

Structural and Optical Analysis of the Role of Modifier Oxides in Multi-Component Silicate Glasses for Laser Applications [†]

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Abstract: Multi-component silica calcium phosphate glasses doped with modifiers of alkaline and transition metal oxides of Mg^{2+} , Fe^{3+} , and Bi^{3+} were synthesized using the sol-gel method. The glasses were analyzed for structural behavior via XRD analysis. While alkaline metal-doped glasses were purely amorphous, the transition metal oxides induced fractional crystallinity in the material, with bismuth evidencing a high glass–ceramic attribute. FT-IR analysis confirmed the presence of silicate and phosphate linkages in the glass material via the vibration modes around 790 cm^{-1} and 450 cm^{-1} , respectively. The peaks also represented the bridging and non-bridging oxygens of the glass formers. The UV-visible absorption spectra of the alkaline metal-infused glasses demonstrated the absence of sharp absorption peaks, while the transition metal-doped glasses evidenced prominent UV absorption. Tauc's plots of the absorption spectra were employed to predict the band gap energies. While the Fe^{3+} -doped glass exhibited the lowest band gap energy of 2.6 eV approaching a semiconducting nature, the remaining glasses exhibited an insulating behavior with a value of around 4 eV. The high UV absorption and lower bandgap indicate the suitability of the iron-doped glass for photovoltaic devices. Green and red emissions from all the glasses were observed using photoluminescence analysis. While the emission indicates the nature of the glass host, the intensity of its luminescence was altered by the influence of modifiers. Multi-component silicate glasses underscore the efficiency of the modifiers that could be suitably tailored for influencing the laser activity.

Keywords: multi-component glasses; modifier oxides; Tauc's plots; photoluminescence; lasers

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1. Introduction

Optically active glasses have been found in a wide range of applications, from lasers to LEDs and to optical amplifiers [1]. While silica, telluride, fluoride, and germanate glasses have been widely reported, the addition of phosphate is also preferred due to their high luminescence and transparency. However, phosphate glasses have exhibited poor chemical stability, which demands the addition of modifiers in the glass material [2]. The structure and optical activity of the glasses could be enhanced by the addition of modifier oxides such as alkali, alkaline earth metals, and transition metals [3]. A significant enhancement in the Mg^{2+} - and Bi^{3+} -doped glasses has been observed related to the luminescent behavior [4,5]. It has been reported that Fe doping in glasses has greatly reduced the band gap energy, approaching a semiconducting nature [3].

The present study is intended to synthesize the silica calcium phosphate glasses doped with the alkaline earth metal and transition metal modifier oxides of Ca^{2+} , Mg^{2+} , Fe^{3+} , and Bi^{3+} . The behavior of the modifiers relating to the structural and optical influence on the glass properties are compared. Emissions from the glasses are analyzed to understand the laser action.

2. Materials and Methods

The silica calcium phosphate glasses doped with modifier oxides from the alkaline metal groups of calcium and magnesium and that from the transition metals of iron and bismuth were synthesized using the sol-gel method as per the scheme reported [6]. The glasses are, respectively, coded as SPCM, SPCF, and SPCB. The precursors were stirred for two hours at room temperature, followed by gelation and formation of solid glasses.

The glasses were taken for structural analysis via X-ray diffraction using an X-ray Diffractometer (Bruker $\lambda = 1.5418\text{\AA}$). The functional groups present in the glasses were verified using Fourier Transform Infrared (FT-IR) analysis employing a Shimadzu FTIR—8400S. The optical properties were examined by the Shimadzu—UV 3600Plus UV-visible spectrophotometer in the visible range, while photoluminescence studies were carried out with a Horiba Fluoromax-PLUS spectrofluorometer at room temperature of 300 K.

3. Results and Discussion

3.1. X-ray Diffraction (XRD) Studies

The XRD spectra of the samples are shown in Figure 1. The Mg^{2+} -doped sample exhibited an amorphous nature without the formation of crystalline phases [7]. Large crystallinity was observed in the Bi^{3+} -doped glass with the bismuth silicate and SiO_2 phases [8,9]. The Fe^{3+} -doped glass also has fewer peaks related to the SiO_2 phase. This proves that the bismuth- and iron-doped glasses have a larger ceramic attribute, producing physical stability to the glasses.

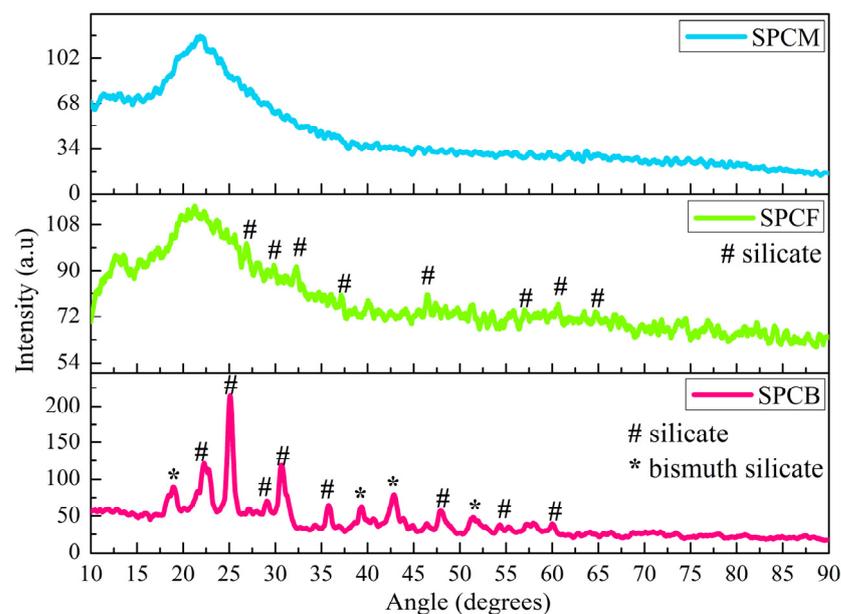


Figure 1. XRD pattern of the glasses.

3.2. FT-IR Studies

The FT-IR spectrum of the undoped silica phosphate glass is shown in Figure 2. The doped samples also exhibited similar spectra without showing the vibrations of the modifier oxides. This is due to the low proportions of the modifiers added as a dopant in the glass. The band at 3548 cm^{-1} is due to the vibrations of the hydroxyl groups. The peaks at 1632 cm^{-1} and 1336 cm^{-1} are due to the bending motions of the remanent water molecules in the glass [10]. The bands at 1108 cm^{-1} and 799 cm^{-1} are due to the asymmetric and symmetric stretching of the phosphate groups, respectively. The existence of silicate groups is confirmed by the bending motion at 450 cm^{-1} [11].

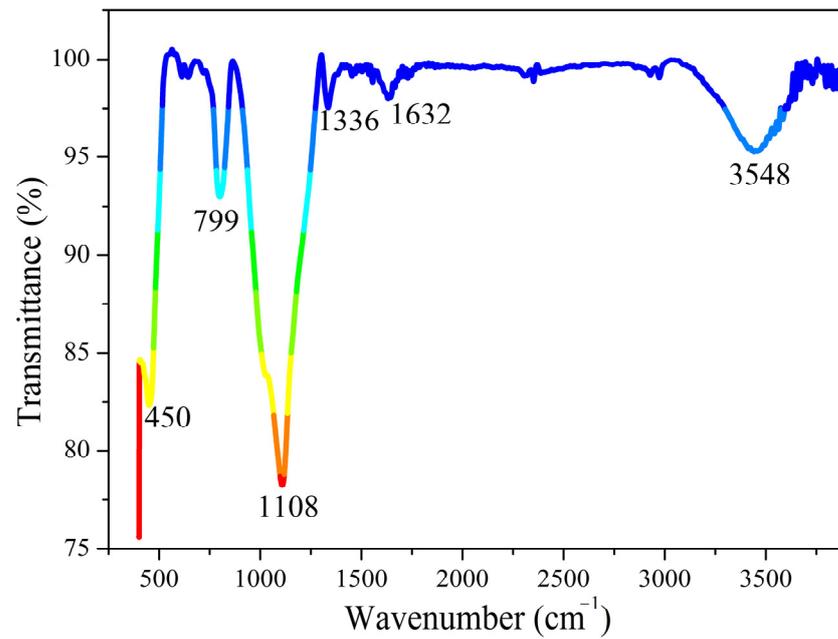


Figure 2. FT-IR graph of pure silica calcium phosphate glass (Variation of transmittance from low to high is indicated by the colors from red to blue).

3.3. Optical Studies

The absorption spectra of the samples are shown in Figure 3.

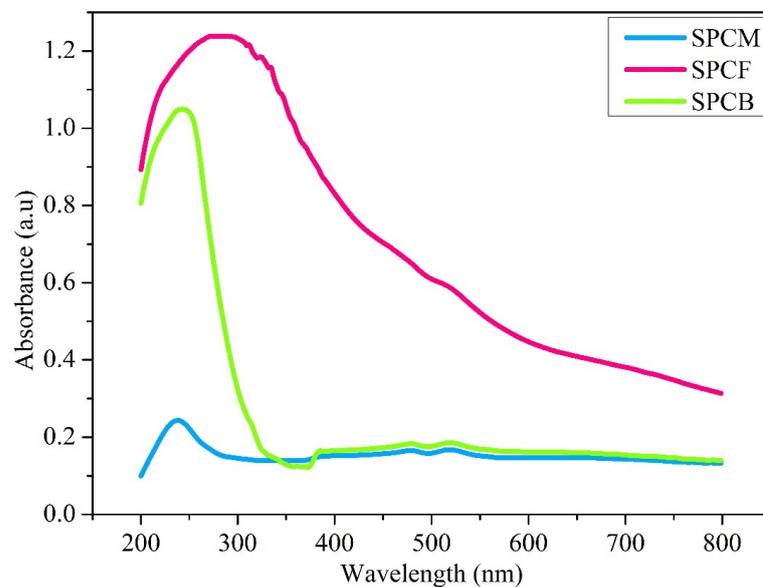


Figure 3. UV-visible absorption spectra.

The glass SPCF shows broad absorption between 200 and 400 nm in the UV region while transmitting light in the visible region. The glass SPCB has minimal absorption in the UV region and provides complete transparency in the visible region [12,13]. The Mg^{2+} -doped glass, however, shows smaller absorptions at 250 nm, 480 nm, and 520 nm in the visible region.

Tauc's plots shown in Figure 4 were used to obtain the band gap energies. The band gap and the related optical parameters were evaluated using the expressions reported [12]. The values of the band gap energy and the optical parameters of SPCM, SPCF, and SPCB are tabulated in Table 1, which agree with the reported values [12,14,15]. This shows that

the iron-doped glass approaches a semiconducting nature, while the rest of the glasses exhibit perfect insulating properties.

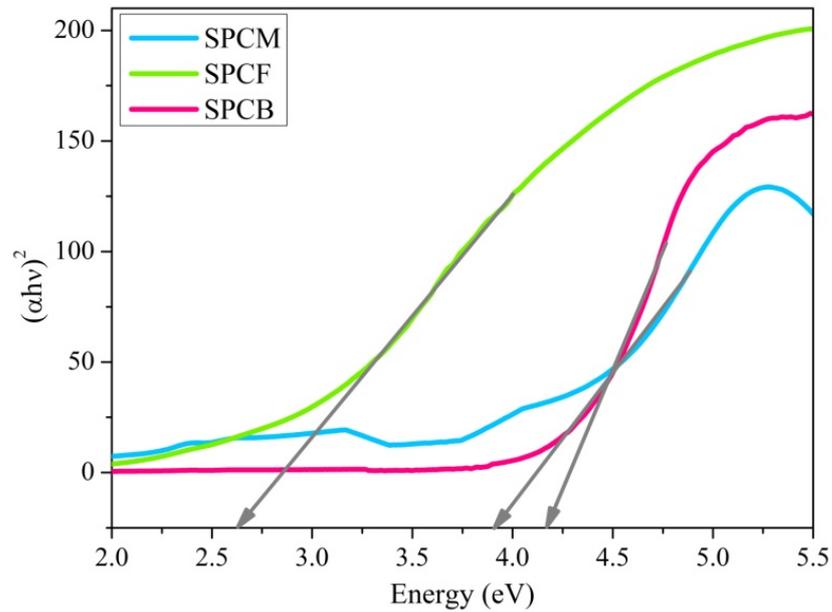


Figure 4. Tauc’s plot (The arrows from the linear fits point to the band gap energy of the respective glass material).

Table 1. Optical parameters.

Parameters/Sample Code	SPCM	SPCF	SPCB
Band gap energy (eV)	3.910	2.610	4.160
Refractive index	2.187	2.510	2.139
Dielectric constant	4.783	6.300	4.575
Reflection loss	0.139	0.185	0.132

3.4. Photoluminescence Studies

The emission spectra of the modifier oxide-doped silica phosphate glasses obtained at an excitation wavelength of 350 nm are shown in Figure 5. All the glasses demonstrated blue emissions around 410 nm, 434 nm, 450 nm, and 470 nm [13]. A prominent yellow emission at 570 nm was observed, along with a relatively low intensity of red emission at 617 nm [16]. A bluish-green emission could be observed at 490 nm in SPCM and SPCF, while it is evident at 505 nm in SPCB. The intensities of emissions in SPCM and SPCF are high, while that in SPCB is relatively low. This would prove the emissive behavior of the silica calcium phosphate glass host, which is more suitable for blue and yellow laser applications. However, the luminescence could be favorably tailored by the modifier oxides. The material could also be considered for doping with rare earth ions to enhance the luminescent behavior with and the glass formers.

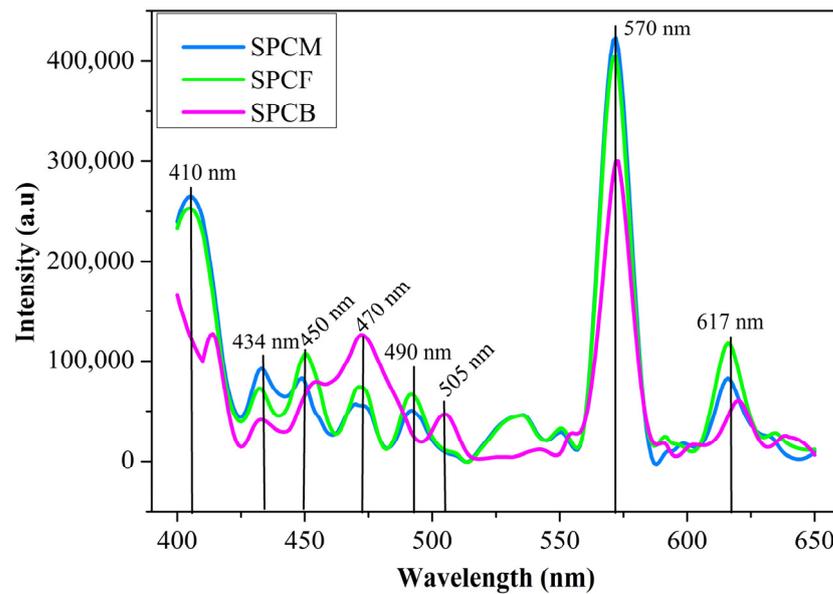


Figure 5. Emission spectra.

4. Conclusions

The silica phosphate glasses were doped using modifier oxides of Mg^{2+} , Fe^{3+} , and Bi^{3+} along with Ca^{2+} and synthesized using the sol-gel method. The XRD analysis confirmed the glass-ceramic nature when modified with bismuth, while a pure amorphous nature was observed in the magnesium-doped glass. The FT-IR analysis confirmed the existence of silica and phosphate groups in the glass material. Tauc's plots with a narrow band gap of 2.6 eV identified a near semiconducting nature for the iron-doped system while retaining an insulating trend in the bismuth- and magnesium-doped glasses. The low bandgap with higher dielectric constant, as well as enhanced UV absorption, indicate the potentiality of the Fe-doped glass for photovoltaic devices. The silica calcium phosphate glass matrix was found to be suitable for blue and yellow emissions, which could be tuned suitably for laser action by optimizing the modifier oxides and doping with rare earth ions.

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