Nanocrystalline Macroporous Wollastonite Ceramics – A Spectroscopic View

R. P. Sreekanth Chakradhar
Department of Physics, Indian Institute of Science, Bangalore 560 012, INDIA.

Abstract
Nanocrystalline macroporous CaSiO$_3$ ceramic powders have been synthesized by a novel low temperature initiated self-propagating, gas producing solution combustion process. The effects of temperature on crystalline phase formation, amount of porogens and particle size of porous CaSiO$_3$ have been investigated. Single phase β-CaSiO$_3$ and α-CaSiO$_3$ are formed at much lower temperatures to the powders obtained via solid state reaction method. On calcination the samples becoming more porous and the pore diameter increases from 2 to 8 µm. The samples calcined at 950 °C has 17.5 % porosity, and the porosity increases to 31.6 % at 1200 °C. The surface area of as formed and calcined at 950 and 1200 °C of CaSiO$_3$ samples were found to be 31.93 m$^2$/g, 0.585 m$^2$/g and 3.48 m$^2$/g respectively. The TL intensity in powdered sample is more when compared to the pelletized CaSiO$_3$ and it is further observed that there is a shift in glow peak temperatures in pelletized sample. This is attributed to the inter particle spacing and pressure-induced defects. The structure of CaSiO$_3$ has been investigated by $^{29}$Si MAS NMR.

INTRODUCTION
In recent years, materials with porous architecture and high surface area are being developed for numerous potential applications in nanotechnology. Since the discovery of the ordered mesoporous silica [1], a lot of porous materials have been synthesized using surfactants as template. However, most of these materials are unstable on removal of the surfactant and the porous skeleton collapse easily when heated above 400 °C. Therefore, new methods of synthesis which give higher stability are desirable.

In the present study, we describe a simple and quick method of preparing nanocrystalline macroporous wollastonite (CaSiO$_3$) ceramic powders. The main advantage of this method is the ability of maintaining porous structure even at elevated temperatures and moreover, the pore diameter increases upon heating. High thermal stability of porous materials can combine porous structure with traditional ceramic science and technology, leading to wide applications.

EXPERIMENTAL
The stoichiometry of the redox mixture used for combustion process was calculated using the total oxidizing and reducing valencies of the ingredients, following the concept used in propellant chemistry. The fuel diformyl hydrazine (C$_2$H$_4$N$_2$O$_2$, DFH), used for combustion synthesis, was prepared in our laboratory by the reaction of formic acid and hydrazine hydrate as described in the literature [2]. For the preparation of wollastonite, the required mole ratio of Ca(NO$_3$)$_2$:4H$_2$O:SiO$_2$:DFH was 1:1:1:2.5. The samples have been studied by various spectroscopic techniques like XRD, TG/DTA, EDS, SEM, FTIR, Thermo luminescence (TL) and MAS NMR. The powder (1mg) as well as the pellets (before and after heat treated) are irradiated with gamma rays (Co$^{60}$ source for a dose of 1 - 5 KGy for TL studies.

RESULTS AND DISCUSSION
The phase evaluation of the as formed and calcined powders of CaSiO$_3$ was examined by powder X-ray diffraction and is shown in Fig. 1. It has been observed that the peaks of CaSiO$_3$ become more and more intense with increase in calcination temperatures from 500-950 °C. On further increase in calcination temperature from 950 - 1200 °C, the simultaneous existence of CaSiO$_3$ in β and α phases could be observed at 1100 °C. Single phases of β-CaSiO$_3$ and α-CaSiO$_3$ can be synthesized at 950 and 1200 °C, respectively. The phase transformation temperatures of combustion derived wollastonite powders were found to be lower to the powders obtained via solid-state reaction method. It was observed that the average particle size of the annealed CaSiO$_3$ samples is in the range 29–50 nm. The nominal composition of the ceramic powders was confirmed by EDS.

The size morphology and distribution of the (a) as formed and calcined at (b) 950 °C and (c)1200 °C CaSiO$_3$ powders was examined using a SEM and are shown in Fig. 2. It is interesting to note that, with increase of temperature the samples becoming more porous and the pore diameter increases from 2 – 8 µm. The as formed sample shows uniform distribution of nanosized particles. The calculated porosity values are 17.5 % and 31.6 % at 950 °C and 1200 °C respectively. The surface area of as formed CaSiO$_3$ and calcined at 950 and 1200 °C are 31.93, 0.585 and 3.48 m$^2$/g respectively.
The large surface area (31.93 m²/g) of as made sample is due to uniform distribution of nano sized particles. On heating the sample at 950 °C, the surface area decreases to 0.585 m²/g might be due to the growth in particle size or agglomeration. On further calcination to 1200 °C the surface area increased to 3.48 m²/g is due to the swelling of agglomerated powder particles.

The TG curve shows about 9% weight loss around 120 °C, which can be attributed to the vaporization of hydrated and coordinated water molecules. From TG curve it is also observed that further weight loss takes place at two stages, one around 530 °C with endothermic peak corresponding to 25% of total weight loss and another one at 745 °C corresponding to total 33% weight loss. Besides to TG-DTA evidence, the IR spectra of the as formed and calcined samples at different temperatures also witnessed the presence of water molecules. This weight loss should be either the release of trapped and very strongly bonded water molecules or correspond to OH groups, in agreement with the ²⁹Si MAS NMR experiments (Fig. 3) showing the transformation of $Q_1$ and $Q_2$ into $Q_3$. The exothermic peak at 890 °C in the DTA curve indicates starting of crystallization of CaSiO₃ and a phase transformation into β-wollastonite in confirmation with XRD results.

Fig. 1. PXRD patterns of combustion derived CaSiO₃ powders (a) as formed (b) 500 °C (c) 700 °C (d) 950 °C (e) 1100 °C and (f) 1200 °C.

Fig. 2. The SEM images of combustion derived wollastonite powders (a) as formed (b) calcined at 950 °C (c) calcined at 1200 °C.

Fig. 3. ²⁹Si MAS NMR spectrum of CaSiO₃  (a) as formed  (b) calcined at 950 °C Deconvoluted Gaussian line shapes for each $Q^n$ obtained from a least-square analysis. MAS spectrum is shown in open circles and the dashed line is the theoretical fit.

The ²⁹Si MAS NMR exhibits the resonances at $-71.29$, $-77.45$ and $-89.52$ ppm and are assigned to $Q_1$, $Q_2$ and $Q_3$ units, respectively. For fully crystalline sample of CaSiO₃ (950 °C 3 h), shows only one fairly narrow peak centered at $-90.31$ ppm indicating a largest amount of silicon in the sample present as $Q_3$ groups. The TL intensity is more in powdered sample compared to pelletized sample. This might be attributed to the physical nature, structure of the sample. The shifts in TL glow peaks as well as reduction in TL intensity in pelletized samples are attributed to inter particle spacing and pressure induced defects.

REFERENCES