Characterization of Ruby Color in Some Special Glass Compositions and Their Corresponding Glass–Ceramic Derivatives

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Abstract
Glasses of the system $\text{B}_2\text{O}_3 - \text{PbO} - \text{MgF}_2 - \text{P}_2\text{O}_5 - \text{SiO}_2$ containing different dopants from $\text{Cr}_2\text{O}_3$, $\text{MnO}_2$, and $\text{SeO}_2$ were prepared by the conventional melt quenching method. The prepared glasses were characterized by their ruby color caused by the effect of dopants. The amorphous nature of the prepared glasses was confirmed by x-ray diffraction (XRD). Differential thermal analysis (DTA) was used to design a heat treatment program to obtain their corresponding transparent glass–ceramic derivatives from parent glasses. Collective spectroscopic measurements were applied to evaluate the optical properties of glasses and their corresponding glass–ceramics. XRD and morphological analysis of glass–ceramics indicated the formation of two crystalline phases ($\text{PbO(B}_2\text{O}_3)_2$) and ($\text{Mg}_2\text{BO}_3\text{F}$). Optical analysis confirmed the stability of the color even after heat treatment. The chromaticity coordinates indicated a deep red color related to the chromium dopant and red wine color for selenium and manganese dopants.

Keywords Glass · optical · glass–ceramics · transition metal

Introduction
Glass materials have been of great interest since ancient times due to their special nature and unique properties. Glass has been defined as an inorganic product of fusion that has been cooled to a rigid condition without crystallization. The structural units in the crystalline materials are arranged regularly, while in the glassy states, units are arranged randomly. For instance, tetrahedral $\text{SiO}_4$ is arranged regularly in the crystalline form, while the same units are irregularly arranged in the glass state forming a random network. The random network is the basic concept in glass formation where cations that can form network-polyhedron are called network formers, while network modifiers can only break down or transform the network. $\text{SiO}_2$, $\text{B}_2\text{O}_3$, and $\text{P}_2\text{O}_5$ are the best glass formers, while alkalis and alkaline earth are the best network modifiers.

The combinations of two of these types in one melt show an increase in the tendency for glass formation. The absence of structural symmetry does not mean that glass has no structure; on the contrary, atoms in the glass network are shaped or arranged in a short-range order that is completely based on the chemical composition of the glass. The ratio of the glass network modifiers such as alkaline or alkali earth oxides to the glass formers such as $\text{SiO}_2$, $\text{P}_2\text{O}_5$, $\text{GeO}_2$, or $\text{B}_2\text{O}_3$ has a clear effect on the glass structure by polymerization of the building network. Extended rings or chains can be formed depending on the glassy network, and this arrangement directly affects the chemical and physical properties of glass. A deeper understanding of these structures can provide a means of predicting many glass behaviors, explaining the empirical results or batch glass design which represent particular useful properties such as high refractive index that can be applied in optical applications. Glasses based on $\text{SiO}_3$ formers are commonly available as commercial glasses due to the ease of fabrication and excellent transparency to visible light. On the other hand, glasses based on $\text{P}_2\text{O}_5$ formers possess several respective applications, for instance, upconversion, optical fibers, photonics, solid-state electrolytes, and biomedical applications. Like the silicate glassy networks, phosphate glassy networks are formulated from several structural
units of phosphate. Phosphate glasses can be obtained at low temperatures compared to silicate glasses.\textsuperscript{1-4} The incorporation of various glass formers yields a glass matrix with an interesting anomalous behavior in some of their chemical and physical properties. Hence, there is a characteristic effect of the melt from which the glass is produced on the resulting glass structure. Silicophosphate is a common glass containing two types of basic glass formers, and due to its scientific interest and potential applications in many domains of recent technology, it has been the subject of many investigations, such as for biomaterial applications.\textsuperscript{5,6} Glass–ceramics can be elaborated from their parent glass by crystallization. Crystallization is considered the opposite process of melting in which crystalline phases can be formed during the cooling of the melt. A controlled crystallization process can improve the mechanical properties and physical properties such as optical, electrical, magnetic, and thermal, as well as their biocompatibility over a large range of glass compositions.\textsuperscript{7} Hence, glass–ceramics have been functionalized in many applications, for instance, heat-resistant cookware, biomedical applications, magnetic memory discs, coatings, and sealing material.\textsuperscript{8} Transition metals are used in coloring glasses and enhance their optical properties. In addition, glass–ceramics containing 3d transition metal ions exhibit an interesting optical and electrical behavior than their parent glasses due to the variations in transition metal (TM) valence or coordination states.\textsuperscript{9-11} According to Min'ko and Nartsev,\textsuperscript{12} nanoparticle coloring agents such as copper, silver, bismuth, or other metals are used for coloring glasses with the aid of special heat-treatment programs. The produced glasses acquire different spectral properties depending on the size of the selected nanoparticles. For instance, silver with an average of 0–25 nm gives blue color, while size from 25 to 55 nm yields green color, and 70–80 and/or 120–130 nm can produce a brown color. They also assumed that different colors can be obtained by coloring glass by regulating the amount of colorant introduced, oxidation–reduction and temperature time-conditions of glass making, and subsequent heat treatment process.\textsuperscript{10-12}

In the course of this work, we aimed at evaluating color defects induced by additions of Cr\textsubscript{2}O\textsubscript{3}, MnO\textsubscript{2}, or SeO\textsubscript{2} to the parent glasses. It was also necessary to investigate and study defects after heat treatment to the parent glasses. The parent glasses and their corresponding glass–ceramics were investigated through collective spectroscopic analysis including XRD, DTA, scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet–visible (UV–Vis) absorption, optical spectrometry, and band gap. Color defects induced by crystallization or transition metal type were estimated according to the CIE1931 chromaticity diagram.

### Materials and Methods

#### Glass Preparation

The prepared glasses are based on the host chemical compositions B\textsubscript{2}O\textsubscript{3}-PbO-MgF\textsubscript{2} together with a minor percentage of SiO\textsubscript{2} and P\textsubscript{2}O\textsubscript{5}. The glass was prepared from pure chemical laboratories including orthoboric acid H\textsubscript{3}BO\textsubscript{3}, Pb\textsubscript{3}O\textsubscript{4}, MgF\textsubscript{2}, SiO\textsubscript{2}, NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}, and selected transition metal ions (Cr\textsubscript{2}O\textsubscript{3}, SeO\textsubscript{2}, and MnO\textsubscript{2}) were added as such. Batches of about 25 g were melted in covered porcelain crucibles in a SiC electric furnace (Vecstar, UK) at 1100 ± 10°C for 60 min. The melts were rotated every 15 min to reach complete mixing and homogeneity. The melts were poured into preheated stainless steel molds with the required dimensions at an annealing temperature ≈ 350°C. The poured glasses were immediately transferred to an annealing furnace regulated at 350°C. The annealing muffle was switched off after 1 h with the glassy samples inside and left to cool to room temperature at a rate of 30°C/h.

#### Measurements

The UV–visible spectra were measured for perfectly polished samples of equal thickness (2 ± 0.1 mm). A recording double-beam spectrophotometer (Jasco, V-630, Japan) was used covering the range from 200 nm to 1100 nm at room temperature.

The differential thermal analysis (DTA) of powdered glasses was measured by an SDTQ600 under N\textsubscript{2} gas. The results of DTA were applied to conduct a controlled crystallization process of the glassy samples.

The prepared samples were examined by x-ray diffraction to confirm their amorphous nature. X-ray diffraction was carried out using a Bruker AXS diffractometer (CD8-ADVANCE) with Cu-K\textalpha radiation, operating at 40 kV and 10 mA. The diffraction data were recorded for 2θ values between 4° and 70°, and the scanning rate was 10°/min.

The morphological textures of the prepared glass–ceramics were detected employing high-resolution scanning electron microscopy (HSEM), on a Quanta Field Emission Gun (FEG) 250 (FEI Company), and high-resolution transmission electron microscopy (HRTEM) on a Philips XL30 attached to an EDX unit, using an accelerating voltage of 30 kV, magnification 10 × up to 400,000 × and wavelength resolution of 3.5 nm.

#### Results and Discussion

Figures 1–3 illustrate the UV–visible absorption spectra of three glasses and their corresponding glass–ceramics from the system based on the glass co-doped with chromium or selenium/manganese. The base undoped glasses (Fig. 1)
reveal characteristic ultraviolet absorption peaks centered at about 242, 324, and 355 nm. The observed UV absorption spectra may be attributed to the trace ferric impurities in the chemicals that are used in glass preparations. The previous assumption was proposed by many previous studies that concluded the sharp UV absorption is correlated with the charge transfer of transition metal impurities that were present during the glass preparations (e.g. Fe$^{3+}$ or Cr$^{6+}$). Therefore, the appearance of the sharp UV absorption peaks in the parent glasses or the other co-doped glasses can be attributed to the presence of Fe$^{3+}$ ions.

The absorption spectra of Cr$_2$O$_3$-doped glasses and their corresponding glass–ceramics are given in Fig. 2. Both spectra exhibit two prominent absorption peaks at 473 and 630 nm. The observed absorption peaks can be attributed to Cr$^{3+}$ (3d) transition states. The absorption peak centered at 473 nm can be attributed to the spin allowed forbidden transition $4A_2(F) \rightarrow 4T_1(F)$ of trivalent chromium octahedral building units, while the peak centered at 630 nm is attributed to $4A_2(F) \rightarrow 4T_2(F)$ transition of Cr$^{3+}$ ions at low-field sites in six-coordinate bonding sites. The absorption peaks centered in the near IR range 600–900 nm are also attributed to Cr$^{3+}$ ions of $3T_1$ transition when overlapping with the $4T_1$ peak of Cr$^{3+}$ octahedral centers. Figure 3 represents MnO$_2$/SeO$_2$-doped glass and glass–ceramics that depicts a spectrum with a characteristic ultraviolet absorption peak at 374 nm followed by a characteristic broad visible peak centered at 508 with no other peaks to the end of measurements. The identified peaks within the spectra indicated that manganese ions exist as trivalent and divalent oxidation states. The characteristic trivalent (Mn$^{3+}$) ions have an identifiable visible peak at 506 nm.

The optical band gaps of the prepared glasses were calculated using the formula of Mott and Davis as follows:

\[ a(h\nu) = B(h\nu - E_{\text{opt}})^n \]  

where $E_{\text{opt}}$ is the optical band gap, $B$ is a constant and $n$ is an index that takes values of 1/2, 3/2, 2, and 3 according to the electronic transition. For direct-allowed and forbidden transitions $n$ will take values 1/2 and 3/2, respectively, while for the indirect-allowed and forbidden transition $n$ will take values 2 and 3, respectively. Hence, the $E_{\text{opt}}$ value can be determined from the linear portion of the plot between $(a(h\nu))^n$ and $1/(h\nu)$.
In the current study, a straight line is obtained when solving Eq. 1 with \( n = 2 \) for all the prepared samples and this linearity indicates the indirectly allowed transitions. Figure 4a, b, and c depicts the linear plot of \( (a\nu)_{1/2} \) versus \( (\nu) \) for undoped and \( \text{Cr}^{3+} \) or \( \text{Mn/Se} \) prepared glasses together with their heat-treated samples at 550°C/3 h. Glassy samples show optical band gap values equal to 2.76, 2.26, and 2.99 eV, while the heat-treated samples show optical band gap values of 2.58, 2.24, and 2.96 eV respectively. The heat-treated samples show a characteristic decrease in the band gap values than those of their parent glasses. According to previous studies, the observed variation in the optical band gap could be correlated to the nature of dopant metal ions. The main reason for this variation is related to the ability of metal ions to form non-bridging oxygen in the glass network that decreases with the addition of modifiers, while the characteristic observed decrease in the optical analysis of the heat-treated samples is due to the disorder decrease in the glass network due to the addition of transition metal ions.

Estimation of the color chromaticity coordinates was carried out applying the CIE1931 chromaticity diagram from three dimensionless quantities \( \bar{x}(\lambda) \), \( \bar{y}(\lambda) \), and \( \bar{z}(\lambda) \) as follows;

\[
X = \int P(\lambda)\bar{x}(\lambda) d\lambda
\]  
\[
Y = \int P(\lambda)\bar{y}(\lambda) d\lambda
\]  
\[
Z = \int P(\lambda)\bar{z}(\lambda) d\lambda
\]

where \( X \), \( Y \), and \( Z \) are the tristimulus values that matched with the three primary red, green, and blue colors. From the tristimulus values the color chromaticity coordinates \( x \) and \( y \) can be determined using the following expression:

\[
x = \frac{X}{X + Y + Z}
\]  
\[
y = \frac{Y}{X + Y + Z}
\]  
\[
z = \frac{Z}{X + Y + Z}
\]

CIE chromaticity coordinates of the prepared glasses together with different color additions after heat treatment at 550°C/6 h with a heating rate of 5°C/min are shown in Fig. 5. It was calculated by using the chromaticity coordinate calculation method based on the CIE1931 (Commission International de l’Eclairage France) system. Chromium, selenium, and manganese act as coloring agents in the prepared glasses. The CIE chromaticity diagram was applied as a helpful tool to detect the actual represented color in each glass sample.
The color coordinates indicated noticeable deep red color for chromium dopant while wine red for selenium and manganese dopants. The observed colors are matched with those that appeared in the photographic (Figs. 1–3). Variations in the shining of the red color can be assigned to the effectiveness of transition metal type, in addition to the coordination state for each one as assumed in previous studies.\textsuperscript{23,24}

Figure 6 represents the DTA data of the main parent undoped glass. The Figure shows a characteristic endothermic peak at about 421°C and a sharp exothermic peak centered at 552°C with an extended additional peak at 645°C. The obtained DTA results can be referred to as the nucleating effect of MgF\textsubscript{2}. It was assumed by many authors\textsuperscript{27–29} that, the addition of MgF\textsubscript{2} to the glass batch can lower the thermal behavior of glass that is correlated to the voluminous nucleation and crystallization of the glass matrix.

Figure 7 represents the x-ray diffraction patterns of the formed glass samples. The analysis of XRD data indicated that no characteristic crystalline phase was detected which reveals the pure amorphous phase of the prepared glasses.

Figure 8 represents the x-ray diffraction of the prepared glass–ceramics after heat treatment at 550°C for 6 h. The obtained results indicate the formation of two characteristic crystalline phases. The formed crystalline phases consist of two phases that correspond to lead oxide borate (PbO(B\textsubscript{2}O\textsubscript{3})\textsubscript{2}) card no. 84–2152 and magnesium fluoride borate (Mg\textsubscript{2}BO\textsubscript{3}F) card no. 19–0753. The XRD data indicated that MgF\textsubscript{2} acts as a nucleating agent in addition to the contribution to B\textsubscript{2}O\textsubscript{3} to form the magnesium fluoride borate crystalline phase that matched with a previous study.\textsuperscript{30} In addition, many studies assumed that\textsuperscript{31–33} the presence of MgF\textsubscript{2} allows the phase separation process in glass matrix; moreover, its nucleating effect leads to the formation of different phases of borate and lead such as in the current studied glasses.

Figure 9 depicts the analysis of the morphology of the corresponding glass–ceramics by transmission and scanning electron microscopy. All samples contain crystals imbedded in the glass matrix. Figure 10 depicts the 3d distributed crystalline structure of PbO(B\textsubscript{2}O\textsubscript{3})\textsubscript{2} and Mg\textsubscript{2}BO\textsubscript{3}F, respectively. The induced crystalline phases from the parent lead borate glass after heat treatment are based on the nucleating agents. The addition of MgF\textsubscript{2} gives an effective role in the nucleation process leading to the formation of two different phases of borate crystalline species.\textsuperscript{27,30,34–36}
Conclusions

Three main glass compositions from $\text{B}_2\text{O}_3$–$\text{PbO}$–$\text{MgF}_2$–$\text{P}_2\text{O}_5$–$\text{SiO}_2$, $\text{Cr}_2\text{O}_3$-doped $\text{B}_2\text{O}_3$–$\text{PbO}$–$\text{MgF}_2$–$\text{P}_2\text{O}_5$–$\text{SiO}_2$, and $\text{MnO}_2$/$\text{SeO}_2$-doped $\text{B}_2\text{O}_3$–$\text{PbO}$–$\text{MgF}_2$–$\text{P}_2\text{O}_5$–$\text{SiO}_2$ were prepared by conventional melting and annealing. The prepared glass contained varying degrees of ruby red color depending on the type of dopant. Differential thermal analysis was applied to design the heat-treatment program for converting the parent glass into their corresponding glass–ceramic. Also, x-ray diffraction was used to verify the amorphous nature of the parent glasses and detection of the formed crystalline phases in the glass–ceramic samples. The formed phases after heat-treatment were $\text{PbO(BO}_3)_2$ and $\text{PbO(BO}_3)_2$ and confirmed with morphological analysis by SEM and TEM. The addition of $\text{CaF}_2$ was effective in the nucleation process leading to the formation of two different phases of borate crystalline species. The observed UV absorption spectra are correlated to the charge transfer of transition metal impurities that were present during the glass preparations and the absorption spectra of $\text{Cr}_2\text{O}_3$-doped glasses and its corresponding glass–ceramics revealed an absorption peak at 473 nm assigned to $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{F})$ of trivalent chromium octahedral building units and a peak at 630 nm assigned to $^4\text{A}_2$ (F) $\rightarrow ^4\text{T}_2$ (F) transition due to $\text{Cr}^{3+}$ (3d) transition states. The optical band gap values of glass–ceramic derivatives show a characteristic decrease compared to those of their parent glasses due to the disorder decrease in the glass network as a result of transition metal ion additions. The color coordinates indicated noticeable deep red color for chromium dopant and red wine for selenium and manganese dopants. Variations in the intensity of the red color can be assigned to the effectiveness of the
transition metal type, in addition to the coordination state for each one. XRD data indicated that no characteristic crystalline phase was detected which reveals the pure amorphous phase of the prepared glasses. The heat-treated samples at 550°C for 6 h indicated the formation of two characteristic crystalline phases that correspond to lead oxide borate (PbO(B₂O₃)₂) card no. 84–2152 and magnesium fluoride borate (Mg₂BO₃F) card no. 19–0753. MgF₂ acts as a nucleating agent in addition to contributing to B₂O₃ to form the magnesium fluoride borate crystalline phase.

Fig. 10 Crystalline structure of the formed phases: (a) PbO(B₂O₃)₂ and (b) Mg₂BO₃F phase.

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