Differences in Vitrification Behaviour of Flint and Opaque Scrap Glass Containing Porcelainized Stoneware Body

A. K. Oluseyi, M. Pal, S. K. Das

In a normal stoneware ceramic composition, feldspar was partially substituted by two types of soda lime silica scrap glass powder (flint-chromium free and opaque-chromium doped). Samples were fired in the temperature range of 1100–1250 °C and their physico-mechanical properties were studied and compared with the normal composition. Samples containing flint glass powder achieved early vitrification at 1200 °C compared to 1250 °C for opaque glass containing sample as well as normal stoneware body. Both bodies achieved more than 40 MPa flexural strength at their vitrification temperature. Formation of needle shaped mullite crystals was observed in all samples. Presence of large number of smaller size mullite crystals was responsible for strength development.

Introduction

Nowadays technically and economically feasible recycling processes and the use of wastes in place of traditional materials become more important due to growing interest in environmental pollution and preservation of traditional materials. Many researchers have used several industrial wastes such as pond ash and fly ash [1], blast furnace slag [2], iron ore tailing [3], rice husk ash [4], scrap glass powder [5, 6] etc. Porcelain of different types are usually produced from a mixture of clay, quartz and feldspar with and without selective additives for special purpose. In porcelain composition, clay provides fine particles which act as binder and good plasticity to give shape and green strength to the body. Feldspar acts as a flux, forming a viscous liquid or glass at commercial firing temperature (~1200–1300 °C) and leads to vitrification. The quartz is mainly a filler and improve mechanical property of the fired material. The toughness, strength, and translucency of porcelain arise mainly from the formation of glass and mullite crystals within the fired body at these high temperatures.

Iqbal and Lee [7] found that clay component dehydroxylated to metakaolin at 550 °C and metastable sanidine formed from decomposition of the feldspar at about 600 °C and dissolved at about 900 °C. Liquid is formed at 1000 °C by the reaction of quartz and clay minerals with feldspar.

Soda lime silica glass powder is vitreous silicate material. It can replace the traditional fluxing agent like feldspar and upto 5 mass-% addition of it reduces Vitrification temperature keeping technological behaviour unaltered. That is why glass powder is widely used in porcelain composition by many researchers [8, 9].

Luz et al. [10] use glass powder in porcelain stoneware tile composition and concluded that during firing glass powder waste accelerates the densification process, with lower open porosity, water absorption, higher values of shrinkage and high closed porosity. The use of small amounts of glass powder in addition with feldspar showed good results of mechanical and technological properties. Unprocessed container cullet is defined as broken or whole scrap glass.

Tucci et al. [5] incorporated scrap glass (soda lime, lead and barium based glasses) into a porcelain stoneware tile mixture. Authors prepared several modified mixes replacing different amounts of the fluxing component in a standard porcelain stoneware body mix, with three types of scrap glass: a soda lime glass from urban wastes, a lead based glass from the neck part of cathode ray tubes (CRTs), and a barium based glass from CRT panels. Replacement of feldspar sand with a soda lime scrap glass, in the range 5–10 mass-%, showed a slight decrease in the water absorption of the fired material at the same vitrification temperature as the reference mix. Furthermore, flexural strength remains high and the microstructural homogeneity enhances reliability. The presence of 2 and 5 mass-%, of lead and barium based scrap glass respectively, both characterised by lower liquid viscosity at higher temperature, resulted a significant decrease in the vitrification temperature of the modified porcelain stoneware products while maintaining good mechanical properties.

Tucci et al. [9] also reported that the replacement of 10 mass-% of sodium feldspar with the same amount of soda-lime scrap glass results in decrease in firing temperature and an increase in mechanical resistance. Same conclusions were drawn by Mustafi et al. [6] as they replaced feldspar partially and fully in ceramic tile composition.

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Tab. 1 Batch composition [mass-%]

Raw Material/ Blend	A1 (Standard)	A2	A3
Kaolin	50	50	50
River sand	25	20	20
Feldspar	25	15	15
Soda-lime scrap glass	Nil	15	Nil
Cr-doped soda-lime scrap glass	Nil	Nil	15

Karamanova et al. [11] compared the effect of the addition of fired scrap on the densification replacing a part of the feldspar and sand in a commercial porcelain composition of kaolin, sand and feldspar. The authors concluded that at temperature below 1200 °C, the addition of fired scrap had no significant influence on densification. At 1300–1350 °C, the molten part of the scrap starts to participate in the dissolution of quartz phase and in the densification process of porcelain. The addition of 15 mass-% scrap glass reduces sintering temperature and better mechanical properties.

Transition metal is the useful colouring agent in glass. Few authors [12] studied the effect of silicate network modifier on colour and electron spectra of chosen transition metal ions. From the analysis of colour and electron spectra of the obtained glasses it follows that the chemical composition of the glass matrix influences the coordination state as well as the oxidation state of the transition metal. The decrease of the electronegativity of the modifiers causes a shift of oxidation/reduction equilibrium towards higher valence of the transition metals (Cr^{6+}, Mn^{3+}).

Meejitpaisan et al. [13] studied the physical properties of Cr_2O_3 doped soda lime silicate glass where less than 0,05 mass-% were used. The authors concluded that the density and refractive index of glass samples were increased and molar volume is decreased with increasing of Cr_2O_3 concentration due to the higher molecular weight of Cr_2O_3 than SiO_2.

The present work is focused on the use of Cr_2O_3 doped opaque type soda-lime scrap glass in stoneware ceramic body and compare their physico-mechanical, phase and microstructural changes with Cr_2O_3 free flint type soda lime silica glass incorporated stoneware body as well as normal stoneware composition.

Experimental procedure

The source of raw materials used in this investigation were similar to the authors' earlier work [14] namely kaolinitic clay from Rajmahal, Bihar/IN; potash feldspar from Hyderabad, A.P./IN; soda lime silicate glass cullet of two types (soda-lime silica glass with and without Cr_2O_3) and river sand from in-home source of CSIR-CGCRI. The glass cullets used was pulverized in high energy ball milling system for 8 h at room temperature. All the raw materials were analysed by standard methods [15].

Three different batches were prepared as provided in Tab. 1, including the normal stoneware ceramic composition (A1). Part of river sand and feldspar were substituted by flint type (Cr_2O_3) soda-lime scrap glass and Cr-doped soda-lime silica scrap glass. The three batches were wet milled separately and grounded by pot milling process in an alumina milling media until the slurry passed through 100 mesh BS sieve. The slurry was then dried at 110 ± 5 °C. The dried material was then crushed and sieved to pass through 60 mesh BS sieve. The powder was then moistened with 5–6 mass-% water to convert it into granules and uniaxially compacted into bar samples (65 mm × 10 mm × 10 mm) at 400 kg/cm^2. The samples were first kept in air for 24 h followed by in an oven at 110 ± 5 °C for 12 h. The dried samples were then heated in the temperature range 1050–1200 °C in an electrically operated furnace. The heating rate was 5 °C/min up to 800 °C and then 3 °C/min up to the highest temperature with a soaking period of 30 min.

The samples were characterised by some physico-mechanical tests like linear shrinkage (LS), bulk density (BD), and apparent porosity (AP) by conventional method. The flexural strength was determined using a universal testing machine (INSTRON 5500R), in three-point bending fixture. Some selected samples were subjected to X-ray diffraction study to identify the phases formed. The X-ray diffraction patterns of the samples were recorded in X'pert Pro MPD diffractometer (PANalytical) [16] using X'Celerator operating at 40 kV and 30 mA using Ni-filtered CuK radiation. The XRD data were recorded in step-scan mode with step size 0,05 and step time 75 s from 10–80°.

For field emission scanning electron microscope study, samples were grinded with SiC powder and water and then the samples were polished with 6, 3, and 1 µm diamond paste respectively. The polished surfaces of each sample were etched for 5 min in 10 % HF solution at room temperature and washed with water and acetone followed by gold coating (Edwards, Scancoat). The microstructural study was done by field emission scanning electron microscopy (FESEM), the images were taken by GEMINI Zeiss Supra TM 35VP Model.

Results and discussion

The chemical composition of the raw materials used are provided in Tab. 2. River sand used in this composition contain 2,28 mass-% Fe_2O_3, which may affect the fired colour of the body. Hence our work refers to stoneware body. Kaolin and feldspar is of normal type. Both the flint and opaque type glasses are almost similar except opaque glass contain small amount of Cr_2O_3 (0,07 mass-%). The oxide composition of the three batches are also provided in Tab. 3. Silica level is almost similar, while A1 contain more alumina than A2 and A3. This is due to substitution of feldspar by scrap glass powder containing negligible amount of alumina.

The total flux content (alkaline + alkaline earth) A2 and A3 is obviously more than A1. It will be interesting to see the vitrification behaviour of these three bodies. Few authors reported the excellent fluxing action of alkaline earth oxide in presence of alkaline earth minerals. A3 contains a very small amount of Cr_2O_3 (0,011 mass-%). The percentual variation in linear shrinkage, bulk density, and apparent porosity of the experimental samples in relation to heating temperature provided in Fig. 1a–c respectively. From these figures it may be seen that A2 sample shrinks more (~9,5 %), achieved highest density (~2,4 g/cm^3) and lowest porosity (≤1,0 %) at 1200 °C. This is

Tab. 2 Chemical composition of raw materials used in the study

	Composition [mass-%]				
Constituent	**Kaolin**	**River Sand**	**Feldspar**	**Soda-Lime Silica Scrap Glass (Flint)**	**Cr-Doped Soda Lime-Silica Scrap Glass (Opaque)**
SiO_2	55,90	89,50	66,81	69,55	70,63
Al_2O_3	30,28	4,31	18,08	1,42	1,71
Fe_2O_3	0,71	2,28	0,24	0,21	0,34
TiO_2	0,86	0,18	Nil	0,13	0,06
CaO	0,13	0,71	1,03	10,57	10,57
MgO	0,07	0,49	0,23	3,53	1,93
Na_2O	0,25	0,27	1,69	13,75	13,77
K_2O	0,09	1,07	10,94	0,47	0,39
Cr_2O_3	Nil	Nil	Nil	Nil	0,07
L.o.I. [%]	11,28	0,60	0,54	Nil	Nil

Tab. 3 Oxide composition of the experimental bodies

Constituent [mass-%]	**A1**	**A2**	**A3**
SiO_2	67,30	66,52	66,47
Al_2O_3	20,74	18,93	18,97
Fe_2O_3	0,99	0,88	0,90
TiO_2	0,48	0,49	0,48
CaO + MgO	0,72	2,64	2,40
$K_2O + Na_2O$	3,67	4,47	4,46
Cr_2O_3	Nil	Nil	0,011
L.o.I. [%]	6,05	6,00	5,84

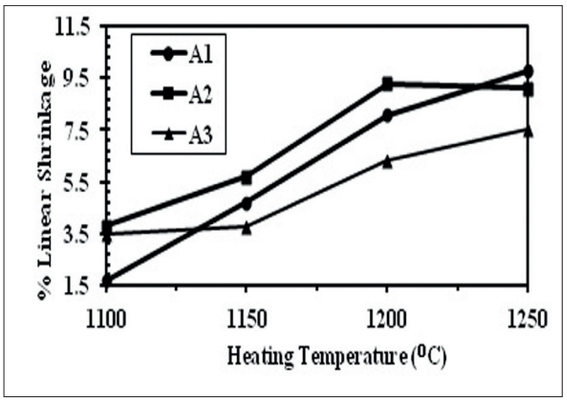

Fig. 1a Variation in linear shrinkage [%] of experimental samples in relation to heating temperature

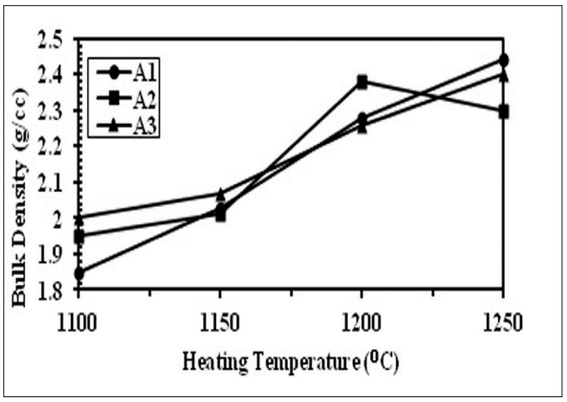

Fig. 1b Variation in bulk density [g/cm³] of experimental samples in relation to heating temperature

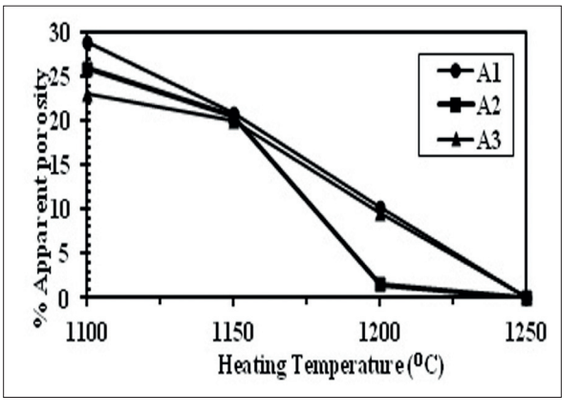

Fig. 1c Variation in apparent porosity [%] of experimental samples in relation to heating temperature

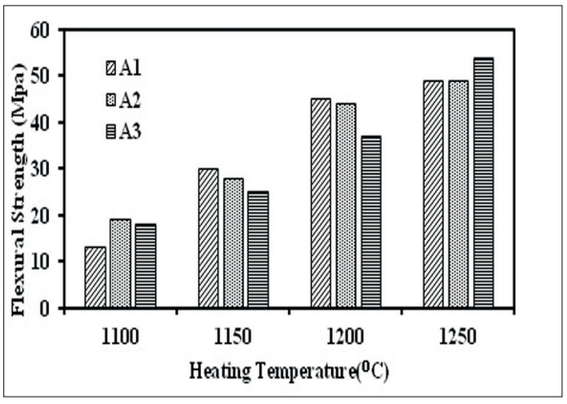

Fig. 1d Variation in flexural strength [MPa] of experimental samples in relation to heating temperature

due to the presence of higher amount of alkali minerals and alkaline earth oxide (total 7,11 mass- %). Beyond 1200 °C the density of body A2 decreases due to over fires. Bodies A1 and A2 achieved fullest vitrification at 1250 °C which is higher than A2. Effect of Cr_2O_3 in body A3 was found to be negligible towards vitrification.

Fig. 1d represents variation in flexural strength in relation to heating temperature. Although beyond 1200 °C the A2 sample works to be over fired but it is retaining its strength at 1250 °C also. However the strength of body A3 is higher than A2 at 1200 °C. Although A3 shows lower strength at all other temperature. Strength of body A1 is more or less similar to body A2. Hence based on the physico-mechanical properties

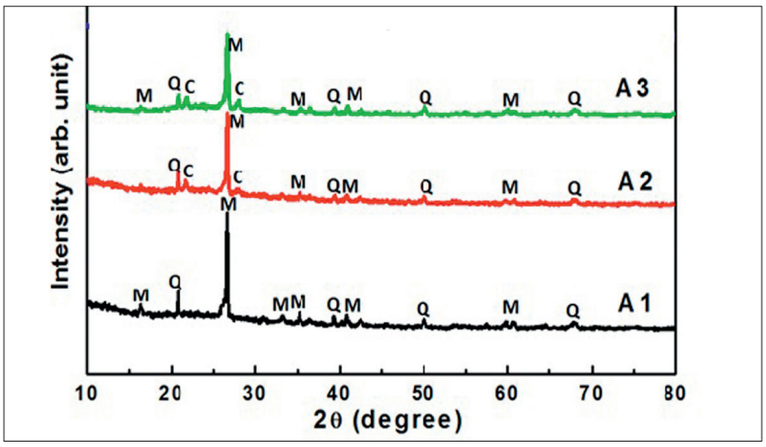

Fig. 2 XRD patterns of the samples A1, A2 and A3 fired at 1250 °C (M = Mullite; Q = Quartz, and C = Cristobalite)

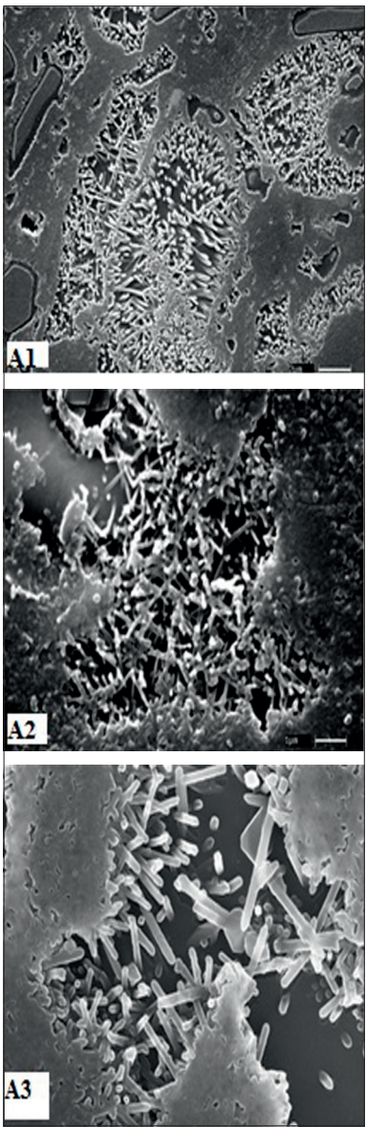

Fig. 3 Microstructure of etched samples of the bodies A1, A2, and A3 fired at 1250 °C

it can be said that naturally available feldspar can be well substituted by soda lime silica scrap glass powder in manufacturing porcelainized stoneware products.

The phase evolution and microstructure development of all the three samples are shown in Fig. 2 and Fig. 3 respectively. No significant phase changes occur due to the presence of scrap glass powder in the body. However some portion of quartz is converted to cristobalite due to the presence of scrap glass powder. Clusters of mullite needles are observed in the microstructure of all the three body. A distinct change in aspect ratio of the mullite needles has been observed in between samples. Cr_2O_3 in body A3 might have promoted the formation of larger mullite crystals.

Conclusion

Partial substitution of feldspar by soda lime silica scrap glass powder in a normal stoneware body has a pronounced effect towards their vitrification. Cr-free flint glass containing body resulted vitrification at lower temperature (1200 °C) compared to Cr-doped glass powder and normal stoneware body. Some part of the quartz converted to cristobalite in presence of scrap glass powder. Clusters of mullite needles are formed in all the bodies. Cr_2O_3 in opaque glass powder produces higher aspect ratio mullite needles.

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