                     | 2.4829                        | 1.5910 | 0.6412 | 3.6573                      |

The increased density resulted from the molecular weight of RE (Sm$_2$O$_3$ is 348.7182 g/mol) that is higher than the molecular weight of the network former (SiO$_2$ is 60.0843 g/mol). In addition, the cause of increasing in molar volume is the ionic radius of the modifier ions (Sm$^{3+}$ is 1.08 Å) that is larger than the ionic radius of the network former (Si$^{4+}$ is 0.40 Å), and it can be suggested the increase in non-bridging oxygen (NBOs) in the glass structure when the concentrations of Sm$_2$O$_3$ increased.

The increased ion concentrations were due to the increase of Sm$_2$O$_3$ contents that led to the increase in Sm$^{3+}$ ions in the glass matrix. This result brings about the decrease of interatomic distance because the distance between Sm$^{3+}$–Sm$^{3+}$ ions decreased when increasing in Sm$_2$O$_3$. Moreover, the declined polaron radius was due to the short-range of the interaction between the free electron and cations (Sm$^{3+}$) leading to the increase in field strength with increasing the concentration of Sm$_2$O$_3$.

3.2. Structural property

This property of the glass samples is investigated using the FTIR spectroscopy technique in the region 400–4000 cm$^{-1}$ shown in figure 1. The absorption bands over 2000 cm$^{-1}$ are the vibration of water groups. As seen in figure 1, the obtained FTIR result was shown the six absorption bands of the glass samples. The carbonate groups and molecular of water band are displayed by the wavenumber at about 1415 and 1640 cm$^{-1}$ respectively [9].

![Figure 1. FTIR spectra of glass samples contained difference mol% of Sm$_2$O$_3$](image)
The wavenumber at about 480 cm\(^{-1}\) is assigned to the Si–O–Si bending vibrations [9]. The Si–O–Si and O–Si–O symmetric stretching of bridging oxygen (BOs) between tetrahedral are indicated by the wavenumber at around 740 cm\(^{-1}\) [10]. The band at about 1040 cm\(^{-1}\) is assigned to the Si–O–Si anti-symmetric stretching of BOs within tetrahedral [10]. Moreover, it also shows the peak at about 930 cm\(^{-1}\) which is the Si–O–Si stretching of NBOs [10]. These results are evidence that supports our discussion about the transformation from tetrahedral (Q\(_4\)) to trigonal (Q\(_3\)) with the formation of NBOs when increasing in Sm\(_2\)O\(_3\) within the glass samples.

4. Conclusion
In summary, doping Sm\(_2\)O\(_3\) in the calcium alimino silicate glass led to increase in density, molar volume, and field strength of this glass. Moreover, the obtained result from FTIR spectra was therefore shown the transformation of network structure from tetrahedral (Q\(_4\)) to trigonal (Q\(_3\)) when increasing in Sm\(_2\)O\(_3\) contents within the glass samples. This result confirms that Sm\(_2\)O\(_3\) act as the network modifier in the glass structure.

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