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 up to 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 and 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.

Keywords: stoneware body, mullite, cristobalite, quartz
The present work is focused on the use of Cr$_2$O$_3$ doped opaque type soda-lime scrap glass in stoneware ceramic body and compare their physico-mechanical, phase and microstructural changes with Cr$_2$O$_3$ 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$_2$O$_3$) 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$_2$O$_3$) 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 XPert 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$_2$O$_3$, 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$_2$O$_3$ (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$_2$O$_3$ (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
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$_2$O$_3$ in body A3 was found to be negligible towards vitrification. Fig. 1d represents variation in flexural strength in relation to heating temperature. 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 of Cr$_2$O$_3$ in body A3 was found to be negligible towards vitrification.
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. \( \text{Cr}_2\text{O}_3 \) 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. \( \text{Cr}_2\text{O}_3 \) in opaque glass powder produces higher aspect ratio mullite needles.

**Acknowledgements**

The authors wish to thank CSIR-TWAS Scholarship Programme and the Director CSIR-Central Glass and Ceramic Research Institute, Kolkata, India for financial support and permission to publish the work.

**References**

[16] www.PANanalytical.com