



Vibrational, Structural and Thermal studies of Debris of 30%CaO-70%B₂O₃

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Abstract

Calcium borate glass debris is the technologically important and plays a significant role in various applications. Calcium borate debris is prepared with melting and quenching. The glass debris of calcium-borate as a simulant material is studied by Raman spectra, Fourier Transform Infrared (FTIR) spectra, structural and thermal analysis. This study is focused on plasma line, Lattice modes, B-O_{ext} out of plane, Deformation modes, B-O_{bridge} stretch, B-O_{ext} stretch with 1050°C temperature. The amorphous nature of the debris glass has been confirmed from XRD profile. The glass transition temperature (740°C) and sharp crystallization peak (792°C) of debris material was analyzed by differential scanning calorimetry (DSC). The thermal stability of calcium glass borate debris is between 420°C to 670°C which is good for sealant application, analyzed by thermo gravimetric analysis (TGA). This composition of debris material was also used in the melt cool-ability experiment because properties of this material are almost same with properties of corium.

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Introduction

Every oxide material is change in glass/glass ceramic after melt and cool. In a severe reactor accident involving core melt and pressure vessel failure in conventional and advanced light water reactors. Corium is a mixture of nuclear fuel and concrete. The properties of corium and CaO-B₂O₃ are same. According to Kulkarni et al. (2014) in actual reactors, when corium falls on concrete and ablates substantial part of it, the resulting mixture comprises metal oxides and silicates which form glass type mixture. Hence, molten glass was chosen as simulant material [1]. Simulant material after quench it converted into debris of glass. It is characterized by a lack of long range order due to absence of periodicity. Two basic approaches are projected for explanation of lawless structures.

The random arrangement hypothesis [2, 3] assumes the fundamental polyhedral present in crystal to be present in corresponding glasses. The existence of larger structural group data is indicated by different data [4, 5]. This proposal has been the source of the Krong-Moe hypothesis [5].

Raman spectra and identification of glass/ glass ceramic forming structural units in alkali borate glasses was analysed also by other authors [6, 7]. The introductions of metal oxides in the glasses lead to the change of the glass structure, metal oxide acting as modifier [8]. In the Raman spectra of glassy of B₂O₃ there is a specific strong bond-807cm⁻¹ assigned to the Boroxol ring [9]. In present work, the vibrational, structural, and thermal properties of glass debris of calcium borate (30% CaO-70% B₂O₃) simulant material have been studied.

Wave number of absorption

The absorption wave number for stretching vibration is related to both the force constant between the two atoms (k) and the mass of the two atoms (m₁ and m₂) by the Hooke's law [10] equation:

$$\bar{\nu} = \frac{1}{2\pi c} \left[k \left(\frac{m_1+m_2}{m_1.m_2} \right) \right]^{1/2} \quad (1)$$

From this relationship, two important trends in the wavenumber for stretching vibrations can be deduced: (i) as the bond strength increases, the wave number increases, (ii) as the mass of one of the two atoms in the bond increases, the wave number decreases.

Experimental

Glass ceramic debris with composition 30%CaO-70%B₂O₃ (by wt.) were prepared by melt and quenching technique. Appropriate amounts of high purity B₂O₃ and CaO were melted in tilt-able and fixed crucible electric furnace, poured in the test section, water apply from bottom in the test section. The amorphous nature of as quenched sample was verified using X-ray diffraction technique. XRD profile was recorded on a X-Ray Diffractometer (Panalytical X Pert Pro) with CuK α radiation ($\lambda = 1.54060 \text{ \AA}$) at 40 kV and 40 mA and $2\theta = 20^\circ$ and 70° at the rate of two degree per minute. FT-IR spectrum of the sample was recorded on FT-IR Spectrum 2 (Perkin Elmer) spectrometer using KBr pellet technique in the range of 4000 – 400cm⁻¹. Raman spectrum was measured using Airix corporation (STR- 500) Micro Raman spectrometer attached with an Ar⁺ laser (532nm) as a excitation source having an output power of 20mW with 600grit. A DSC the power compensation technique (NETZSCH DSC -404F3) was used for recording the non-isothermal behaviour of the glass ceramic debris. The DSC experiment was performed with 8mg as quenched glass ceramic debris sample taken in alumina crucible under continuous nitrogen purging. The DSC curve was recorded in the temperature range 25-950 °C for the 10 K min⁻¹ heating rate. The glass transition temperature (T_g) and sharp crystallization peak (T_c) temperature were determined from the DSC data. The measurement of TGA was carried out on STA 6000 (Perkin Elmeris) at a heating rate of 10°C/min. with N₂ as the purging gas.

Results and Discussion

XRD profile reveals in Figure 1 diffused peak at 2θ (20-50°) could be noticed in debris glass sample, which clearly indicates their amorphous nature. Figure 2 presents the FT-IR spectrum of CB (CaO-B₂O₃) glass debris, describing the structure of vitreous borate consisting of random network of BO₃ triangles with certain fraction of boroxol (six membered) rings but with the inclusion of the network modifier such as alkaline/alkaline earth metals (Ca), formation of BO₄ network modifier takes place in the borate glass network. The FT-IR has shown characteristics peaks at 524cm⁻¹, 685 cm⁻¹, 1015 cm⁻¹, 1419 cm⁻¹, 2857 cm⁻¹, 3425 cm⁻¹. The broad bands are due to combination of factors such as high degeneracy of vibrational state, thermal broadening of lattice dispersion band and also mechanical scattering in the debris glass. In the infrared spectral region, the vibrational modes of borate show three regions [11], the first region at 1200-1600 cm⁻¹ band is due to an asymmetric stretching of relaxation of the B-O bond of trigonal BO₃ units, the second region at 800-1200 cm⁻¹ due to the B-O bond stretching of tetrahedral BO₄ units, and third region bands at 600-800 cm⁻¹ is originating from the bending vibrations of B-O-B linkages in borate network [12].

In the present debris of glass, the absence of peak at 806cm⁻¹ indicates the absence of boroxol ring. The substitution of boroxol rings by triborate and tetraborate groups has been observed. The band at 466cm⁻¹ is assigned (Fig.3) to the characteristic vibration of Ca cation [13]. The band at 685cm⁻¹ is due to the bending vibrations of B-O-B linkage in the borate network [14], a big band at 1015cm⁻¹, is due to stretching vibrations of B-O in BO₄ units from tri-, tetra-, and penta borate groups [15]. The band at 1419cm⁻¹ is due the stretching of B-O bonds of various borate arrangements containing planar six membered groups, exhibiting a compositional dependence that originates from different species. The small band at 2857cm⁻¹ can be attributed to Hydrogen bonds and broad band at 3425cm⁻¹ is due to the hydroxyl group (due to stretching of OH) [16].

The contribution due to borate network dynamics is mostly in the mid infrared region of the profile, where as for calcium cation motion dominates in the low frequency region. Thus, CB glass debris has demonstrated the presence of principle bands at the three regions.

Raman spectrum of Calcium oxide and Borate oxide (CB) debris glass is shown in Figure 4 exhibiting bands at 131cm⁻¹, 300 cm⁻¹, 640 cm⁻¹, 745 cm⁻¹, 1100 cm⁻¹, 1300 cm⁻¹, 1470 cm⁻¹. It is reported that pure B₂O₃ reveals a strong band at 806 cm⁻¹ and which is assigned to the boroxol ring oxygen breathing vibrations involving a very little boron motion [17, 18]. In the CB debris glass, with the availability of Cao (30%), the B₂O₃ transforms into a complex network which involves a boroxol ring coupled with fourfold-coordinated boron (BO₄) because of the non-bridging oxygens. The peak 745 cm⁻¹ is assigned due to breathing vibrations of six member rings with BO₃ triangles replaced by BO₄ tetrahedral units [19-21]. The band at 640cm⁻¹ is attributed to a bending mode (B-O-B) of BO₃³⁻ units [22]. The peak band at 960 cm⁻¹ is due to di-borate group [23] and the peak 1100 cm⁻¹ is due to the vibrations of di-borate groups formed from six membered rings that contain two BO₄ tetrahedral units in the structure [24-26]. The peaks in the higher frequency region are due to BO₂O⁻ triangles linked to BO₄ units and BO₂O⁻ triangles linked to the other triangular units [27, 28]. In the lower frequency range, a peak is observed in the debris glass of Calcium borate at 164cm⁻¹ that could be attributed to librational mode of BO₃ and BO₄ units [29]. Two peaks at 1300 cm⁻¹ and 1470 cm⁻¹ are because of the overlap of different modes such as: (i) B-O⁻ in BO₂O⁻, (ii) BO₂O⁻ triangles linked to BO₄ units and (iii) stretching in BO₃ triangles which are asymmetrically

connected [30-31]. Assignments of measured Raman and IR band position of CaO-B₂O₃ have been listed in Table 1.

Table 1: Assignment of measured Raman and IR band position of CaO-B₂O₃

Assignments	Raman/ Range Literature	Raman Observed	Infrared/Range Literature	Infrared Observed
Plasma line	Below 170	164 cm ⁻¹	Below 155 cm ⁻¹
Lattice modes	170 to 329 cm ⁻¹	300 cm ⁻¹	185 to 350 cm ⁻¹
B-O _{ext} out-of-plane	387-523 cm ⁻¹	466 cm ⁻¹
Deformation modes	550-805 cm ⁻¹	640 cm ⁻¹	637 to 772 cm ⁻¹	536 cm ⁻¹
B-O _{bridge} stretch	1003-1410 cm ⁻¹	745 cm ⁻¹ 960 cm ⁻¹	1163 cm ⁻¹	685 cm ⁻¹ 1015 cm ⁻¹
B-O _{ext} stretch	1427-1597 cm ⁻¹	1100 cm ⁻¹ 1300 cm ⁻¹ 1470 cm ⁻¹	1441-1500 cm ⁻¹	1419 cm ⁻¹

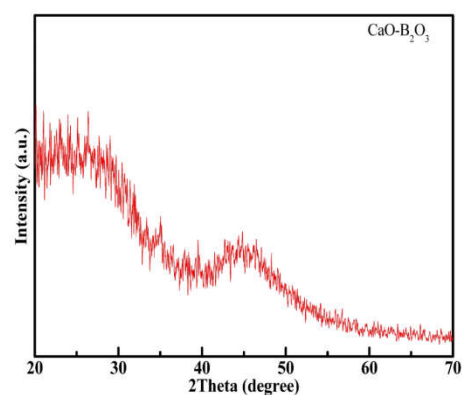


Figure 1: XRD of Debris of CaO-B₂O₃

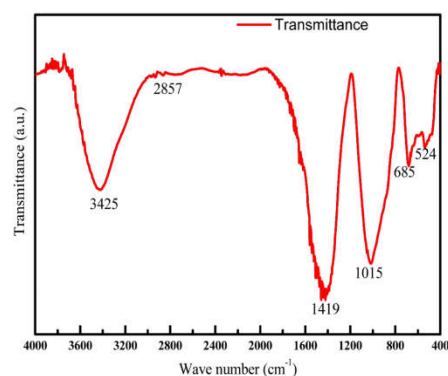


Figure 2: FT-IR spectrum (4000-400 cm⁻¹) of Calcium oxide and Borate Oxide (CaO-B₂O₃) debris.

Thermal analysis

DSC curve of CaO-B₂O₃ debris shows in fig. 5 (a) recorded under a constant heating rate of 10 Kmin⁻¹. A glass debris composition of CaO-B₂O₃ exhibited a glass transition marked by endothermic base line shift within the temperature range of 740-760°C. The glass transition temperature of 30%CaO+ 70%B₂O₃ was 745± 2 °C. The sharp crystallization peaks was observed at 792±2 °C.

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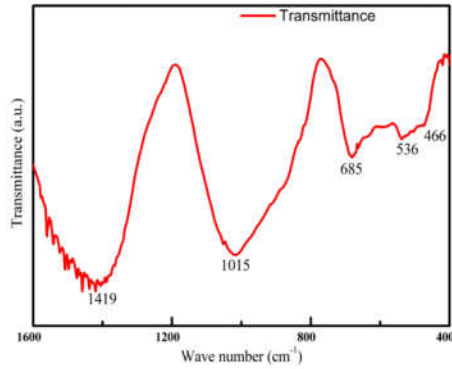


Figure 3: FT-IR spectrum (1600-400 cm⁻¹) of Calcium oxide and Borate Oxide (CaO-B₂O₃) debris.

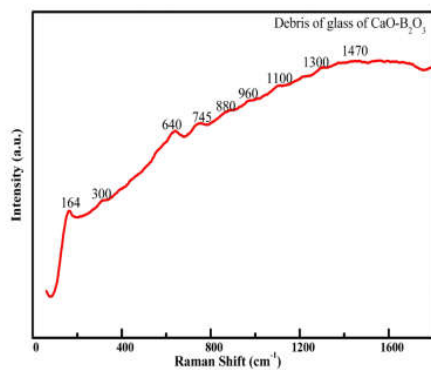
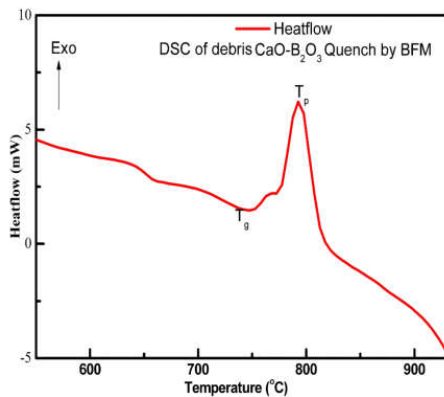
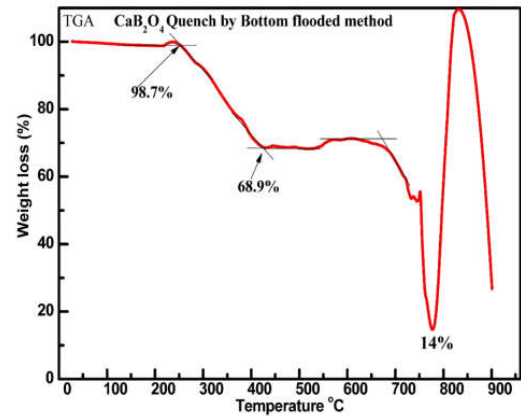


Figure 4: Raman spectrum of CaO-B₂O₃ debris glass

TGA is commonly used to determine the selected characteristics of materials that exhibit mass loss or gain due to decomposition, oxidation, or loss of volatiles. The thermogravimetric characteristic of the debris is shown in figure 5(b). A total loss in weight of 86% was observed throughout the heating range (25 - 770°C). The initial gradual drop in the weight of the debris powder 1.3% from room temperature to about 230°C can be attributed to the removal of small molecules, due to dehydration of compound. The linear drop in weight of debris powder 30% from 250 – 420°C due to decomposition of debris.



(a)



(b)

Figure 5: (a) DSC characteristics of debris (b) Shows the TGA characteristics of 1050°C quench by bottom flooded method at 10K/min heating rate

This phase is meta-stable at 420 °C to 670 °C because of the ordering process without any weight loss, again decompose linerly and suddenly after 670°C, remaining residue 14.5%.

Conclusions

A systematic study of non-isothermal behaviour of 30%CaO+70%B₂O₃ glass debris has been carried out. The glass debris of calcium-borate as a simulant material is studied by Raman spectra, Fourier Transform Infrared (FTIR) spectra, structural and thermal analysis. This study is focused on plasma line, Lattice modes, B-O_{ext} out of plane, Deformation modes, B-O_{bridge} stretch, B-O_{ext} stretch with 1050°C temperature. The amorphous nature of the debris glass has been confirmed from XRD profile. The glass transition temperature (740°C) and sharp crystallization peak (792°C) of debris material was analyzed by differential scanning calorimetry (DSC). The thermal stability of calcium glass borate debris is between 420°C to 670°C which is good for sealant application, analyzed by thermo gravimetric analysis (TGA). This composition of debris material was also used in the melt cool-ability experiment because properties of this material are almost same with properties of corium.

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