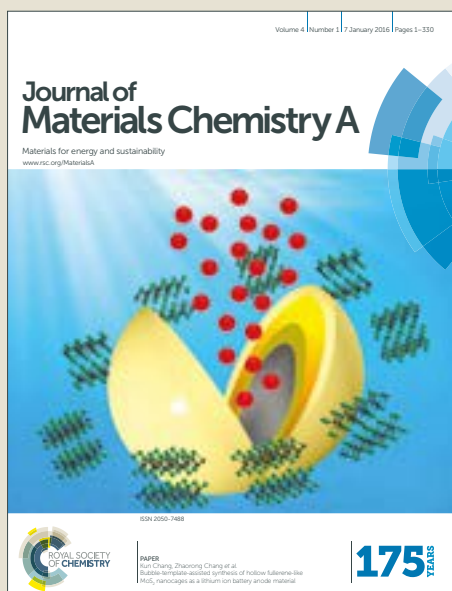


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Germanium Incorporated Lithium Silicate as Highly Efficient Low Temperature Sorbents for CO₂ Capture

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Carbon dioxide emission from massive point sources such as industries and power plants is perceived to be a major contributor towards global warming and associated climate changes. Lithium silicate with the highest capacity for CO₂ sorption (8 mmol g⁻¹) suffers from kinetic limitations during the sorption process, particularly at temperatures below 500 °C. Herein, we report a facile strategy for the development of germanium incorporated lithium silicate composites, which display enhanced CO₂ absorption capacity as well as kinetics in the temperature range of 150 to 700 °C. The absorption capacity of 324 mg g⁻¹ at the rate of 117 mg g⁻¹ min⁻¹ was measured at 680 °C and 49 mg g⁻¹ at the rate of 36 mg g⁻¹ min⁻¹ was measured at 300 °C for the samples with the Si: Ge molar ratio of 1: 0.183. The study thus highlights the possibility of employing germanium incorporated lithium silicates for the absorption of CO₂ at a wide range of temperatures, including the in-situ removal of CO₂ from chemical and petrochemical reactions such as water gas shift reaction occurring at low temperature ranges of 150 °C - 450 °C, that has hitherto been not possible with pure Li₄SiO₄.

1. Introduction

The atmospheric concentration of CO₂ went up dramatically in the post-industrial era reaching the present value of ~400 ppm. This has, in turn, created severe environmental issues like global warming and climate destabilization inducing undesirable weather patterns and natural calamities. For the sustainable balance of carbon cycle in the biosphere, selective and controlled removal of CO₂ followed by its reuse or sequestration is essential. It is, therefore, necessary to develop sustainable technologies for the effective removal of CO₂ from the point sources to reduce carbon foot prints in the atmosphere¹⁻¹⁵. In order to realize this, most often we rely on post-combustion CO₂ capture and proven

approaches like the use of amine-based absorbents and oxy-combustion techniques are adopted to reduce the increasing level of CO₂ in the atmosphere.

Out of various high-temperature CO₂ absorbents¹⁶⁻¹⁸ available presently, Li₄SiO₄ qualifies as a potential material by virtue of its high absorption capacity with appreciable kinetics at elevated temperatures (450-700 °C)¹⁹⁻²³. However, Li₄SiO₄ suffers from poor absorption capacity and slow kinetics in the low-temperature range (150-450 °C) where several chemical and petrochemical reactions occur. This necessitates the need for the development of materials that display appreciable absorption capacities at lower temperatures. Conventionally synthesized lithium silicate materials^{24,25} in the pure form absorb CO₂ in the temperature range of 650-700 °C. Nevertheless, the kinetics gets affected due to strong lattice enthalpy and the diffusion resistance arising from the absorption product layer. The addition of second phase eutectics can promote CO₂ absorption at lower temperatures to some extent. Several synthesis approaches such as sol-gel, hydrothermal,

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thermal oxidation and plasma irradiation are adopted to control the morphology and composition of the lithium silicate particles²⁶⁻²⁸. The solid-state approaches often use high calcination temperatures leading to particle agglomeration and non-uniform particle size distributions. Wet chemical approaches such as hydrothermal, co-precipitation are effective in morphological control but are time-consuming. Radiative techniques such as plasma oxidation^{29,30} are recently used for the preparation of Li_4SiO_4 . However the use of high temperature can induce compositional changes due to the sublimation of lithium during irradiation leading to poor absorption and kinetics during the sorption process. We have earlier reported the synthesis of Li_4SiO_4 through microwave assisted sol-gel process resulting in the formation of Li_4SiO_4 nano-rods that displayed near theoretical absorption capacity with enhanced sorption rates³¹⁻³². However, the CO_2 absorption properties of the pure Li_4SiO_4 powder were found insignificant below 450 °C.

In the present investigation, we aim to enhance the kinetics and absorption capacity of Li_4SiO_4 material at low as well as elevated temperatures through the development of germanium incorporated Li_4SiO_4 nanostructures. Since silicon and germanium exhibit similar physical and chemical properties, substitution of silicon by germanium is possible, due to which a lattice expansion and thereby an increase of CO_2 absorption is expected. Germanium compounds exhibit higher electronic conductivity and lithium diffusivity than that of silica, but its lack of economic viability imposes restrictions in wide spread applications. Fuller and Severiens revealed that lithium has an ability to migrate as a singly-charged positive ion in single crystals of both Ge and Si in the temperature ranges of 150-600 °C and 360-860 °C respectively³³. Further, Graetz et al. reported that lithium-ion diffusivity in Ge matrices is approximately 15 times higher than that of silica at 360 °C and can hence be used in lithium batteries³⁴. In view of such favourable diffusion properties of germanium, it is expected that the lithium-ion hopping in germanium containing lithium silicate structures should be larger than the Li_4SiO_4 matrices. It is also known that Li_4SiO_4 and Li_4GeO_4 are iso-structural. Hence, the incorporation of germanium to the crystal lattice of Li_4SiO_4 could be considered as an option to process high-performance absorbent

materials. Nobuaki et al. compared the absorption capacity of Li_4TiO_4 , Li_4SiO_4 and Li_4GeO_4 , however their results showed that the absorption performance of Li_4GeO_4 in its pure form is lower than that of Li_4TiO_4 ³⁵ & Li_4SiO_4 ^{36,37}. In this work, the possibility of employing germanium substituted Li_4SiO_4 for the absorption of CO_2 at temperatures as low as 150 °C is demonstrated for the first time. Moreover, the sorbent structure is tailored to be nano-sized to minimize diffusion resistance during the CO_2 capture as well as during its regeneration. The present investigation thus reveals the development of germanium incorporated lithium silicate (Ge-LS) for the reactive absorption of CO_2 . By employing a microwave sol-gel approach, we made nanorods of substituted structures that displayed enhanced CO_2 absorption with significantly improved kinetics at low as well as elevated temperatures.

2. Experimental

a. Synthesis of Germanium incorporated lithium silicate

$\text{Li}_4\text{Si}_x\text{Ge}_{1-x}\text{O}_4$ having Si: Ge molar ratios of 1:0.040, 1:0.084, 1:0.183 and 1:0.447 was synthesized by sol-gel method employing lithium nitrate (Alfa Aesar, USA), colloidal silica (purity 99.8%, Aldrich Chemicals, USA) and germanium tetrachloride (Alfa Aesar, USA) as the starting precursors. Initially, 11.495 g of lithium nitrate dissolved in 40 ml of distilled water was hydrolysed by the slow addition of ammonium hydroxide solution and pH was raised to 8. Subsequently colloidal silica and germanium tetrachloride were added drop wise to this reaction mixture with constant stirring and the resulting solution was stirred for 1h. The resulting gel was subjected to microwave irradiation for 4 min, dried at 150 °C for 15h and calcined at 800 °C for 3h to obtain germanium incorporated lithium silicate (Ge-LS).

The phase pure lithium silicate (Li_4SiO_4) sample for comparison was also made by sol-gel method, starting from lithium nitrate and colloidal silica as precursors. For this, lithium nitrate (11.495 g) was dissolved in 40 ml distilled water and by the slow addition of ammonium hydroxide solution (25%, s. d. fine-chem. Ltd, India) the pH was increased to 8 with constant stirring. Further, 8.5 g of colloidal silica sol (50 wt %, purity 99.8 %, Aldrich Chemicals, USA) was added drop wise

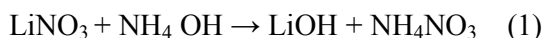
to the reaction mixture. The mixed sol thus obtained was subjected to microwave irradiation for 2 min followed by oven drying at 150 °C for 15 h. The mixture was calcined at 800 °C for 3h to obtain phase pure lithium silicate sample.

b. Characterisation

The crystalline phases of the synthesized samples were analysed employing X-ray diffraction (Philips X'pert Pro diffractometer) in the 2θ range of 9-55 using Cu Kα radiation (λ= 0.154 nm). Raman spectra of pure and germanium added lithium orthosilicate samples were recorded using a WI-Tec Raman microscope (WI-Tec, Inc., Germany, alpha 300R) with a Peltier cooled CCD detector. The 633 nm excitation wavelength laser was used for the excitation of the sample and the spectra were collected in the range of 400-3000 cm⁻¹ with 1 cm⁻¹ resolution. The morphological and micro structural analyses of the materials were carried out using a scanning electron microscope (JEOL JSM-35) operated at 15 kV. The morphology and topographical data of the samples were investigated using a HR-TEM (FEI Tecnai 30G2 S-T win) operating at 300 kV. The Thermo gravimetric analysis of the prepared samples were done using a Perkin Elmer STA 6000 instrument (Netherlands) in the temperature range of 50-900 °C at a heating rate of 10 °C/min. In the set up used, actual temperatures close to sample were typically 5-10 °C lower than the set temperatures. CO₂/nitrogen flow rate through the sample chamber was ~50 ml /min. X-ray photo electron spectroscopy (XPS) was carried out on PHI 5000 versa probe II with a monochromated Al K - X-ray source.

3. Results and discussions

During the microwave sol-gel process, lithium hydroxide formation occurs due to the hydrolysis of aqueous lithium nitrate.



The addition of germanium chloride into the reaction mixture results in the formation of germanium hydroxides, as reported in the literature³⁸.



Hydrolysed products in the reaction mixture undergo poly condensation reactions with

silica, leading to the formation of the gel network. The calcination at 800 °C results in the formation of LS and Ge-LS samples. Structural, morphological as well as CO₂ absorption studies of the as-synthesized samples are carried out and are described in the following sections.

X-ray diffraction patterns of Ge-LS sample synthesized through sol-gel route at different molar concentrations are shown in Fig. 1.

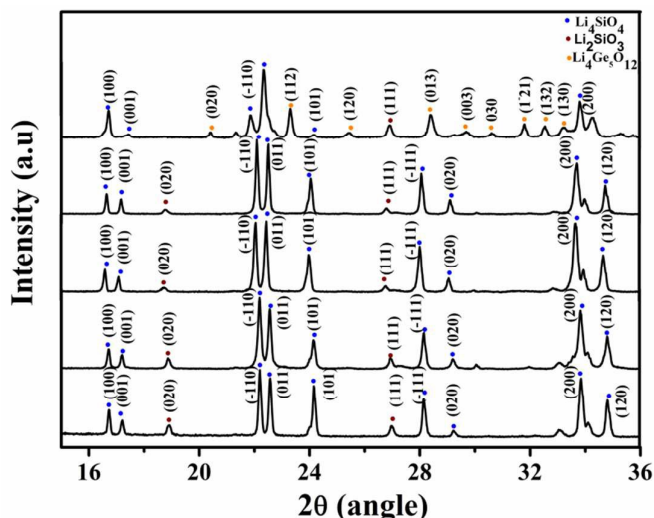


Fig. 1. X-ray diffraction patterns of (a) pure Li₄SiO₄ (b) Ge-LS samples at different (Si: Ge) molar ratios 1:0.040 (c) 1:0.088, (d) 1:0.183, (e) 1:0.447.

The expected characteristic reflection peaks of monoclinic lithium silicate phases were observed in all (Si: Ge) compositions, the major reflections from the planes (-110), (011) and (200) with the 2θ angles of 22.1, 22.6 and 33.8 were seen and are in accordance with JCPDS (037-1472) data. The addition of germanium to the lithium silicate sample resulted in the slight shifting of maximum intensity peak towards lower 2θ values, compared to that of the Li₄SiO₄ sample. The peak shift can presumably be attributed to the substitution of silicon by germanium in the crystal lattice of Li₄SiO₄ leading to a lattice expansion in accordance with Vigards law. The peak shifts in Ge-LS samples are highlighted in the XRD patterns provided in Fig. 2.

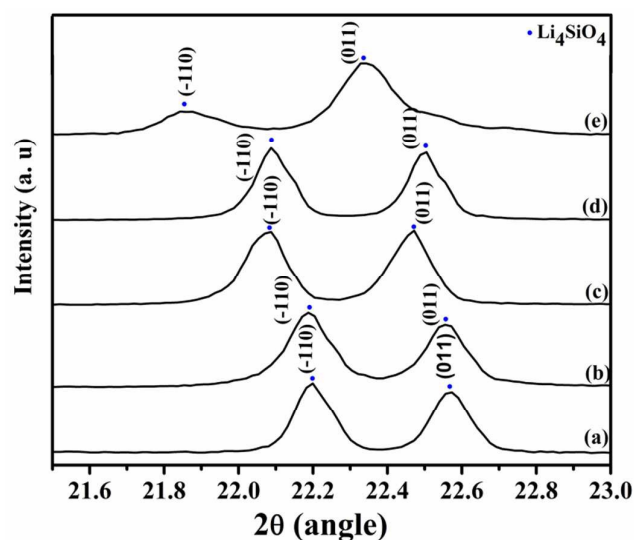


Fig 2. X-ray diffraction patterns of (a) pure Li_4SiO_4 (b) Ge-LS samples with different (Si: Ge) molar ratios 1:0.040 (c) 1:0.084 (d) 1:0.183, (e) 1:0.447.

The XRD patterns in Fig. 1 and 2 of the composition containing the highest amount of germanium (1:0.447) clearly revealed that other phases of germanium ($\text{Li}_4\text{Ge}_5\text{O}_{12}$) coexisted along with the lithium silicate phase. The identification of such phases was done in conjunction with the Raman spectroscopic analysis (Fig. 3).

The characteristic vibrational frequencies of GeO_4 tetrahedra were found in the range of $850\text{--}650\text{ cm}^{-1}$ and the external modes of GeO_4 were found below 370 cm^{-1} . In pure LS, the characteristics peaks are seen at wave numbers of $1086, 822, 163$ and 95 cm^{-1} . The addition of germanium to the Li_4SiO_4 resulted in the slight shift of peak at 822 cm^{-1} to the lower wavelength region due to the substitution of silicon by germanium in the crystal lattice of Li_4SiO_4 (Fig. 3). In the sample having silicon and germanium in the molar ratio (1:0.040), apart from the peak shift to the left, splitting of peaks was also observed at 829 cm^{-1} . As the germanium content was increased, the shifts corresponding to the molar ratio (1:0.084), (1:0.183) were $791, 789\text{ cm}^{-1}$ respectively. At the highest composition (1:0.447) the peak intensity at 822 cm^{-1} decreased due to the decrease in silica content in contrast to the increasing intensity of 1093 cm^{-1} band indicating silica substitution with germanium or the formation of the higher phase of lithium germanates in the samples.

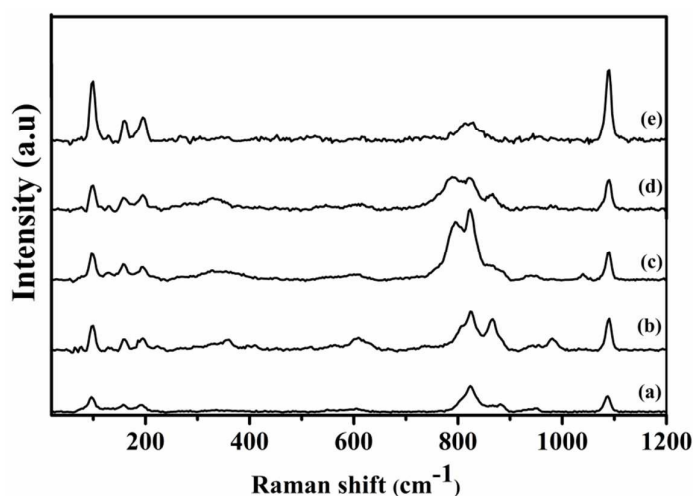
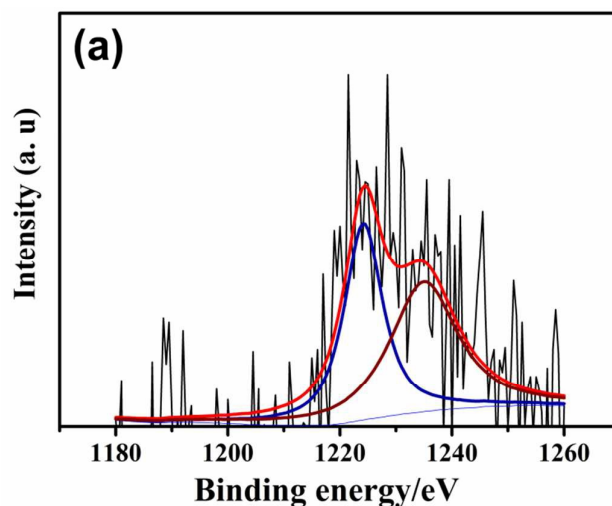


Fig 3. Raman spectrum of (a) pure Li_4SiO_4 (b) Ge-LS samples with different (Si: Ge) molar ratios 1:0.040, (c) 1:0.084, (d) 1:0.183 (e) 1:0.447.

The substitution of silicon by Ge in the crystal lattice of Li_4SiO_4 was again confirmed by the XPS spectral analysis shown in Fig. 4 (a & b). In Fig. 4a the main peak of $\text{Ge } 2p^{3/2}$ appeared at 1224 eV which is related to Ge^{4+} and the loss feature may be observed between the spin components at 1235 eV and is consistent with results reported in literature³⁹. The Fig. 4(b) XPS spectrum was deconvoluted to three peaks to fit the $\text{O } 1s$ spectra, corresponding to Ge-O (+4), Si-O and O-O. The peak of $\text{O } 1s$ appeared at 531.3 eV , was related to Ge-O bond and the core level shift of oxidation state at 532.1 eV corresponded to Si-O bond. The conformation of localized oxygen arising from the O-O scattering was observed at around 530.5 eV .



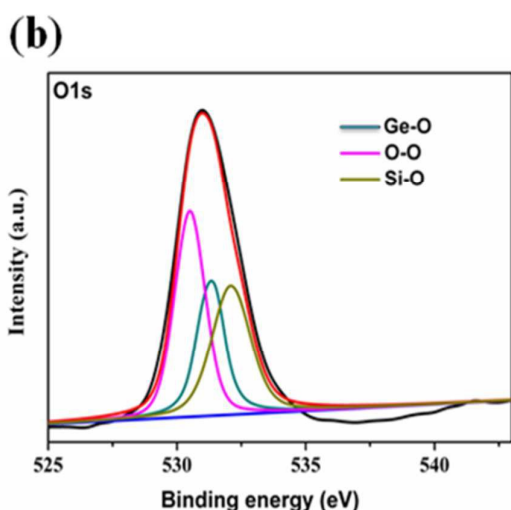


Fig. 4. XPS analysis of Ge-LS sample in the molar ratio 1:0.183 (a) Ge 2p core level spectra (b) O1s core level spectra of oxide formation.

Morphological characterization of the pure LS and Ge-LS samples with the molar ratios of 1:0.040, 1:0.084, 1:0.183 and 1:0.447 are presented in Fig. 5. From morphological observations, it can be noticed that in the sample containing lower amounts of germanium (1:0.040) the particles had flower-like morphology Fig. 5a. In samples having molar ratio 1:0.084, the particles appeared uniformly as stacked sheets (Fig. 5b) and as the molar ratio was further increased (1:0.183) the particles appeared as needle shaped structures with a lesser degree of agglomeration (Fig. 5c). Samples having still higher concentration of Ge (1:0.447) showed larger particles with needle-shaped morphology Fig. 5d.

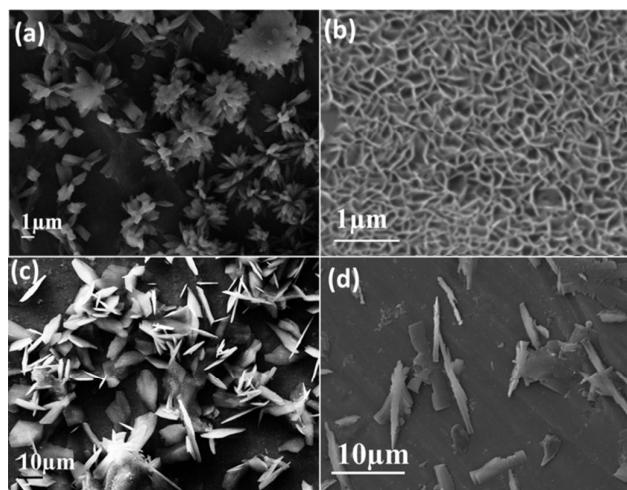


Fig. 5. SEM images of Ge-LS samples with different molar compositions of Si: Ge (a) 1:0.040, (b) 1:0.084, (c) 1:0.183 and (d) 1:0.447.

Micrographs of samples containing low molar concentration (1:0.084) of germanium indicated that the needle formation was less apparent in such samples. The presence of Ge in these samples was confirmed from EDAX analysis presented in Fig. 6. Although some differences between the molar composition used for synthesis and measured were detected, the EDAX results more or less reflected the synthesis composition.

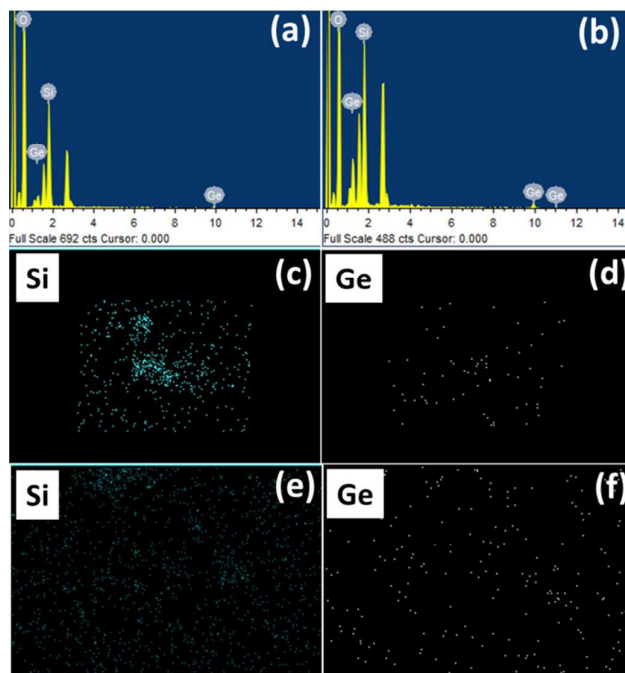


Fig 6. (a) EDAX of Ge-LS sample in the molar ratio 1:0.084 and its elemental mapping in c & d. (b) EDAX of Ge-LS sample in the molar ratio 1:0.183 and its elemental mapping in e & f.

Table 1. EDAX analysis of the Ge-LS sample with different molar composition.

Sl.No	Molar composition of (Si: Ge) (as per composition used for synthesis)	Measured molar composition of (Si: Ge) (EDAX analysis of samples)
1	1: 0.040	1: 0.029
2	1: 0.084	1: 0.077
3	1: 0.183	1: 0.116
4	1: 0.447	1: 0.244

The morphology and microstructure of the samples with the molar ratio of 1:0.183 and 1:0.084 are investigated using a high-resolution transmission electron microscopy (TEM) and the images are shown in Fig. 7 (a & b). From high magnification images, the particles were

observed as needle structures with pointed edges as has been revealed by the SEM images.

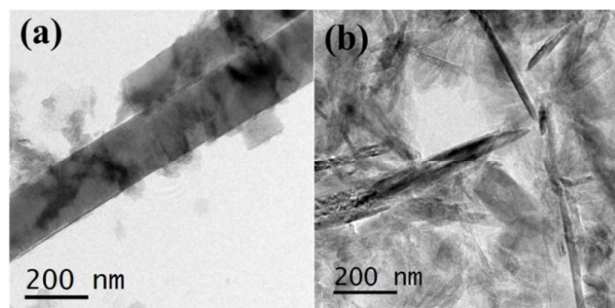
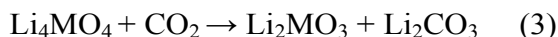


Fig 7. TEM Images of Ge-LS samples having the molar ratio (a) 1:0.183 and (b) 1:0.084.

CO₂ absorption studies

CO₂ absorption studies were carried out by gravimetric techniques using a thermal analyzer (TGA) in the temperature range of 100 to 800 °C. In the sample chamber, CO₂/N₂ flow rates were approximately 50 mlmin⁻¹. The mechanism of CO₂ absorption in Li₄SiO₄ is well known and widely reported. Absorption of CO₂ in the case of Ge-LS sample also lead to the formation of lithium metasilicate and carbonate phases and the reaction could be represented in the following generalized form



Where M = Si_xGe_{1-x}

Ge-LS samples of molar ratios 1:0.040, 1:0.084, 1:0.183, 1:0.447 were initially heated to a temperature of 800 °C at a heating rate of 20 °C min⁻¹ under 100 % CO₂ flow to obtain dynamic thermogram. The dynamic thermograms of these samples are shown in Fig. 8 and the low-temperature absorption behaviour is highlighted in Fig. 9. The absorption of CO₂ in LS became significant only after the temperature reaches 500 °C; the kinetics of absorption was always negligible below 500 °C. Compared to this, Ge-LS materials exhibited four distinct absorption steps during the sorption process. CO₂ absorption was initiated at a very low temperature of 150 °C as clearly visible from the low-temperature absorption part highlighted in Fig. 9. When the temperature was slightly above 250 °C, a sudden weight increment occurred. After the completion of this step, two more distinct steps around 500 °C and 600 °C were visible in the dynamic TG patterns.

Finally, as the temperature reached around 680 °C, the desorption of CO₂ from the samples occurred due to the reverse reaction forming the initial Ge-LS phase. The comparative absorption rates depended on a great deal on the composition of the samples. The absorption capacity increased with increasing germanium addition up to the Si: Ge molar ratio of (1: 0.183). As the Si: Ge molar ratio was increased to 1: 0.447, the absorption capacity in the higher temperature range above 600 °C was reduced. As shown, Ge-LS samples exhibited significant CO₂ absorption at very low temperatures of 150 °C. The absorption of CO₂ at low temperatures increased with increase in the concentration of germanium in lithium silicate samples.

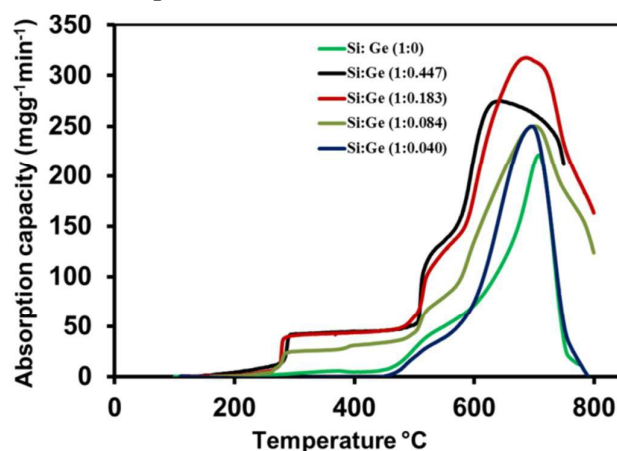


Fig 8. Dynamic thermo gravimetric analysis of Germanium incorporated lithium silicate samples measured at 20 °C min⁻¹ (100 % CO₂) with respect to temperature.

In the present investigation, a sample with the molar ratio of 1:0.183 (Si: Ge) exhibited enhanced absorption capacity and kinetics at both low and elevated temperatures compared to samples with molar ratios of 1:0.084 and 1:0.040. Sample with a molar ratio of 1:0.447 showed similar absorption properties with that of the sample of molar ratio of 1:0.183, at low temperatures. However, the absorption capacity of such samples was lower at elevated temperatures. The variation in absorption capacity at different molar ratios of silicon and germanium can be clearly correlated to the phase composition as analyzed through XRD and Raman spectroscopy. The low absorption values observed at elevated temperatures could lead to the conclusion that at higher concentrations, excess un-substituted germanium appears as oxide phases, resulting in a reduction of absorption capacity. For e.g.

the formation of $\text{Li}_4\text{Ge}_5\text{O}_{12}$ phase in the sample of Si: Ge (1:0.447) molar composition could effectively reduce the CO_2 absorption capacity as the Li: M (Ge) ratio in this material is 4:5 compared to the value of 4:1 in Li_4SiO_4 . The appreciable absorption capacity of (1:0.447) and 1:0.183 Si: Ge samples at low temperatures should be due to the presence of germanium incorporated lithium silicate phase.

The enhancement in the kinetics of CO_2 absorption capacity at lower as well as at elevated temperatures of Ge-LS sample having the molar ratio of 1:0.183 should be mainly due to the incorporation of Ge into the lattice of lithium silicate. It is reported that the diffusivity of lithium in germanium is 15 times higher than that of lithium in silicon at 360°C ³⁴. Hence the substitution of Si by Ge in the Ge-LS samples should have influenced the diffusion kinetics of lithium ion in the substituted silicates. Moreover, the needle like morphology of the samples obtained by the microwave sol-gel process should also have contributed in the enhancement of the absorption kinetics as has been reported in a recent study on phase pure lithium silicate³².

Conventionally low-temperature absorption ($\sim 400^\circ\text{C}$) was observed in lithium silicate samples modified with low melting fluxes. In the present work, we have successfully enhanced the kinetics as well as the absorption capacity of the material at much lower temperatures through the incorporation of germanium in lithium silicate.

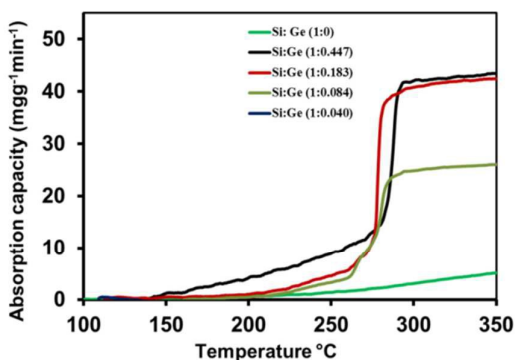


Fig. 9. Dynamic thermogravimetric analysis of Ge-LS samples in the temperature range $100\text{--}350^\circ\text{C}$.

From the highlighted dynamic thermogram (Fig. 9), it can be observed that the absorption is initiated from the lower temperature of 150°C and at temperatures above 250°C the absorption becomes significant. CO_2 absorption

studies of the samples are also performed by heating the sample from ambient temperature to the respective absorption temperatures ($300\text{--}680^\circ\text{C}$) at a heating rate of $10^\circ\text{C}/\text{min}$ under 100% CO_2 flow. As expected, the absorption increased with increase in temperature. The detailed absorption-desorption isotherms at various temperatures of the Ge-LS sample with the molar ratio 1:0.183 are shown in Fig. 10.

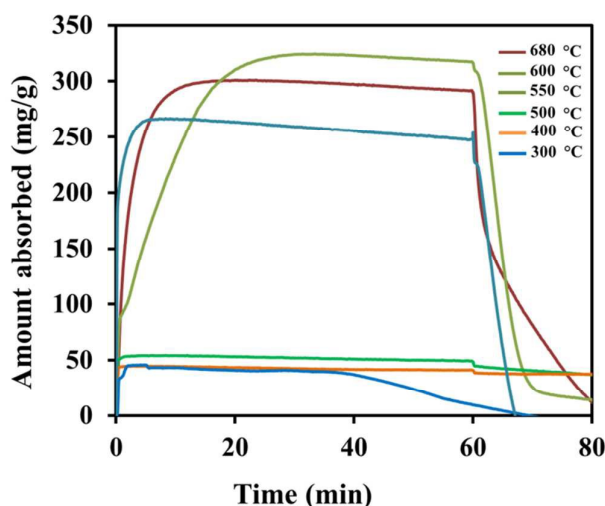


Fig. 10. A detailed comparison of the absorption performance of the synthesized Ge-LS sample in the molar ratio (1:0.183), measured under isothermal conditions.

The sorption at higher temperatures was carried out by holding the sample at 600 and 680°C for one hour under 100% CO_2 gas flow and complete desorption was obtained by switching the gas to N_2 . At lower temperatures ($300\text{--}500^\circ\text{C}$) the sample was held for one hour under 100% CO_2 flow and the desorption was attained by heating the sample to higher temperatures (700°C) as switching the gas to N_2 alone at the absorption temperatures did not facilitate desorption of CO_2 .

The absorption capacity of the 1:0.183 sample, reached the maximum value of 320 mg g^{-1} at 600°C within 25 min of CO_2 flow and complete desorption was realized by switching the gas to N_2 at the same temperature. The absorption capacity was slightly lower (300 mg g^{-1}) at the measurement temperature of 680°C though the maximum capacity was attained much earlier with a faster absorption kinetics. Complete desorption was achieved at this temperature also by the gas switching to N_2 . The sample at 300°C reached its maximum absorption capacity of 49 mg g^{-1} within 6 minutes of CO_2 exposure. This value

increased only slightly even at the measurement temperature of 500 °C. However, desorption could not be achieved by switching the gas to N₂ at the measurement temperatures of 300 °C, 400 °C and 500 °C. The desorption in such cases was realized by increasing the temperature to 700 °C. The full isotherm for a sample at 300 °C adsorption temperature and 700 °C desorption temperature is shown as a typical example in Fig 10.

In order to elucidate the CO₂ sorption mechanism of Ge-LS samples, the phase identification of the sorption products at 300 °C, 500 °C, 600 °C and 680 °C have been carried out using XRD analysis Fig. 11. From the characterization data, it could be observed that the Ge-LS samples at T > 300 °C contained lithium carbonate and Li₂GeO₃ as sorption products indicating the conversion of Ge-LS samples at temperatures as low as 300 °C. Increasing the temperature from 300 °C to 680 °C, lithium orthosilicate phase diminishes and an increase in the intensity of lithium metasilicate phase was observed. The presence of Li₂GeO₃ phase but not Li₂SiO₃ in the sorption products at 300 °C confirms the role of germanium in low temperature CO₂ absorption.

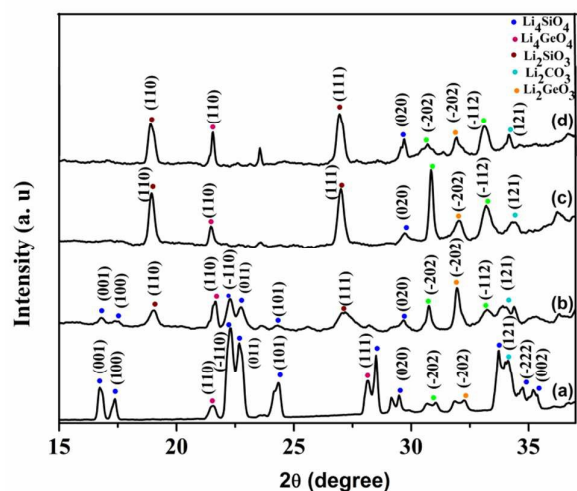


Fig 11. X-ray diffraction patterns of germanium incorporated lithium silicate after CO₂ sorption at (a) 300 °C (b) 500 °C (c) 600 °C (d) 680 °C

The absorption rate at different temperatures was measured from the data in Fig. 12 and is shown in Fig. 13. Ge-LS samples showed absorption rate values of 36 mgg⁻¹min⁻¹ & 44 mgg⁻¹min⁻¹ at the low temperatures of 300 °C and 400 °C respectively. At 500 °C, 600 °C and 680 °C calculated absorption rates were 52, 91 & 118 mgg⁻¹min⁻¹ respectively for this sample. Absorption rates were determined by

calculating the absorption capacity within one minute in all cases. These observations clearly indicated that the Ge-LS samples exhibited enhanced kinetics that of pure LS sample than at low as well as elevated temperatures.

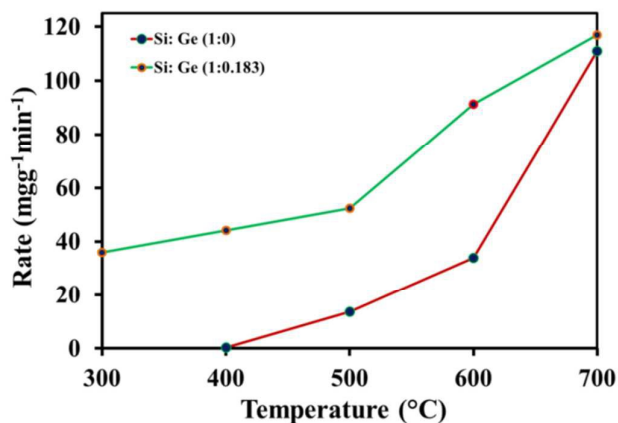


Fig. 12. Absorption rate of Si :Ge (1:0) and Si :Ge (1:0.183) samples at different temperatures

Different models have been proposed in the literature to understand the kinetic behaviour of the CO₂ chemisorption process. The kinetic calculations were performed on the absorption isotherms of 1:0.183 (Si: Ge) sample at different temperatures and fitting the curves with the well-accepted double exponential model²². The isotherms at various temperatures are fitted with the equation

$$Y = A \exp^{-K_1 x} + B \exp^{-K_2 x} + C$$

Where Y indicated the amount of CO₂ absorbed at time x and K₁, K₂ are exponential constants for the CO₂ chemisorption produced directly over the particles and the CO₂ chemisorption kinetically controlled by diffusion processes, respectively. We assume that chemisorption and diffusion occur during the sorption process. In chemisorption process, the Li atom on the surface of the sorbent reacts with CO₂ to form Li₂CO₃ shell over the sorbent particle. In diffusion process, the sorption completely relies on the diffusion of Li from the core of the material to the surface of the particle. The K₁, K₂ values calculated for the sample are listed in the Table. 1. The activation energy values for the measured samples were calculated as 131.36 kJ/mol for the chemisorption process and 110.57 kJ/mol for the diffusion process (Fig. 13). The higher

activation energy value for the chemisorption process confirmed higher absorption of CO₂ by the surface reaction with lithium silicate particles.

Table 2. Kinetic parameters obtained from the isotherms of composites at different temperatures fitted to a double exponential model

Kinetic parameters of Ge-LS sample (1:0.183)			
Temperature (K)	$k_1(s^{-1})$	$k_2(s^{-1})$	R^2
673	0.0011	0.0011	0.999
873	0.1227	0.1227	0.987
953	1.6368	0.3608	0.994

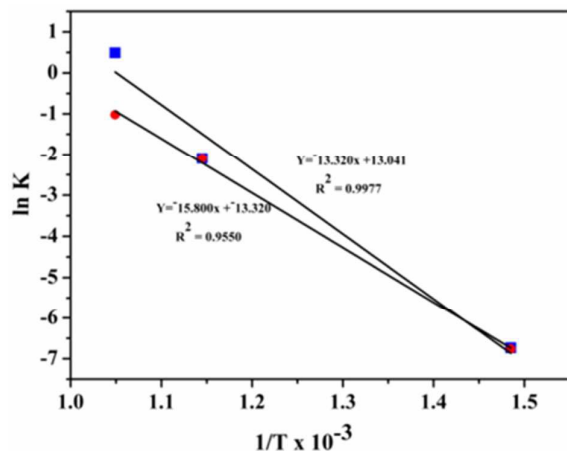


Fig. 13. The plot of $\ln K$ versus $1/T$ for the two different process chemisorption (k_1) and diffusion (k_2) observed on the germanium composite.

One cycle regenerability of the sample at 300 °C, 600 °C and 680 °C is shown in Fig. 10. The cyclic absorption-desorption data of the Ge-LS sample (of the molar ratio 1:0.183) at 550 °C is also carried out and is shown in Fig. 14. The measurement was carried out at a static temperature of 550 °C by switching between 100% CO₂ and 100% N₂. From the cyclic measurement data, it can be observed that the sample shows no reduction in the original absorption capacity even after 9 cycles.

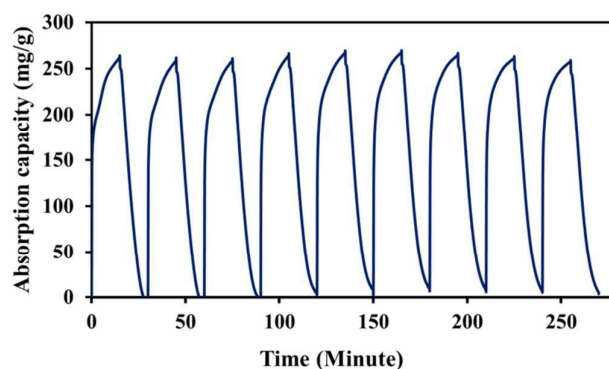


Fig 14. Cyclic absorption-desorption results of the Ge-LS sample with the molar ratio (1:0.183) at 550 °C. Desorption was carried out at the same temperature by changing 100% CO₂ to 100% N₂ gas.

The study thus indicated the possibility of employing germanium incorporated lithium silicate for the low-temperature absorption of CO₂ at temperatures as low as 150 °C. Samples having Si: Ge molar ratio of 1:0.183 exhibited enhanced CO₂ absorption capacity as well as the kinetics in the temperature range of 200 °C-680 °C compared to pure Li₄SiO₄ absorbents. Due to its excellent performance in capacity and kinetics the samples may find use in facilitating CO₂ sorption during the water gas shift reaction as well as other petrochemical reactions in the temperature range of 300-400 °C. The study thus provides a facile synthetic pathway to realize a ceramic sorbent that displays favourable kinetics at low and high-temperature ranges (150-700 °C) without the use of any eutectic additives.

3. Conclusions

In summary, germanium incorporated lithium silicates synthesised via microwave assisted sol-gel process displayed enhanced CO₂ absorption capacity as well as kinetics in the temperature range of 150-700 °C compared to pure Li₄SiO₄ absorbents. The needle-shaped morphology of synthesised particles coupled with the presence of germanium significantly altered the absorption kinetics of the material. Absorption capacity of 324 mgg⁻¹ at the rate of 117mgg⁻¹ was attained at 680 °C for the samples with the Si: Ge molar ratio of 1:0.183. Moreover, an appreciable capacity of 49 mgg⁻¹ at the rate of 36 mgg⁻¹min⁻¹ was obtained at temperatures as low as 300 °C. The study thus indicated the possibility of employing germanium incorporated lithium silicate for the insitu removal of CO₂ from reactive

environments such as water gas shift reaction in the temperature range of 150-450 °C

Acknowledgements

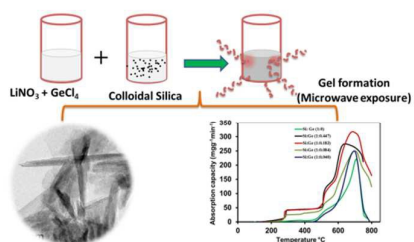
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Table of Content



Germanium incorporated lithium silicate nanostructures with exceptional carbon dioxide absorption kinetics and capacity in the temperature range (150-700 $^\circ\text{C}$)