Advanced Ceramics Progress: Vol. 10, No. 1, (Winter 2024) 18-21

Materials and Energy Research Center
MERC

Contents lists available at ACERP

Advanced Ceramics Progress

Journal Homepage: www.acerp.ir

Original Research Article

Investigating the Effects of CeO_2 Addition on the Structure of $MgO-Al_2O_3-SiO_2$ Glass Using FTIR and Raman Analysis

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URL: https://www.acerp.ir/article_207692.html

ARTICLE INFO

Article History:
Received: 29 January 2024
Revised: 07 February 2024
Accepted: 08 February 2024

Keywords:
Silicate Glass,
Structural Analysis,
FTIR,
Raman,
Cerium Oxide

ABSTRACT

The $MgO-Al_2O_3-SiO_2$ (MAS) glass system has long been of interest due to its potential to be converted into glass-ceramics containing spinel and cordierite phases. This study investigated the effect of adding varying amounts of cerium oxide (1-5% by weight) on the structure of the $MgO-Al_2O_3-SiO_2$ glass system. After mixing the raw materials, the samples were melted at 1600°C, and the density of the glass samples was measured using the Archimedes method. FTIR analyses, covering both far and mid-infrared ranges, as well as Raman spectroscopy, were conducted on the glass samples. To improve detection accuracy, the obtained spectra were deconvoluted. The results showed that the addition of cerium oxide increased the density from 2.53 g/cm³ to 2.69 g/cm³. Furthermore, the data indicated that cerium oxide in concentrations below 5% acts as a modifier. At lower concentrations, cerium predominantly exists in the Ce^{3+} state, increasing the number of non-bridging oxygens (NBOs), while at higher concentrations, Ce^{3+} is mostly converted to Ce^{4+}, which in turn reduces the NBO concentration.

https://doi.org/10.30501/acp.2024.435473.1145

1. INTRODUCTION

The $MgO-Al_2O_3-SiO_2$ (MAS) glass system has long been of interest due to its ability to be converted into glass-ceramics containing spinel and cordierite phases (Chen et al., 2007; Holand et al., 2012)(Rezvani et al., 2005). These glass-ceramics have been applied in various fields, including military uses such as anti-bullet armor and radomes, as well as anti-wear tiles in the construction industry (Soleimani et al., 2015; Zou et al., 2013). The properties of glass-ceramics are strongly influenced by the structural and physical characteristics of the base glass. Glass transition temperature, dilatometric and crystallization temperature, thermal expansion coefficient, and various physical and chemical properties of glass-ceramics are all affected by the base glass structure (Komatsu, 2015). Research has shown that $[SiO_4]$ and $[AlO_6]$ groups, along with smaller amounts of $[MgO_4]$ groups, are the most important structural groups in MAS glasses (El-Damrawi et al., 2018). It is well known that the introduction of certain transition cations leads to structural changes in glass and alters its properties. For instance, Zhang et al. (Zhang et al., 2020) demonstrated that the addition of Cr^{+} increases the number of non-bridging oxygens (NBOs), leading to

Please cite this article as: Soleimani, F., Aghababaei, H., Kargar, M., Torkashevand, M. & Hemmati, A. (2024). Investigating the Effects of CeO2 Addition on the Structure of MgO-Al2O3-SiO2 Glass Using FTIR and Raman Analysis, *Advanced Ceramics Progress*, 10(1), 18-21. https://doi.org/10.30501/acp.2024.435473.1145

changes in the glass network. The presence of cations like chromium has also been shown to affect the physical properties of MAS glass, such as luminescence.

Cerium oxide (CeO_2) is another oxide compound of interest, and its incorporation into glass compositions induces significant structural changes. CeO_2 has been identified as an intermediate in glasses (M. B. Volf, 1984), meaning it can act as either a modifier or a glass former depending on the glass composition, the amount of cerium oxide present, and the production conditions (Soleimani et al., 2012). In silicate and phosphate glasses, cerium oxide typically increases density and imparts luminescent properties.

The objective of this study is to investigate the structural effects induced by the addition of small amounts of cerium oxide to MAS glass using structural analysis techniques.

2. MATERIALS AND METHODS

A composition of 41 wt% SiO_2 with 5 wt% MnO and ZrO_2 (in equal amounts, making up the balance) was considered for the study. To prepare the raw materials, high-purity oxides (≥99%) were used according to the specified composition. To investigate the effect of adding CeO_2, 1 wt% (G-Ce1), 3 wt% (G-Ce3), and 5 wt% (G-Ce5) of cerium oxide were substituted for SiO_2 in the base composition. After mixing the raw materials, 50 g of each batch was poured into alumina crucibles and melted at 1600°C in an electric furnace. After one hour of holding at the maximum temperature, the molten glass was cast into a preheated steel mold. The cast parts were then immediately transferred to a furnace set at 600°C, where they were slowly cooled to ambient temperature.

The density of the samples was measured using the Archimedes method. Samples were then prepared from each piece for structural analysis. For this purpose, the glass pieces were ground using an agate mortar. The resulting powder samples were mixed with KBr powder at a ratio of 1:100 and pressed to create suitable samples for FTIR analysis. FTIR analysis was performed on the samples across two spectral ranges: the far-infrared range (100-400 cm^{-1}) and the mid-infrared range (4000-2000 cm^{-1}).

Raman analysis was also conducted on pure powder samples of the glasses. The deconvolution technique was applied to the FTIR spectra to more accurately determine the positions of the peaks.

3. RESULTS AND DISCUSSION

Table 1 shows the results of density measurement. It is determined that with the addition of CeO_2, density increases, given the atomic weight of Ce.

TABLE 1. Density of glass samples (g/cm3)

Code	Density
Ge-Ce0	2.55±0.03
Ge-Ce1	2.57±0.02
Ge-Ce3	2.64±0.03
Ge-Ce5	2.69±0.01

The FTIR absorption spectrum of the glass samples was measured in the range of 400-2000 cm-1, as shown in Figure 1.

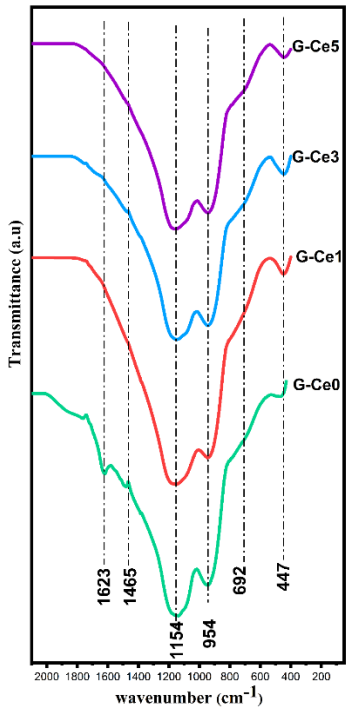

Figure 1. FTIR absorption spectrum of G-Ce0, G-Ce1, G-Ce3, and G-Ce5 glass samples.

The band in the range of 450 cm^{-1} is attributed to the bending vibrations of O-Si-O and Si-O-Si bond (Handke et al., 1993)(Aguiar et al., 2009)(Abdelwahab et al., 2021). The peak observed around 692 cm^{-1} corresponds to the bending vibrations of Si–O–Al and Si–O–Si bonds, and no significant changes were detected in the spectrum with the addition of CeO_2 (Yan et al., 2012). The strong absorption band in the range of 900–1120 cm^{-1} exhibits the highest intensity in the IR spectra of various glasses, attributed to the stretching vibrations. Two distinct absorption bands are observed at 1954 cm^{-1} and 1154 cm^{-1}, with the vibration intensity at 1154 cm^{-1} being higher than that at 1954 cm^{-1}. These bands are associated with the stretching vibration of Si–O–Si in Q^2 (1154 cm^{-1}) and the asymmetric vibration of Si–O–Si in Q^3 (1954 cm^{-1}), respectively (Handke et al., 1993)(Kazancioglu et al., 2021)(Fang et al., 2020).

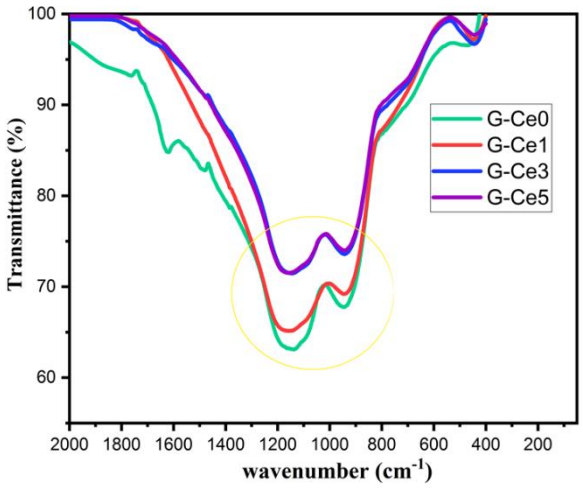

Figure 2. FTIR absorption spectrum of G-Ce0, G-Ce1, G-Ce3, and G-Ce5 glass samples.

Figure 2 clearly demonstrates that the addition of CeO_2 reduced the intensity of the bands at 1954 cm^{-1} and 1154 cm^{-1}. The weak peak at 1465 cm^{-1} is attributed to the stretching and deformation vibrations of the CH_2 group (Liu et al., 2020). The peak at 1623 cm^{-1} corresponds to the bending vibrations of H_2O molecules (Abdelwahab et al., 2021). To further examine the effect of CeO_2 addition, the Raman spectra of G-Ce0, G-Ce1, G-Ce3, and G-Ce5 glasses were analyzed, as shown in Figure 3.

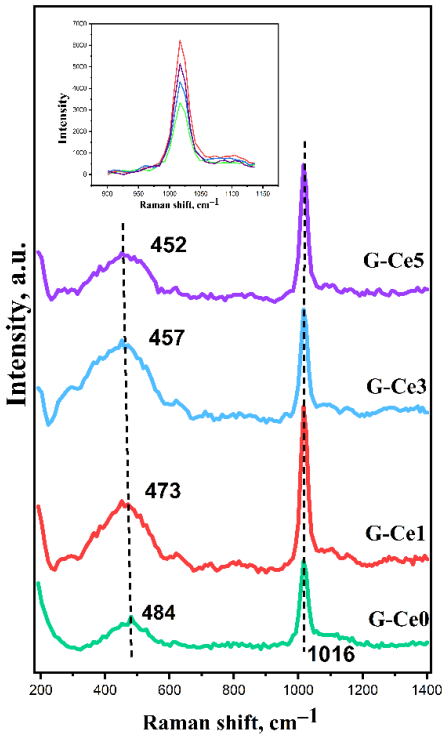

Figure 3. Raman spectrum of G-Ce0, G-Ce1, G-Ce3, and G-Ce5 glass samples.

The Raman spectra of G-Ce0, G-Ce1, G-Ce3, and G-Ce5 glasses are shown in Figure 3. Based on the results, the peak around 490 cm^{-1} corresponds to the bending vibrations of Si–O–Si bonds (Aguiar et al., 2009). The addition of CeO_2 to the glass caused a shift of this peak to a lower wavenumber, indicating changes in Si–O–Si vibrations. At higher wavenumbers, a sharp peak near 1016 cm^{-1}, associated with Si–O vibrations in the Q^3 structure, was observed, and the addition of CeO_2 increased the intensity of this peak (Fang et al., 2020). A decrease in the intensity of the bands at 954 cm^{-1} and 1154 cm^{-1} in the FTIR spectrum, which are related to Si–O–Si vibrations, along with the shift of the peak at 1490 cm^{-1} to a lower wavenumber and an increase in the intensity of the band at 1016 cm^{-1} in the Raman spectrum upon the addition of CeO_2, is attributed to non-bridging oxygens (NBOs). This suggests that cerium oxide disrupts Si–O–Si bonds. In this study, it is assumed that alumina integrates into the Si–O tetrahedral network and remains unaffected by the addition of CeO_2. As seen in previous studies on aluminosilicate glasses (Lin et al., 1996), borosilicate (Deshpande et al., 2010), and lead silicate glasses (Wang et al., 2016) cerium oxide acts as a network modifier. The results of this study similarly show that the addition of cerium oxide increases the number of non-bridging oxygens, indicating its role as a silicate network modifier. The addition of cerium oxide to glass exhibits non-linear behavior in the Raman spectrum regarding peak intensity. This behavior is likely due to the multivalent states of cerium oxide in the glass melt. As expressed in the redox reaction (Equation 1), Ce^{3+} ions promote the formation of NBOs.

$$Ce^{4+} + O^{-} \Rightarrow Ce^{3+} + O \quad (1)$$

At lower concentrations, cerium predominantly exists in the Ce^{3+} state, producing more NBOs. However, at higher concentrations, Ce^{3+} is mostly converted to Ce^{4+}, reducing NBO concentration. Thus, the variation in NBO concentration as a function of cerium content has a significant impact on the non-linear changes in the connectivity of the silicate network (Wang et al., 2015).

4. CONCLUSIONS

Glasses containing cerium oxide in the MAS system were successfully prepared. It was demonstrated that the addition of cerium oxide increased the density from 2.55 to 2.69 g/cm^3 in glasses containing 5 wt% cerium oxide. The incorporation of CeO_2 also reduced the intensity of the bands at 1954 cm^{-1} and 1154 cm^{-1}. At lower concentrations, cerium primarily exists in the Ce^{3+} state, leading to an increase in non-bridging oxygens (NBOs). However, at higher concentrations, Ce^{3+} is largely converted to Ce^{4+}, resulting in a reduction in NBO concentration.

5. Acknowledgement

The authors would like to express sincere appreciation to Malayer University for financial support.

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