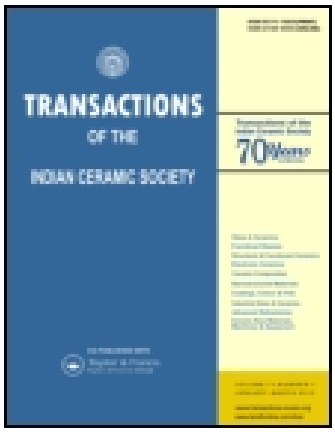

Transactions of the Indian Ceramic Society
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tcer20

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Published online: 09 Apr 2013.

To cite this article: Reshma Raut Dessai , J. A. E. Desa , D. Sen & S. Mazumder (2012) Nano-Porous Structure of a Porous Ceramics from Rice Husk, Transactions of the Indian Ceramic Society, 71:4, 243-246, DOI: 10.1080/0371750X.2013.775764

To link to this article: http://dx.doi.org/10.1080/0371750X.2013.775764

Trans. Ind. Ceram. Soc., vol. 71, no. 4, pp. 243-246 (2012).

ISSN 0371-750X (Print), ISSN 2165-5456 (Online)
http://dx.doi.org/10.1080/0371750X.2013.775764

Nano-Porous Structure of a Porous Ceramics from Rice Husk

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[MS received November 15, 2012; revised copy received January 10, 2013]

A porous ceramics is obtained using rice husk as the source of silica. The modification of mesoscopic structure under different sintering conditions has been investigated using neutron scattering techniques and scanning electron microscopy. X-ray diffraction confirmed the purity of silica by comparing the diffraction pattern from pure silica. Thermogravimetry data show that a phase transition occurs at 750°C. X-ray data confirms that sodium calcium silicate is formed after the latter transition. Small angle neutron scattering measurements reveal the presence of nanopores of two distinct size ranges; viz. 162 and 30 nm. Porosity of the compact by bulk density measurement has been found to be ~50%.

[Keywords: Sintering, Sol-gel processes, Electron microscopy, Nanopores, Scattering]

Introduction

Many industries such as rice mill and biomass power plant have been using rice husk which is a by-product of rice mill as the source of energy. Combustion of rice husk gives mainly ash, termed rice husk silica (RHS),[1] and some alkali metal impurities.[2] Due to relatively high silica content, rice husk has been used as a source for the preparation of various silicon compounds such as solar grade silicon.[3, 4] RHS may also be used in preparing glass ceramics, filler material in cement,[4, 5] zeolite, aerogel and as an adsorbent of minor vegetable oil components.[1, 6] Importance of rice husk silica ceramic composites is due to its non carcinogenic and biodegradable nature. Bioactive glasses and ceramics are brittle and this property makes them good candidates for application in the field of bone defect reconstruction (replacement biomaterial).[7, 8] Specifically, these biomaterials have found clinical applications as bone filler, vertebral substitution and, in a porous form, as bone substitutes. It has also been reported that the specific surface area and pore volume of bioactive glasses may greatly enhance their bioactive behaviour.[9–11] Nanopore characterization in such ceramics is important in such applications.

The objective of this research is to prepare ceramics from a natural source, that is by silica extracted from rice husk. Structural properties of amorphous silica in this ceramics sintered between 800° and 1000°C were also examined by X-ray diffraction (XRD). Thermal features were measured by thermogravemetry (TG-DTA). The microstructure of compacts at sintering temperatures was studied by scanning electron microscopy. Ceramic compacts showed presence of nanopore which plays a very important role in filtration. The structures of nanopores were studied by small angle neutron scattering (SANS), as this technique is well suited to obtain information in nanometric range.

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Experimental Methods

A local variety of rice husk was repeatedly washed with water before being acid leached with HCl (1 N) for 1 h. The husk was subsequently washed with hot distilled water and dried overnight at 110°C. The husk was fully combusted in air at 700°C for 6 h.[1, 2, 12] The product was a whitish ash, termed rice husk silica (RHS). The size of silica particles thus obtained was reduced by grinding. The structural properties were investigated by SEM and X-ray diffraction. The RHS was then used to prepare a porous glass-ceramics by the process[4, 13] summarized in Fig. 1 which finally yielded sodium calcium silicate.

500 mg of ceramic powder obtained after firing at 700°C was compacted at a pressure of 2 T and sintered at 800° and 1000°C. A Rigaku X-ray diffractometer (40 kV and a current of 50 A) with incident CuKα was used to observe crystalline peaks. The samples were measured in step scan mode (steps of 0.02) and speed 2°.min^{-1}. Surface morphology and composition were measured by scanning electron microscopy (JOEL, 15 kV). TGA-DTA data were obtained with a NETZSCH STA 409 PC instrument (10°C.min^{-1}). Ultra small angle neutron scattering measurements were performed on the porous ceramic samples with a medium resolution instrument which has a double-crystal arrangement at Guide tube laboratory of Dhruva reactor at Trombay, India.[14, 15] The instrument uses two perfect silicon (111) crystals with the sample located between them. The scattered intensities were measured as a function of wave vector transfer: $Q = (4\pi\sin\theta/\lambda)$, where 2θ is the scattering angle and λ is the wavelength of incident neutrons. The accessible Q (wave vector transfer) range was 0.003 to 0.173 nm^{-1} with an incident neutron wavelength of 0.312 nm.

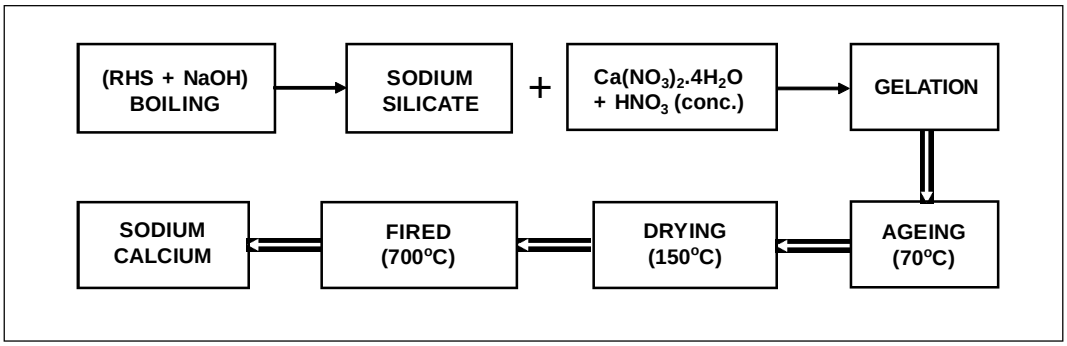

Fig. 1 – Scheme of preparation of porous glass-ceramics from rice husk silica

Results and Discussion

The absence of sharp crystalline reflections and the appearance of a broad peak at 22° in the X-ray diffraction pattern of RHS indicate that rice husk ash is in an amorphous state; comparison with commercially obtained SiO_2 shows that the RHS is indeed pure (Fig. 2a).

Scanning electron micrograph of RHS (Fig. 2b) shows that the particles in the fired samples possess irregular shape of sizes of ~600 μm length and 100 μm diameter. Shape of silica obtained is similar to that of rice husk having smaller size. The silicon content of RHS was estimated from energy dispersive X-ray (EDX) spectroscopy and is shown in Table I. Carbon is seen to be one of the principal elemental components and is likely to arise from the initial phase of preparation of RHS by combustion. Despite the atomic percentage of carbon being in excess of 12%, the overall structure of the RHS remains similar to pure silica.

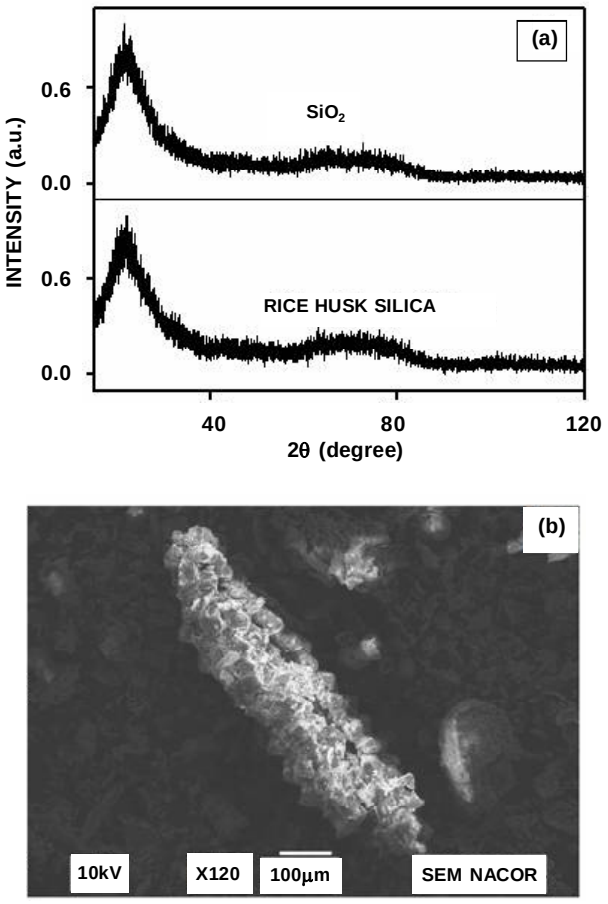

Fig. 2 – (a) X-ray diffraction comparison of rice husk silica with commercial silica, (b) scanning electron micrograph of rice husk silica (120X)

Table I : Elemental composition of silica rice husk by EDX

Element	Weight%	Atomic%	Formula
C	8.26	12.41	CO_2
Na	0.10	0.08	Na_2O
Mg	0.05	0.04	MgO
Al	0.34	0.23	Al_2O_3
Si	32.05	20.59	SiO_2
Ca	0.12	0.06	CaO
Ti	0.22	0.08	TiO_2
O	58.86	66.51	O_2
Total	100	100	–

The porous glass-ceramic samples sintered at 800° and 1000°C for 2 h were also examined by X-rays over a limited scattering angular range as shown in Fig. 3. The powder fired at 800° and 1000°C show the presence of two phases of sodium calcium silicate, viz. $Na_6Ca_3Si_6O_{18}$ (JCPDS-77-2189) and $Na_2Ca_2Si_2O_7$ (JCPDS-10-0016).[4, 13]

The thermogravemetric measurements show weight loss at about 140°, 660° and 780°C (Fig. 4) corresponding to different endothermic reactions as observed from the differential thermal analysis curve. The first weight loss at 140°C is due to loss of gel water which corresponds to a large endothermic peak at 98°C. The endothermic peak at about 237°C, which is not accompanied by weight loss, may be due to structural change. The weight loss of about 6.2% may be due to the decomposition of the nitrate

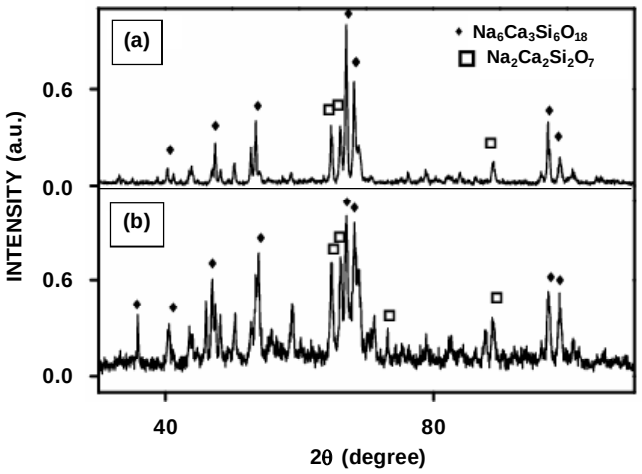

Fig. 3 – X-ray diffraction patterns of rice husk silica ceramics fired at (a) 1000°C and (b) 800°C

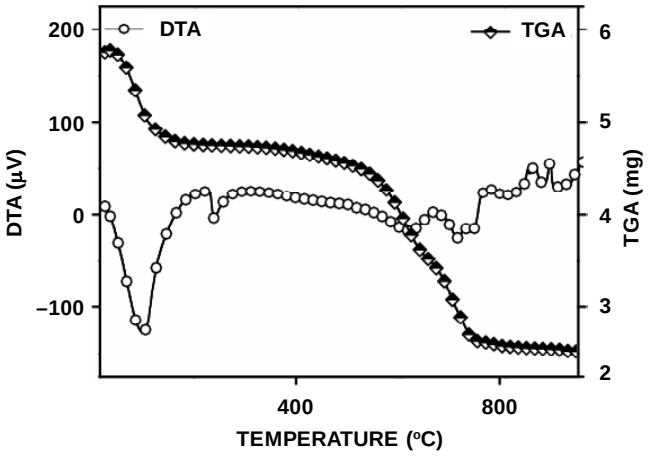

Fig. 4 – TGA-DTA curve of RHS ceramics fired at 800°C

Table II : Densities and porosities of the compacts of porous ceramics

Sample no.	Temperature (°C)	Geometric density ($g.cm^{-3}$) ± 0.005	Density by water displacement ($g.cm^{-3}$) ± 0.001	Porosity (%)
1	800	1.456	2.270	54
2	1000	1.415	2.159	50

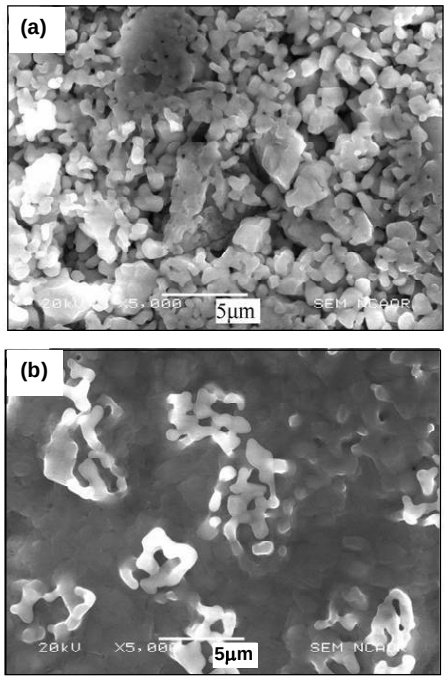

Fig. 5 – SEM images of ceramic compact at (a) 800°C, (b) 1000°C fired for 2 h (5000X)

compound and residual water. The decomposition of sodium nitrate and calcium nitrate occurs at 750°C. The peak in the DTA at 237°C may be due to crystallization of sodium nitrate or/and calcium nitrate.

Bulk densities for the two samples sintered at 800° and 1000°C, each for 2 h, were measured by the water displacement method. The density of the sample fired at the higher temperature is lower. However, comparison of the X-ray data of the two samples shows the "higher temperature" sample to have better signal to noise ratio and crystallinity. From Table II it is observed that the density and porosity go down for higher temperature in order to reconcile these two observations, with improved crystallinity. The presence of substantial number of blind / unconnected pores is proposed. Evidence of coalescence of smaller particles and reduction of pore concentration is confirmed from the SEM data (Fig. 5).

Morphological characterization of the compacts regarding surface modifications that occurred during sintering of compacts at 800° and 1000°C for 2 h are observed from the SEM images (Fig. 5). It is seen that the ceramic compact fired at 800°C is highly porous. As the sintering temperature is increased to 1000°C, the ceramic structure coalesces while reducing its porosity.

The porous ceramics contains nanopores along with pores of micron dimensions. In order to obtain pore size in these compacts of nanometer range, small angle neutron scattering (SANS) is used. Although pore size can be determined by various methods like mercury intrusion and nitrogen adsorption, SANS has the special advantage of being able to determine pores of nanometer dimension[16] as well as being sensitive to the presence of isolated pores. This method can be used to obtain pore size distributions and pore size in the range of 30 to 2000 nm depending on the parameters of the particular instrument that is used. The measured intensity from SANS were corrected for background transmission and resolution broadening.[17] The broad profiles in SANS data (Fig. 6) with two distinct zones in scattering profile indicate that the scattering originated from pores with two widely separated length scale within

the compacts. The SANS data have been fitted to a model assuming spherical shapes of scattering centres in which there are two main size domains, viz. 30 and 162 nm with a fractal dimension of 2.87.

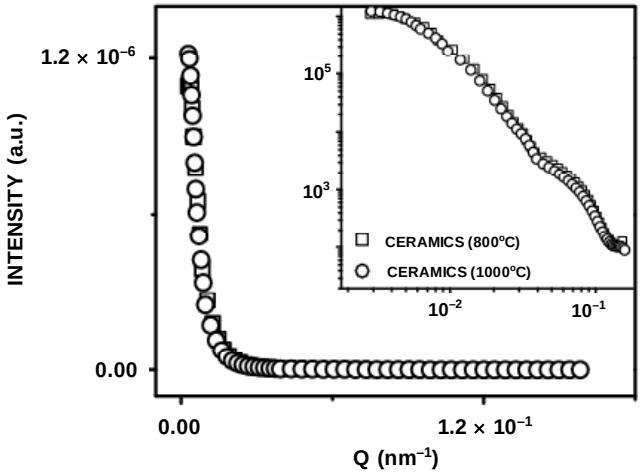

Fig. 6 – Scattering profile of ceramics sintered at 800° and 1000°C; inset shows profiles on a log-log scale

Conclusions

A porous ceramics has been prepared from rice husk as the starting material. The ceramics has been found to have a hierarchical range of pore sizes spanning over from micrometric to nanometric dimension. From bulk density measurements, porosities (due mainly to macroscopic pores) of the compacted and sintered ceramics (at 800° and 1000°C) have been found to vary between 50 and 54%. Scanning electron microscopy has shown pores of micron sizes ranging from ~0.5 to 5 μm. The particles have also been seen to coalesce at higher temperatures giving rise to reduction of pore concentration, especially of the larger ones, and an increase in numbers of isolated pores. Small angle neutron scattering measurements data show a good intensity of scattering indicating the presence of nano-sized scattering centres. Further, fits to the SANS data to spherical scattering centres give 30 nm as the individual size with 162 nm as the aggregate size having a fractal dimension of 2.87.

Acknowledgements: The authors gratefully acknowledge funding of this work by UGC-DAE CSR (CRS-M-148). The authors are also grateful to the Director, National Centre for Antarctic and Ocean Research, Vasco da Gama, Goa for their generous help with the SEM micrographs and EDX data.

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