



# Nanocrystalline glass ceramics: Structural, physical and optical properties



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## HIGHLIGHTS

- Effect of transition ions on nanocrystalline phase formation in glass ceramics.
- Correlation of structure and properties of glass ceramics.
- Higher content of ZnO increases the optical band gap.

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## ABSTRACT

Four different transition metals contained nanocrystalline glass ceramics are synthesized by melting and quenching technique. The transition metal oxides play as former, modifier or both the roles depending on their oxidation states, field strength and covalent characteristics. The optical band gaps are observed in the range of 3.2–5.5 eV. The presence of nano-crystalline phases dominates the optical band gap. The softening temperature ( $T_s$ ) is mainly affected by the residual glass in glass ceramics. These glass ceramics can be used as shielding materials for nuclear waste.

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## Introduction

Glasses and glass ceramics are an important class of materials and exhibit very attractive properties [1,2]. These materials are being used in aerospace industry, telecommunications, photonics, solid oxide fuel cells, waste materials management and medical applications, etc. [3]. Structurally, glassy materials lack the long range order. However, they maintain the short range order at the local level. The lack of grain boundaries makes most of the glasses to be transparent, which leads to lots of applications. The local structure of the glasses, many times can be changed according to the desired properties by employing some compositional changes or by some other means, like by developing some crystalline phases by controlled heat treatment of the glass i.e. glass ceramics. The presence of crystalline phase in the glass matrix significantly changes the molecular structure and subsequently the other properties of glass. The properties of the glass ceramics depend upon the glass matrix composition and also on the kind and amount of the crystalline phase present in the glass matrix [4]. Glasses and

glass ceramic materials generally absorb electromagnetic energy in the ultraviolet and infrared region due to the electronic transitions in interior molecules and molecular vibrations, respectively. Widely varying optical characteristics of the glass and glass ceramics are further tailored when elements from transition series are included in the glass composition. In general, these properties are associated with variable oxidation state of the transition elements [5–7]. Actually, the different oxidation states of the elements exhibit different field strengths. The changes in field strength of the cation causes modification to the glass network and properties [8]. In addition to this, the field strength of the cation affects the polarization of its neighboring ions, which in turn affects their interaction with light. Glasses, usually consist of three components, namely, glass formers, modifiers and intermediates. The incorporation of the network modifier, like alkali and alkaline earth metal oxides, into the glass, leads to a wide range of different structural configuration possibilities along with unique physical properties [3]. Network modifiers create non-bridging oxygens (NBOs) in the glass network. The amount of these negatively charged NBOs plays a crucial role in determining the optical, thermodynamic and structural properties of glass and glass ceramics [9]. Not only alkaline and alkaline earth metal oxides, but oxides

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of the transition elements also act as a modifier or former depending upon their valence state, amount and initial composition [10,11]. Many studies have reported the effect of different transition metals on the formation of the glass and glass ceramics and their properties [12–14]. Apart from this, lots of studies have been carried out to investigate the optical properties of nanocrystalline ZnO, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>. However, the nano particles of these transition elements required some capping agents to prevent the agglomeration for their application. So, in the present case, high contents of TiO<sub>2</sub>, ZnO, MnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> were taken purposely, so that, they can act as nucleating agents and increase the tendency to form nanocrystalline phases in the glassy matrix. In this situation, glass matrix will act as a capping agent. The objective of the present study is to investigate the effect of different transition metal oxides on structural, physical, thermal and optical properties of nanocrystalline phases contained glass ceramics. Additionally, the selection of these transition metal oxides is based on their initial valence states. The transition metal cations are taken by their decreasing valence states such as Ti<sup>4+</sup>, Mn<sup>4+</sup>, Fe<sup>3+</sup> and Zn<sup>2+</sup> in four different compositions. Moreover, their field strength decreases with increasing covalent bond characteristic. Therefore, it is worthwhile to study the effect of their valence states, change in covalent characteristics and electronegativity on glass formation, physical, thermal, structural and optical properties.

In the present study, glass ceramic samples with composition 45SiO<sub>2</sub>–25CaO–10Na<sub>2</sub>O–5P<sub>2</sub>O<sub>5</sub>–15TO, where TO = TiO<sub>2</sub>, MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and ZnO were prepared using the melting and quenching technique. The structural investigations of the as prepared samples were carried out using X-ray diffraction, Fourier Transform Infrared Spectroscopy (FTIR) and dilatometry. The optical parameters were calculated from the absorption spectra obtained using UV–visible spectroscopy. Observed characteristics were correlated in the light of field strength, polarization power of the transition metal cations and the structural modifications by the addition of transition elements.

## Materials and methods

Glass samples were prepared by melting and quenching technique. Raw materials in the form of oxides and carbonates were taken as SiO<sub>2</sub>, CaO, Na<sub>2</sub>CO<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, MnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and ZnO (Loba Chemie, ≥99% Pure). The compositions (mol%) and their label are given in Table 1. The chemicals were grounded in an agate mortar pestle for 1 h in an acetone medium. After grinding, the mixtures were put in a recrystallized alumina crucible and melted at 1550 °C in a programmable electric furnace. The melt was held at this temperature for 1 h to get bubble free and homogeneous melt. This melt was air quenched between two thick copper plates. As quenched samples were crushed into the powder form for the characterizations. The density of the quenched samples was measured by Archimedes' principle in xylene using a sensitive microbalance. The least count of the balance was 0.01 mg. Density is the simplest measurable physical quantity of any solid material. It gives valuable information about the structure of the given material. The density of the samples is calculated as follows:

**Table 1**  
Compositions of the samples along with labels.

Label	SiO <sub>2</sub>	CaO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	MnO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	ZnO
15-T	45	25	10	5	15	0	0	0
15-M	45	25	10	5	0	15	0	0
15-F	45	25	10	5	0	0	15	0
15-Z	45	25	10	5	0	0	0	15

$$\rho_{\text{Sample}} = \frac{W_a}{W_a - W_x} \times \rho_x \quad (1)$$

where  $\rho_{\text{Sample}}$  is the density of the sample,  $\rho_x$  is the density of xylene at 30 °C,  $w_a$  is the weight of the sample in air and  $w_x$  is the weight of the sample in xylene. Density of xylene is 0.863 g/cc at room temperature.

The amorphous nature of the samples was studied using X-ray diffraction patterns on PANalytical X'Pert PROX-ray diffractometer with Cu K $\alpha$  radiations ( $\lambda = 1.54 \text{ \AA}$ ). During the experiment the step size was 0.017° and scan rate was  $\sim 3^\circ \text{ min}^{-1}$ . Infrared spectroscopy can be employed to acquire deeper insight of the structure of the glasses. Information about the competitive roles played by each oxides in the glass network was investigated by analyzing the FTIR spectra of the present samples. Perkin Elmer-Spectrum-RX-IFTIR spectrometer was used to record Fourier Transform Infrared (FTIR) in the range 450–4000 cm<sup>-1</sup>. Powdered samples were mixed with KBr and the recorded spectrum was normalized to the spectrum of KBr. The softening temperature of all glass ceramics was measured by horizontal type dilatometer (DIL402PC, Netzsch) with 5 °C/min heating rate in the air. UV–visible absorption spectra of the samples were obtained using Hitachi U-3900H UV–visible spectrophotometer in the spectral range of 200–800 nm. To obtain the absorption spectra, the powder samples were dissolved in 38% HCl, which was diluted further 10 times before sonication for 20 min. Contribution of HCl part was nullified for each sample by normalizing it to the base dilute HCl spectra.

## Results and discussion

### Density and molar volume

Apparent densities of the glass ceramics are given in Table 2. The density of the samples depends on the densities of its individual constituent [3]. However, in the case of glasses and glass ceramics, many other factors also marginally influence the final density of the sample. Some of these factors include the thermal history of the sample, measurement temperature, crystallization, creation of NBOs, the field strength of the modifier, etc. Molecular weights of the intermediate oxides, in the present compositions, follows as TiO<sub>2</sub> < ZnO < MnO<sub>2</sub> < Fe<sub>2</sub>O<sub>3</sub>. The density of the samples should have followed the similar trend, but 15-Z was found as an exception in the present study, as shown in Table 2. The density of the 15-Z is greater than the 15-M sample. This can be explained on the basis of the fact that the addition of divalent cations (Zn<sup>2+</sup>) forms higher NBOs than other intermediate oxides. It is reported that the breaking of the glass network by the modifier increases the compactness of the glass. Secondly, the XRD patterns clearly indicate that the 15-Z sample has a higher degree of crystallinity as compared to the 15-M sample. As crystalline ordering increases in any system, the compactness of the network also increases and leads to an increase in the density of the system [15]. 15-F, containing iron oxide, is the densest sample among the present series. On the other hand, 15-T sample due to the lowest molecular weight in all the intermediate oxides has the lowest density.

The structure of the glass and glass ceramic samples can be explained in terms of molar volume as it represents the spatial distribution of the ions that form the structure. Molar volume can be calculated using the following equation:

$$V_m = \frac{M}{\rho} \quad (2)$$

where  $M$  is the molecular weight and is the density of the sample.  $V_m$  represents the volume in the space occupied by one mole of the sample. The molar volume depends on  $M$  and  $\rho$ , so as molecular weight and density of the samples among the present series do not

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