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Photocatalytic study on $SrBi_2B_2O_7$ ($SrO\text{-}Bi_2O_3\text{-}B_2O_3$) transparent glass ceramics

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ABSTRACT

$SrO\text{-}Bi_2O_3\text{-}B_2O_3$ transparent glass ceramic was fabricated via conventional melt-quenching technique. Structural analysis like X-ray diffraction, Raman and Fourier transform infrared spectroscopies were performed to confirm SBBO glass ceramic formation. As-quenched glass samples exhibited X-ray diffraction peaks corresponding to $SrBi_2B_2O_7$ which were further confirmed through Field Emission Scanning Electron Microscope. UV–vis transmission spectra revealed 60%–80% transparency in 500–800 nm spectral range. Absorption study revealed direct bandgap of 2.58 eV. Resazurin (Rz) ink was used as an indicator to monitor photocatalytic activity for self-cleaning purposes. Digital photographic method was performed to examine photoreduction of Rz ink. Further, the pseudo-first order kinetics was istimated for Methylene blue (MB) degradation. Nucleation of nanoparticles of $SrBi_2B_2O_7$ over glass surface were found responsible for photocatalytic activity. Contact angle with water droplet for SBBO glass ceramic was 63.43°. Reduced Young's modulus (E_r) and Vickers hardness (H_v) were found 59.9 GPa and 5.01 GPa, respectively.

1. Introduction

Now a day's photocatalytic materials are extensively endorsed for self-cleaning purposes. Several metal oxides like TiO_2, ZnO, WO_3, V_2O_5, SnO_2 and numerous perovskite similar to $SrTiO_3$, $K_2La_2Ti_3O_{10}$, $La_2Ti_2O_7$ and many other materials are known for photocatalytic activity [1–6]. While using the photocatalytic material in its powder form, during pollutant degradation under waste water treatment, it gets drained out or settle down in the bottom, where sun light never reaches. Some other disadvantages associated with powder are the energy loss during stirring for dispersion of powder to get enhance photocatalytic activity as well as the separation of powder from waste water after the photocatelytic treatment. Monetarily, separation of photocatalytic powder after waste water treatment is essential for using it multiple time. On the other side without separation, powder contamination behave as intrusion of new pollutant [7]. Therefore, to evade the disadvantage of powder, researchers are exploring to integrate the photocatalytic powder with tiles, glass, block, paints and cement matrices [8,9]. At the moment, TiO_2 coated as thin films over glass or tiles are frequently utilizing for self-cleaning function [10]. Already several self-cleaning automotives, building materials, windows and solar panels are in use [11]. However, still several other disadvantages are observed with the above mentioned integration of photocatalytic material with different matrix: (1) quantum efficiency of powder reduces very much after integration with any matrix (2) photocatalytic material start to leach out from the matrix during sanitation and (3) mostly commercialized photocatalytic materials are UV active [12–14].

In this context, photocatalytic glasses could be the possible solution. Usually amorphous glass does not show any photocatalytic properties. It is only possible by appropriate selection of glass compositions and the controlled crystallization which having photocatalytic activity and known as photocatalytic glass ceramics. In addition to the photocatalytic properties, enclosing transparency in glass ceramics are found suitable for the effective technological elucidation with easy fabrication of bigger photocatalytic panels and reactors in any shape and size at large scale [15]. One can control the transparency in glass-ceramics by controlled crystallization with comparable refractive index of glass and crystal phases. To obtain transparent glass ceramics, the size of nucleated crystals in glass must be remain in nanorange. Most prominently, inbuilt photocatalytic nanocrystals in transparent glasses is an effective alternative which will evade coating and leaching issues of material during sanitation with easy handling and low cost maintenance of the system developed for the function under crucial weather condition such as hot, cold, humid or dust prone environments intended for the removal of pollutants [15].

In glass matrix, size of growing crystals mainly depend on the glass compositions and its heat treatment [16–18]. By now few limited glass ceramics like; $(70B_2O_3–29Bi_2O_3–1Dy_2O_3)–x(BaO–TiO_2)$,

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$20WO_3$–$50ZnO$–$30B_2O_3$, (42-x)P_2O_5–$8MgO$–$50ZnO$–xTiO_2, $70TiO_2$–$30P_2O_5$, and SnO added CaO–B_2O_3–Bi_2O_3–Al_2O_3–TiO_2 are reported with crystallization of nanocrystals with transparency, photocatalytic activity and self-cleaning property [7,18–21]. Paramesh et al. fabricated transparent colourless BaO–TiO_2–B_2O_3 glasses having nanocrystalline phase of TiO_2 with 5–15 nm size [17]. Bulk crystallization of α-$ZnWO_4$ nanocrystals with a diameter of ~10 nm is demonstrated in 20 WO_3–$50ZnO$–$30B_2O_3$ glass [18]. Photocatalytic activity in 20 WO_3–$50ZnO$–$30B_2O_3$ glass is reported due to α-$ZnWO_4$nanocrystals.Ismail et al.reported self-cleaning properties in (42-x)P_2O_5–$8MgO$–$50ZnO$–xTiO_2 glass ceramic accompanied with TiO_2 nanoparticles [19]. Crystallisation was achieved and their photocatalytic activity was examined by adding SnO in CaO–B_2O_3–Bi_2O_3–Al_2O_3–TiO_2 glass, Masai et al.demonstrated the nucleation of rutile TiO_2 nanocrystals with higher photocatalytic activity [21]. Fu et al. grown crystalline phases of nasicon-type crystals, $MTi_4(PO_4)_6$ or $RTi_2(PO_4)_3$ in MO–TiO_2–$P2O_5$ (M = Mg, Ca, Sr and Ba) and R_2O–TiO_2–P_2O_5–SiO_2 (R = Li, Na and K) glasses, respectively [22]. Thus, crystallized transparent glasses have a huge prospective for application as photocatalytic materials and self-cleaning purposes.

Incidentally, few resent studies show Bi-based compounds like oxides, halides or oxyhalides having quick and effective visible light active photocatalytic performances than TiO_2 [23]. However, their counterpart glasses and glass ceramics have not been explored for photocatalyst activity explicitly. This article reports simple and effective way to introduce photocatalytic properties on SrO-Bi_2O_3-B_2O_3 (SBBO) glass surface. Selection of glass for the photocatalytic applications was due to the exceptional formability with high mechanical strength and its stability. This composition has not been investigated neither in crystal or glass-ceramics forms for photocatalytic applications. In this work, SBBO transparent glass ceramic with $SrBi_2B_2O_7$nanocrystalshave prepared. The photocatalysis of Rz ink over SBBO glass ceramic is performed to quantify self-cleaning activity which is reported in subsequent sections.

2. Experimental

SrO-Bi_2O_3-B_2O_3(SBBO) transparent glass ceramic was prepared by conventional melt quench technique. Sr, Bi and B constituents of SBBO glass were obtained in accordance to their molar ratio from$SrCO_3$, Bi_2O_3 and H_3BO_3precursors, respectively. All materials were of analytical grade. First, appropriate amounts of each precursor were thoroughly mixed in agate mortar-pestle for 30 min. For homogeneous mixing, again the whole mixture was transferred to a jar which belongs to the ball mill. Agate jar was containing 20 balls. Acetone was used as a mixing medium. Mixing of the material was done for 5 h at 200 rpm. The mixture was then poured in a platinum crucible and placed in a Nabertherm furnace for melting at 1000 °C. At last, melt was quenched on a stainless steel plate which was preheated at 200 °C. This process produced as mooth and transparent yellowish thin glass plates which further annealed at 200 °C for 5 h to remove the thermal stress presented in the glasses.

The resazurin (Rz) self-cleaning indicator ink was prepared by previous reported method. 5 mg of Rz dye (75% Na salt) was mixed with 10 g of a hydroxyethyl-cellulose (HEC) solution (1.5 wt% aqueous), 1 g of glycerol and 10 mg of Tween 20 surfactant. To investigate the photocatalytic performance of the SBBO as quenched transparent glass ceramic, the resazurin (Rz) indicator ink was used as a pollutant. Approximately equal amount of resazurin (Rz) ink was coated over SBBO transparent glass. Before starting the experiment, glass sample with the coated surfaces were subjected under 420 nm light irradiation such that it become fully exposed to the light. The photocatalytic reduction process of resazurin (Rz) ink was initiated by exposing the glass sampleunder 420 nm light irradiation. At different time intervals, we removed the glass sample and obtained its real time images by using digital optical camera.

To investigate the photocatalytic activities of as-quenched SBBO glass ceramic the solution of hazardous Methylene blue (MB) in deionized water with concentration 5 ppm was used. SBBO glass ceramic plate of 1 cm^2 size was immersed into 10 ml of MB solution, separately. Before photocatalytic experiment, to attained equilibrium of adsorption-desorption process SBBO glass ceramic plate dipped in MB solution was subjected under dark for 6 h and monitored at specific time intervals. Photocatalytic experiment was performed in a chamber with Hitachi FL8BL-B light tubes having maximum emission of 420 nm and intensity of 3200 lx. During photocatalytic degradation samples were exposed to 420 nm light irradiation and examined at a different time intervals.

SBBO transparent glass ceramic was characterized by X-ray diffraction (XRD) using a 9 kW rotating anode (Cu Kα) based Rigaku powder diffractometer. Samples were scanned with the scan rate of 2°/min in the scanning range (2θ) starting from 10° to 80°. Raman scattering was performed on HORIBA (Model-Lab RAM HR Evolution) with a grating of 1800 lines/mm and a Peltier cooled charge coupled device (CCD) detector working at −60 °C. The green laser (535 nm) was adopted as the excitation source. A microscope from HORIBA (Model-LabRAM HR Evolution) was attached with the spectrometer that focuses the laser light onto the sample. The LabSpec-6 software was used for data collection. The micrographs were recorded with FE-SEM Inspect™S50. Optical absorption as well as band gap calculation was estimated by using double beam UV–vis spectrophotometers SHIMADZU-2450. The contact angle was measured with a Ramé-Hart Goniometer model 250. FTIR spectra was obtained by using Model no. K8002AA, Agilent Technologies. Nano indentation was performed using Hysitron Tribo indenter T1950 with Berkovich diamond indenter @ loading rate of 200 μN/s.

3. Results and discussion

Fig. 1(a–c) shows the XRD pattern, Raman spectra and FTIR transmittance spectra of as- quenched SBBO glass ceramic, respectively. The X-ray diffraction shown in Fig. 1(a) confirms the existence of few broad as well as sharp peaks in as-quenched glass ceramic plates. Presence of broad peaks bellow 2θ at 25° confirms glass formation. While, overall diffraction pattern clearly reveals the crystallisation in the sample. The 2θ position of all observed sharp peaks matches well with the diffraction peaks corresponding to (004), (113), (006), (306), (413), and (103) planes of $SrBi_2B_2O_7$(JCPDS file no. 60-0269). It is important to note that it was desirable to have only glass phase after quenching which was not noticed as we noticed sharp diffraction peaks in XRD. In order to avoid crystallization in glasses, we could perform quenching from higher temperature (above 1000 °C). However, as bismuth starts evaporation above 1000 °C, we could not perform melting at higher temperature. Instead the 2θ position, XRD peak intensity of sharp peaks of $SrBi_2B_2O_7$ reported in literature as well as in JCPDS file no. 60-0269 discloses an anomaly in present glass ceramic sample [24]. Peak at 41.28° for (006) plane shows enormously high intensity, relatively. When we anneal the sample at 400 °C for 12 h the intensity of the peak for (006) plane restrain, relatively (Not shown here). After annealing, the XRD peak intensity ratio in present glass ceramic sample almost matches with the reported XRD peak intensity ratio. This anomaly in peak intensity is due to the crystallisation of $SrBi_2B_2O_7$ crystals in SBBO glass matrix which could be grown as isolated crystallites in glass matrix with preferred orientation along (006) plane on the surface of the sample [24].

Raman spectra for SBBO transparent glass ceramic sample obtained in the range of 50–1500 cm^{-1}at RT, shown in Fig. 1(b). Raman scattering is a flexible technique for fast and non-destructive study to evaluate crystalline as well as amorphous nature present in the lattice. In present case, Raman spectrum for SBBO glass ceramic shows broadening for all bands in 50–1500 cm^{-1} range. Usually the broadening in glass samples is because of the structural disorder. The present Raman modes in SBBO glass ceramic are well matched with the