

Synthesis and characterization of indium-borate glass-ceramic containing $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ via an incorporation method

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Glass in the system $5\text{In}_2\text{O}_3.94\text{Na}_2\text{B}_4\text{O}_7$ was fabricated via a melt quenching technique. The amorphous nature of the quenched glass was confirmed by X-ray powder diffraction. The infrared spectrum shows no boroxol ring formation in the structure of this glass. Differential thermal analysis shows a glass transition temperature of 696 °C and a crystallization temperature of 1151 °C. A cerium–zirconium mixed oxide $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ and Eu-doped cerium-zirconium mixed oxide were obtained by a solid-state method. Then the glass powder and Eu-doped cerium-zirconium mixed oxide were mixed. The mixture was heated in a crucible. The glass-ceramic sample was obtained by pouring the melts onto stainless steel plates. The samples obtained were annealed at 450 °C for 1 h to remove the thermal strain. Gas phase catalytic oxidation of toluene was studied over these nanostructures. The results showed that the catalytic activity of $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ was higher than $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ for conversion of toluene. Differential thermal analysis for a glass-ceramic sample shows a glass transition temperature of 648 °C and a crystallization temperature of 1134 °C. A scanning electron microscopy study of the glass-ceramic indicates that the crystallized glass consists of crystals with an average diameter of about 86 nm dispersed in glassy regions.

Key words: Glass, Nanostructure, Incorporation method, Cerium–zirconium.

Introduction

A well-known paradigm in glass science states that the atomic constituents of oxide glasses can be grouped into network formers (SiO_2 , B_2O_3 , GeO_2 , . . .) and into network modifiers (Na_2O , K_2O , Rb_2O , . . .). The network formers establish a three-dimensional network of coordination polyhedra bridged by twofold coordinated oxygen atoms. In borate glasses the B_2O_3 network is transformed with increasing modifier content from trigonal planar coordinated BO_3 units to tetragonally coordinated $(\text{BO}_4)^-$ units which act as charge compensating centres. The modifier oxide becomes part of the glass by modifying the three dimensional network and the modifier cations reside in the interstitial spaces of the network as positive ions [1]. Nowadays, their potential for modern high-technological applications as vitreous electrolytes in solid-state batteries, fuel cells, and chemical sensors attracts considerable attention. Borax is a type of sodium borate glass that consists of one-third of sodium oxide and two-thirds of boron oxide. This type of borate glass draws great attention due to its enhanced electrical and optical properties when modified by phthalocyanine or by rare earths. In our previous studies, we prepared the $x\text{Tb}_2\text{O}_3.(1-x)\text{Na}_2\text{B}_4\text{O}_7$ glass system with $0 \leq x \leq 0.2$ [2] and $x\text{Nd}_2\text{O}_3.(10-x)\text{In}_2\text{O}_3.90\text{Na}_2\text{B}_4\text{O}_7$ ($x = 0, 1, 3, 5$ mol%) [3] and

characterized with XRD, UV-Vis, infrared spectroscopy, fluorescence, SEM and TG/DTA.

Glass ceramic materials are polycrystalline solids containing nanometers to micrometers size crystals embedded in a residual glass matrix and are produced by devitrification of glasses. Glass ceramics derive particular interest for several end applications, such as thermal, chemical, biological and dielectric ones, because these systems provide great possibilities to manipulate their properties, such as transparency, strength, resistance to abrasion and coefficient of thermal expansion by selecting the suitable constituent oxides [4]. The first step involves conventional techniques for glass production, followed by controlled crystallization; this process leads to the separation of a crystalline phase from the glassy parent phase in the form of tiny crystals, where the number of crystals, their growth rate and their final size are controlled by a suitable heat treatment [5]. However, some crystals are not precipitated easily from the glass by heat treatment. On the other hand, this method sometimes causes the crystallization of unexpected crystalline phases. Thus the “incorporation method” was proposed by Komatsu *et al.* [6]. In our a previous studies, we prepared indium- borate glass-ceramics containing $\text{Ho}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ via an incorporation method and characterized with XRD, infrared spectroscopy, SEM and DTA analysis [7].

In recent years, ceria and ceria-based composite oxides have been extensively investigated for a variety of reactions such as the preferential oxidation of CO gas, steam reforming of ethanol, a low-temperature water-gas shift reaction, apart

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from the conventional three-way catalytic applications to reduce the emissions of noxious pollutants such as CO , NO_x and hydrocarbons from automobile exhausts [8]. It has been found that the addition of ZrO_2 into CeO_2 can enhance the reduction of CeO_2 by lowering the reduction energy, and the formation of a solid solution ($\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$) can improve both the reduction and thermal stability properties of CeO_2 [9]. $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ has a better redox property and a higher oxygen storage capacity than the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ($x \leq 0.5$) sample. The purpose of this study was the synthesis of indium-borate glass-ceramics containing $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ with an “incorporation method” and characterization with XRD, FT-IR, SEM and DTA analysis.

Experimental

A cerium-zirconium mixed oxide ($\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$) and Eu-doped cerium-zirconium mixed oxide ($\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$) were obtained by a solid-state method. The required amounts of CeO_2 , ZrO_2 and Eu_2O_3 were mixed in a mortar and calcined in static air at 1000°C for 90 minutes. Boron-based indium oxide glass ($94\text{Na}_2\text{B}_4\text{O}_7\text{-}5\text{In}_2\text{O}_3$) was obtained using reagent grade $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$ and $\text{In}(\text{NO}_3)_3$. At first the base $\text{Na}_2\text{B}_4\text{O}_7$ glass was prepared by melting dehydrated borax at 1000°C for 30 minutes. Then the melt was quenched on a refractory steel block. The base glass obtained was crushed and powdered by an agate ball mill. Then appropriate amounts of $\text{Na}_2\text{B}_4\text{O}_7$ glass powder and $\text{In}(\text{NO}_3)_3$ were mixed and melted at 1300°C for 1 h. The glass samples were obtained by pouring the melts onto stainless steel plates. The steel plate was pre-heated to 400°C to prevent the glass samples from cracking. Finally the glass samples obtained were annealed at 450°C for 1 h to remove the thermal strain.

Glass powder and $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ were mixed (the amount of $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ crystals was 10 wt%) and heated in a crucible at 1210°C for 1 h. The glass-ceramic sample was obtained by pouring the melts onto stainless steel plates. The sample obtained was annealed at 450°C for 1 h to remove the thermal strain.

Physical measurements

The glassy nature of the glass sample and the crystal structure of Eu-doped cerium-zirconium mixed oxide were confirmed by XRD using a D5000 Siemens with $\text{Cu-K}\alpha$ line of wavelength $\lambda = 1.5406 \text{ \AA}$ at the scanning rate of $1^\circ/\text{minute}$ and 2θ was varied from 4 to 70° . The FT-IR transmission spectrum in the region $400\text{-}4000 \text{ cm}^{-1}$ was recorded for the glass sample using a Shimadzu Tensor27 by the KBr pellet technique. The catalytic activities of crystals were studied for the gas phase combustion of volatile organic compounds (VOCs). Toluene was used as the VOC model compound. The activities of the catalysts were tested for the combustion of toluene in a U-shaped-quartz tube placed in an electric furnace working under atmospheric pressure. A catalyst of 0.2 g was used in the toluene combustion tests. The concentration of VOCs in the feed gas was

0.2% (mol mol^{-1}), the hourly gas flow space velocity (GHSV) was 15000 h^{-1} , and the reaction temperature ranged from $150\text{-}400^\circ\text{C}$. Reactants and products were analyzed by gas chromatography (Shimadzu 2010), equipped with a flame ionization detector (FID). The conversion rate was obtained by calculating the concentration of reactants (inlet and outlet) at different temperatures. Differential thermal analyses (DTA) (DTG-60AH Shimadzu) were carried out from ambient temperature to 1200°C at a heating rate of $10^\circ/\text{minute}$. The morphologies of the glass-ceramic samples were observed with a scanning electron microscope (SEM), type LEO440I after coating with gold.

Results and Discussion

Characterization

Fig. 1 gives photographs of the glass and the glass-ceramic.

The glassy state for the glass sample was confirmed by the absence of peaks in X-ray powder diffraction patterns. The XRD patterns exhibit a broad diffuse scattering at low angles instead of crystalline peaks, confirming a long-range structural disorder characteristic of an amorphous network. Fig. 2 shows the X-ray diffraction pattern of the glass sample. Typical XRD patterns of the oxides and mixed oxides (CeO_2 , ZrO_2 , $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$, $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$) are shown in Fig. 3. The mean crystallite sizes were estimated using the Scherrer equation, $D = k\lambda/\beta \cos\theta$, where $k = 0.89$, $\lambda = 0.15418 \text{ nm}$ (Cu), β is the half peak width of the X-ray reflection and θ is the diffraction angle.

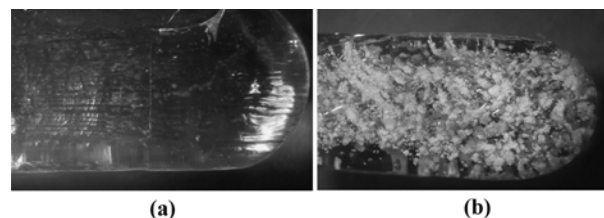


Fig. 1. photographs of glass (a) and glass-ceramic (b).

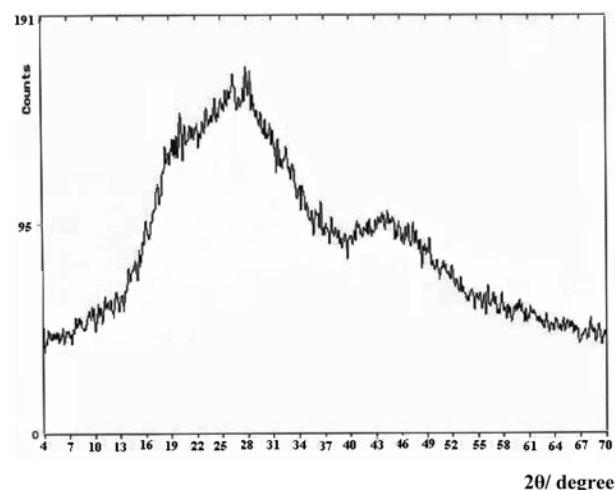


Fig. 2. X-ray diffraction pattern of the glass sample ($94\text{Na}_2\text{B}_4\text{O}_7\text{-}5\text{In}_2\text{O}_3$).

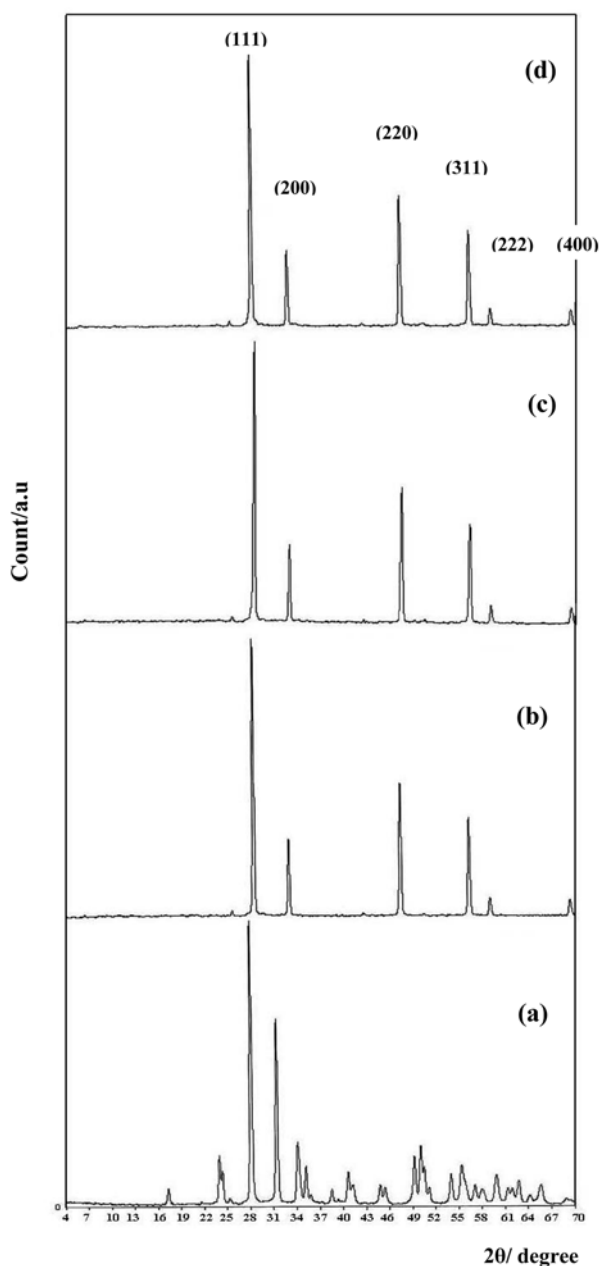


Fig. 3. The XRD patterns of ZrO_2 (a), CeO_2 (b), $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (c), $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ (d).

It is apparent that the patterns consist of six main reflections, typical of a cubic, fluorite structure of CeO_2 , corresponding to the (111), (200), (220), (311), (222), and (400) planes. The results suggested that crystals preferably crystallize into a cubic structure. The presence of only the cubic phase in $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ indicates that Ce and Zr are highly homogeneously distributed and ZrO_2 is incorporated into the CeO_2 lattice to form a solid solution. A slight shift of the main diffraction peaks to higher 2θ values is seen. This observation indicates that the substitution of the Ce^{4+} cation (Ce^{4+} cation radius 0.97 Å) with the smaller Zr^{4+} cation (Zr^{4+} cation radius 0.84 Å) causes a lowering of the symmetry and a decrease in the unit

cell parameters. Also no separated CeO_2 , ZrO_2 , Eu_2O_3 are detected by XRD in the 2θ region from 4 to 70° , which indicates that Eu ion is doped into the ceria-zirconia mixed oxide framework forming CeO_2 - ZrO_2 mixed oxides. The average particle sizes were determined to be approximately 42 and 45 nm from the XRD pattern parameters of the $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ and $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ respectively according to the Scherrer equation. The XRD pattern of the glass-ceramic sample is shown in Fig. 4. As seen in the figure, the peaks belonging to $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ crystals can be observed, but the intensities of these peaks are small. A SEM micrograph of $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ is shown in Fig. 5. The average particle size was determined to be approximately 47 nm. The IR spectroscopy of borate-containing compounds show that the vibrational modes of the network present are mainly active in three infrared spectral regions [10]:

(i) the first group of bands which occur at $1200\text{--}1600\text{ cm}^{-1}$

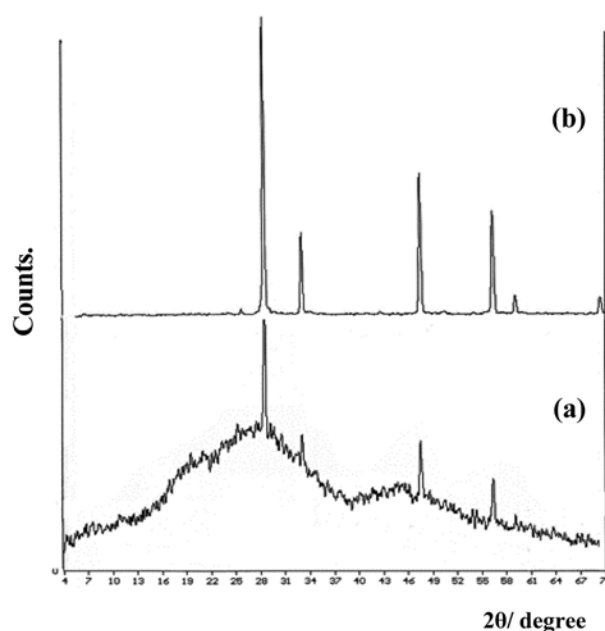


Fig. 4. The XRD pattern of glass-ceramic (a) and $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ (b).

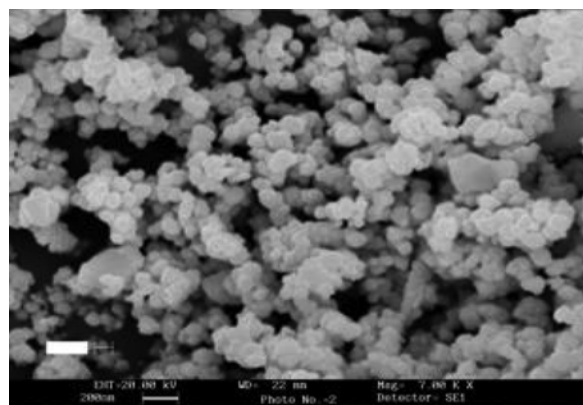


Fig. 5. SEM micrograph of $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$.

is due to the asymmetric stretching relaxation of the B-O bond of trigonal BO_3 units.

(ii) the second group lies between 800 and 1200 cm^{-1} is due to the B-O bond stretching of the tetrahedral BO_4 units.

(iii) the third group is observed around 700 cm^{-1} is due to bending of B-O-B linkages in the borate networks.

These speculative (rich) features are based on the fact that boron has the smallest mass compared to other network-forming cations and thus the main vibrational modes associated with the glass network appear well above 500 cm^{-1} in the mid-infrared. The broad composite bands extending from 3200 – 3600 cm^{-1} are attributed to hydroxyl or water groups [11]. The spectroscopic features given evidence by these spectra, namely the absorption bands at about 450 , 700 , 900 , 1030 , 1270 , 1390 cm^{-1} are characteristic of the base $\text{Na}_2\text{B}_4\text{O}_7$ glass [12]. The FT-IR spectra of indium-sodium borate glasses were obtained using a KBr pellet technique in the range of 1000 – 4000 cm^{-1} . Fig. 6 shows the IR spectra recorded for the glass sample.

The IR spectral features of the glass samples are very broad due to the vitreous nature of the samples [13]. In pure B_2O_3 glass, the 806 cm^{-1} frequency is a characteristic of the boroxol ring. In the present glass, the absence of an absorption peak at 806 cm^{-1} indicates the absence of boroxol ring formation. The absorption peak in the region of 450 cm^{-1} can be associated with B-O-B bending modes [14]. The band around 700 cm^{-1} is assigned to the bending vibration of B-O-B linkage in the borate network [15]. The absorption band around 1000 cm^{-1} may be assigned to B-O stretching modes of BO_4 groups. The shoulder at around 1270 cm^{-1} is assigned to oxygens bridging trigonal borons [16]. The band at 1400 cm^{-1} is due to B-O symmetric stretching vibrations of BO_3 in various borate groups [17]. In the high frequency region (1630 cm^{-1}) an absorption peak is seen that is attributed to the bending modes of -OH groups present due to the absorbed water [18]. The band at 2360 cm^{-1} could be caused by stretching vibrations of atoms in the C-O bond of gaseous CO_2 sorbed in the powder analyzed [19].

The density of the glass and its value is important and stands on its own as intrinsic property capable of casting the light on the short range structure. Also, boron oxide

in its glassy form is a laminar network consisting of boron atoms 3-fold coordinated with oxygen which can form 6-membered boroxol rings (B_3O_6). When an alkali oxide modifies the pure boron oxide, the additional oxygen, obtained by the oxide dissociation, causes a conversion from the trigonal boron atoms BO_3 into 4-fold coordinated boron atoms as BO_4 . Each BO_4 structural group is negatively charged and the four oxygen's are included in the network as bridging oxygen. These units are responsible for the increase in the connectivity of the glass network. As a result, the degree of the structural compactness, modification of the geometrical configuration in the glass network can vary with a change in the composition [2]. The density of glass samples was measured using Archimedes's principle. The measurements were carried out using Shimadzu Aw 200 balance and xylene as an inert immersion liquid. The density was obtained from the relation $d(\text{g/cm}^3) = [a/a-b] \times (\text{density of xylene})$, where a is the weight of the glass sample in air, b is the weight of the glass sample when immersed in xylene. The density of xylene is $0.865(\text{g/cm}^3)$. The density values for $\text{Na}_2\text{B}_4\text{O}_7$ (2.310 g/cm^3) and $94\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{In}_2\text{O}_3$ (2.77 g/cm^3) and IR data indicated the conversion of BO_3 into BO_4 structural units leading to a less compact structure of the glass matrix ($94\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{In}_2\text{O}_3$) and consequently to a decrease of its density.

Activities of crystals

Catalytic activity is known to be influenced by mass transfer at high conversions, and comparisons of activity were made in terms of "light-off". It is convenient to define the "light-off" temperature as the temperature when the conversion reaches either 10% or, as in this case, 50%. Catalytic activity is related to the redox properties of the mixed oxide. In addition, the catalytic activity of mixed oxide samples depends on the structural properties of the mixed oxide samples [20]. Toluene was chosen as the model molecule of VOC to investigate the catalytic activities of crystals for combustion of toluene.

A control test without catalysts was performed under the same conditions. At first the conversion of toluene was studied without a catalyst (thermal combustion) whose related light-off curve is shown in Fig. 7. The maximum conversion of approximately 35% was obtained at temperature of 400°C .

In the control test, toluene was not oxidized when the temperature was below 150°C . The activities of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ and $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ for the combustion of toluene are plotted in Fig. 8. The results showed that the activities of the $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ calcined at 900°C are incomparable to $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$. The catalytic activity of $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ was higher than $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ for the conversion of toluene. The conversion was over 50% with $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ as the catalyst when the temperature was 295°C . In $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ nano-crystal conversion increases with temperature. One can postulate that Eu which has been incorporated into the Ce-Zr-O lattice to form a solid solution influences the

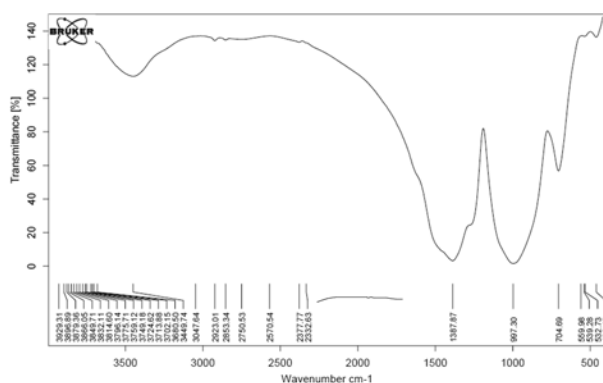


Fig. 6. The infrared absorption spectra of In_2O_3 - $\text{Na}_2\text{B}_4\text{O}_7$ glass.

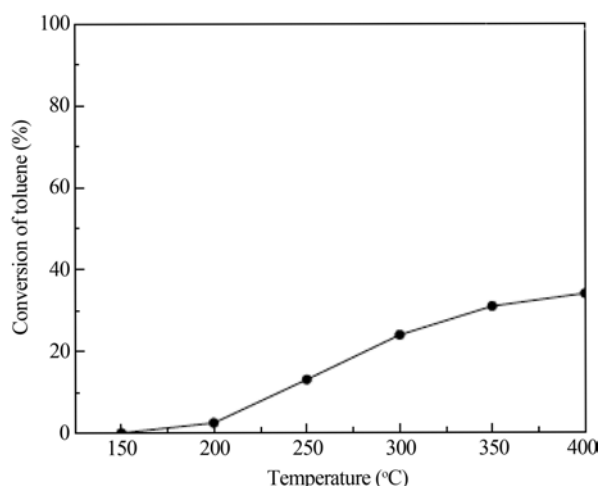


Fig. 7. Light-off curve for toluene in air without catalysts.

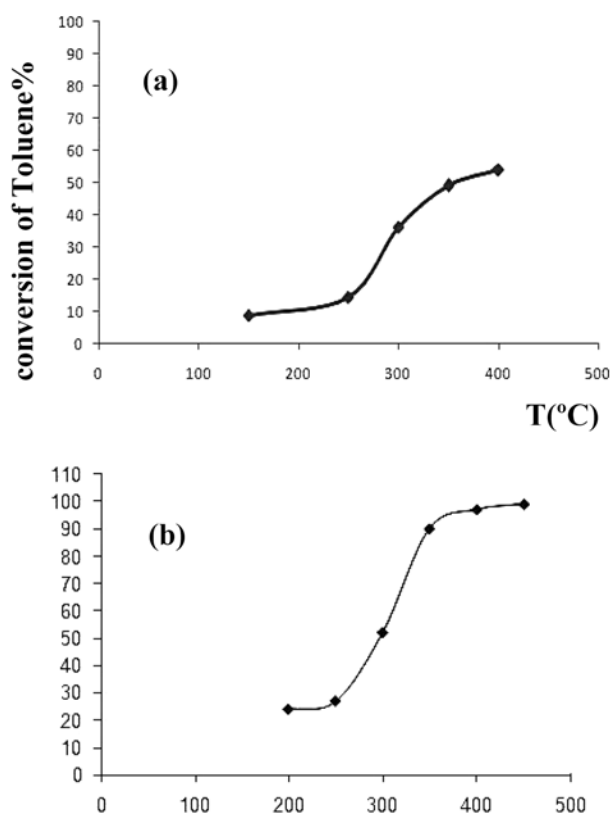


Fig. 8. Light-off curves for toluene in air on $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ (a) and $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ (b).

catalytic activity for the combustion of toluene. Differential scanning calorimetry (DSC) or differential thermal analysis (DTA) monitors the heat absorbed or evolved by a material as a function of time, most commonly during heating or cooling. If a kinetically impeded process such as crystallization or a chemical reaction which is accompanied by absorption or evolution of heat occurs within the sample, DSC and DTA can be used to characterize the kinetics of the process [21]. The glass sample was subjected to DTA in order to determine glass transition (T_g) and

crystallization (T_{cr}) temperatures. A typical DTA plot obtained for the present sample is depicted in Fig. 9(a).

DTA analysis of the glass sample confirms its glassy state. This figure shows an endotherm (696°C) corresponding to the glass transition and an exotherm (1151°C) corresponding to the crystallization temperature. T_g represents the strength or the rigidity of the glass structure. Fig. 9(b) shows the DTA curve for the glass-ceramic. This curve shows an endotherm (648°C) corresponding to the glass transition and an exotherm (1134°C) corresponding to the crystallization temperature and phase separation. The difference between T_g and T_x (i.e. $\Delta T = T_x - T_g$) is larger for the $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ containing specimen, indicating that the thermal stability of the glass-ceramic is higher than that of the glass without crystals.

A SEM micrograph of the glass-ceramic sample is shown in Fig. 10. The average particle size was determined to be approximately 86 nm.

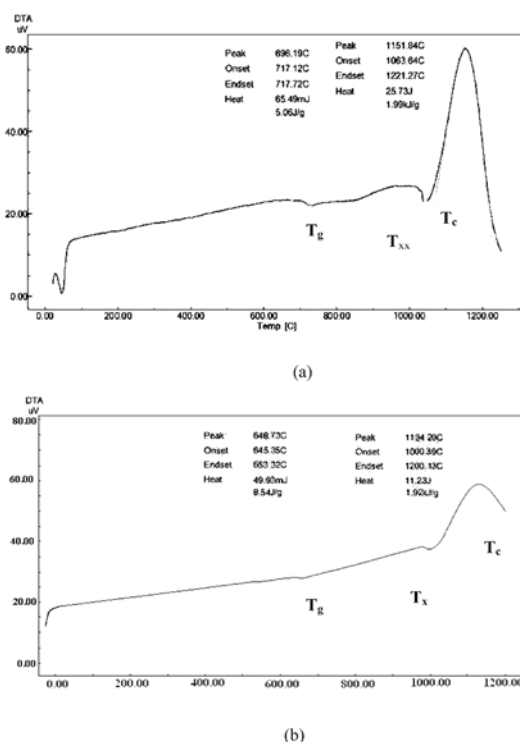


Fig. 9. DTA curves of glass (a) and glass-ceramic (b) samples.

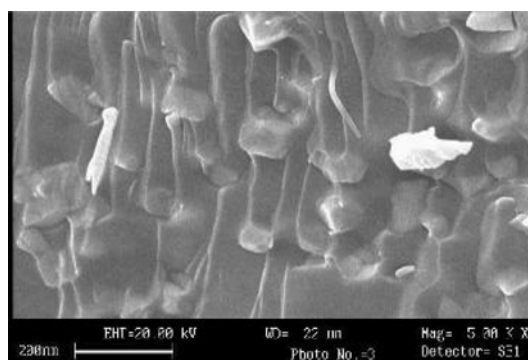


Fig. 10. SEM micrograph of the glass-ceramic synthesized.

Conclusions

Glass in the system $5\text{In}_2\text{O}_3\cdot 94\text{Na}_2\text{B}_4\text{O}_7$ was fabricated via a melt quenching technique. The amorphous nature of the quenched glass was confirmed by X-ray powder diffraction. The infrared spectra of the glass show no boroxol ring formation in the structure of this glass. A cerium-zirconium mixed oxides ($\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ and $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$) were obtained by a solid-state method. Gas phase catalytic oxidation of toluene was studied over these nanostructures. The results showed that the catalytic activity of $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ was higher than $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ for the conversion of toluene. One can postulate that Eu which has been incorporated into the Ce-Zr-O lattice to form a solid solution influences the catalytic activity for the combustion of toluene. Glass powder and $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ were mixed. The mixture was heated in a crucible. The glass-ceramic sample was obtained by pouring the melts onto stainless steel plates. The samples obtained were annealed at 450°C for 1 h to remove the thermal strain. DTA analysis of the glass and glass-ceramic samples show an endotherm corresponding to the glass transition and an exotherm corresponding to the crystallization temperature. The difference between T_g and T_x (i.e. $\Delta T = T_x - T_g$) in the DTA curves is larger for the $\text{Eu}_{0.01}\text{Ce}_{0.74}\text{Zr}_{0.25}\text{O}_{1.995}$ containing specimen, indicating that the thermal stability of the glass-ceramic is higher than that of the glass without crystals. A scanning electron microscopy study for the glass-ceramic indicates that the crystallized glass consists of crystals with an average diameter of about 86 nm dispersed in glassy regions.

Acknowledgements

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