

# Sodium-doped lithium zirconate nano squares: synthesis, characterization and applications for CO<sub>2</sub> sequestration

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**Abstract** Nano squares of sodium-doped lithium zirconate have been synthesized by a simple citrate based sol–gel method at room temperature in the presence of cetyl trimethylammonium bromide (CTAB) as a surfactant. The structural and morphological properties were investigated by X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) respectively. XRD analysis of sample calcined at 900 °C for 4 h shows the formation of monoclinic lithium zirconate phase. The TEM shows the interesting morphology of formation of nano squares of sodium doped lithium zirconate sample. The carbon dioxide sorption capacity was carried out by TGA analysis at different high temperatures. It is observed that the sample shows ~20 wt% carbon dioxide sorption at higher temperature (650 °C) within 20 min which are better than the known reports.

**Keywords** Lithium zirconate · Sodium doped lithium zirconate · Sol–gel · CTAB · Carbon dioxide · XRD · TEM

## 1 Introduction

The demand for energy in India, and across the globe, has been steadily increasing in recent years, and is projected to

continue to increase for years to come. Much of this demand is met through the production of electric power from inexpensive coal in combustion systems, which emit large quantities of carbon dioxide to the atmosphere in the process. In order to manage the conflict between increasing demand for affordable electric power and increasing concerns over climate change, strategies for supplying low-carbon power are being pursued. In the event that serious CO<sub>2</sub> emission limitations are adopted, technological solutions will be needed to avoid CO<sub>2</sub> emissions while the use of coal is continued.

Therefore, development of CO<sub>2</sub> reduction techniques is an urgent necessity. Since the flue gas from a coal-burner is hot (for example, around 400 °C after the economizer), it is highly desirable to separate CO<sub>2</sub> from flue gas at a high temperature without cooling the flue gas to room temperature or even lower. Transformation of the captured warm CO<sub>2</sub> into usable or valuable products (e.g., fuels or chemicals), if it becomes possible, will improve further the efficiency and economics of overall processes for power generation and CO<sub>2</sub> sequestration [1].

The high-temperature CO<sub>2</sub> separation process using an inorganic adsorbent or membrane is one of the most promising ways for CO<sub>2</sub> capture, utilization, and sequestration. Various adsorbents have been studied for many years for use in adsorption processes for separation of CO<sub>2</sub> from gas mixtures. However, most of the studies for CO<sub>2</sub> separation were at ambient temperature. Carbon-based adsorbents [2, 3], metal oxide sorbents [4], and hydrotalcite-like compounds [5, 6] show CO<sub>2</sub> sorption properties at relatively high temperature. However, CO<sub>2</sub> sorption capacity is still low (e.g. 0.65 mol/kg at 400 °C for hydrotalcite) [5, 6]. A review covering these topics can be found in a paper by Yong et al. [7]. Zeolite membranes (especially of Y type) offer good permselectivity and high permeance for CO<sub>2</sub> over N<sub>2</sub> at low

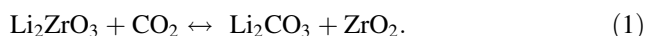
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temperatures (<100 °C) [8]. Sol–gel derived silica membranes exhibit good separation factors at temperatures below 200 °C [9]. These membranes also have a high CO<sub>2</sub> permeance (up to about  $3 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ ). However, all these inorganic membranes do not offer sufficiently high perm-selectivity for separation of CO<sub>2</sub> over N<sub>2</sub> at temperatures >350 °C.

Li-containing materials are promising candidates with high CO<sub>2</sub> capture capacity and high stability. Nakagawa et al. [10] reported that lithium zirconate can theoretically hold CO<sub>2</sub> in amounts up to 28 weight percent at high temperatures according to the following reaction:



The high capture capacity and stability at 450–600 °C of lithium zirconate make it promising for application in both pre- and post combustion systems. However, CO<sub>2</sub> capture kinetic is very slow. Pure lithium zirconate powder is conventionally prepared by solid state methods [11]. Many efforts have been made to reduce the particle size of lithium zirconate by using wet chemical preparation routes to increase the capture rate of carbon dioxide.

In this study, we report a new sol–gel based synthesis for the preparation of lithium zirconate nanoparticle and sodium doped lithium zirconate nano squares in presence of surfactant. We also report non-alkoxide route (using water based sols of inorganic metal salts as a starting reagents) for the synthesis of nanomaterials and their capacity evaluation for high temperature carbon dioxide sorption.

## 2 Experimental

### 2.1 Materials

All the chemicals were of analytical grade and were used without any further purification. Lithium carbonate (Loba Chemie), zirconium oxychloride (Univesal Laboratories), sodium carbonate (SD-Fine Chem), CTAB (Loba Chemie) and citric acid (Loba Chemie) were used as a starting material. The surfactant is selected from the cationic type.

According to the stoichiometric composition of reactant, for lithium zirconate; 3:2:1 molar ratio of citric acid: lithium carbonate: zirconium oxychloride is selected and for sodium doped lithium zirconate; 3:1.6:0.4:1 molar ratio of citric acid: lithium carbonate: sodium carbonate: zirconium oxychloride is selected.

### 2.2 Preparation of lithium zirconate nanoparticles with surfactant

Zirconium oxychloride and lithium carbonate are used as Zr and Li precursors respectively. 3 M citric acid solution

was prepared in 300 mL de-ionized water. To this solution 0.05 M CTAB was added and the mixture was stirred till homogeneous. The stoichiometric amount of reactants, 1 M zirconium oxychloride and 2 M lithium carbonate was dissolved in the above solution. Here the molar amount of citric acid is equal to total molar amount of precursors in the solution. Ammonium hydroxide was added slowly to adjust the pH value of the solution in the range of 8–9 and stabilize the citrate solution. After completion of addition of ammonium hydroxide, the solution is kept for stirring for 1 h at ambient condition, resulting in a clear and homogeneous sol. The sol was kept at 110 °C for gelling and drying for 24 h. The dried powder was calcined at 900 °C for 4 h.

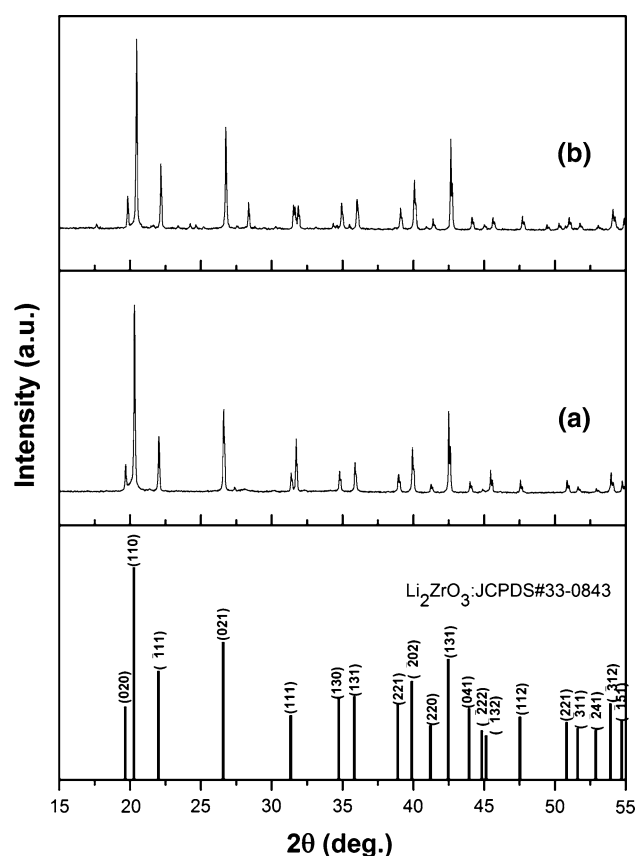
### 2.3 Preparation of Na-doped lithium zirconate nanoparticles with surfactant

Sodium doped sample was prepared in the similar manner as that of lithium zirconate, with a difference that sodium carbonate was added as Na precursor. Zirconium oxychloride, lithium carbonate and sodium carbonate are used as Zr, Li and Na precursors respectively. 3 M citric acid solution was prepared in 300 mL de-ionized water. To this solution 0.05 M surfactant (CTAB) is added and the mixture is stirred till homogeneous. The stoichiometric amount of reactants, 1 M zirconium oxychloride, 1.6 M lithium carbonate and 0.4 M of sodium carbonate was dissolved in the above solution. Here the molar amount of citric acid is equal to total molar amount of precursors in the solution. Ammonium hydroxide was added slowly to adjust the pH value of the solution in the range of 8–9 and stabilize the citrate solution. After completion of addition of ammonium hydroxide, the solution is kept for stirring for 1 h at ambient condition, resulting in a clear and homogeneous sol. The sol was kept at 110 °C for gelling and drying for 24 h. The dried powder was calcined at 900 °C for 4 h.

## 3 Results and discussion

### 3.1 XRD analysis

The crystallographic phase of the obtained materials was characterized by XRD (Philips Xpert pro-3040 equipped with CuK $\alpha$  with 40 kV, 30 mA at scanning rate of 5°/min). Results of the XRD analysis of the obtained lithium zirconate (1a) and sodium doped lithium zirconate (1b) are shown in Fig. 1 along with JCPDS pattern of monoclinic lithium zirconate. All the diffraction peaks of samples which can be readily indexed to the monoclinic phase of Li<sub>2</sub>ZrO<sub>3</sub> (JCPDS#33-0843) and also matching that of reported literature [1, 12]. The powder were calcined at



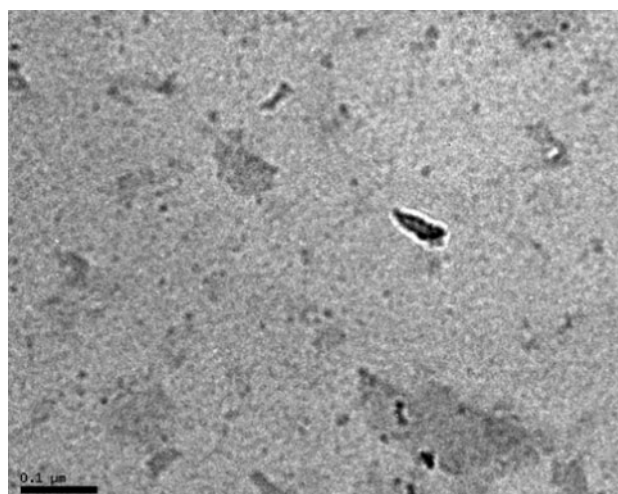
**Fig. 1** XRD analysis of (a) lithium zirconate and (b) sodium doped lithium zirconate samples calcined at 900 °C for 4 h

900 °C which led to the formation of monoclinic  $\text{Li}_2\text{ZrO}_3$  which was found as the predominant crystalline phase without any mixed phase indicating high purity of the product.

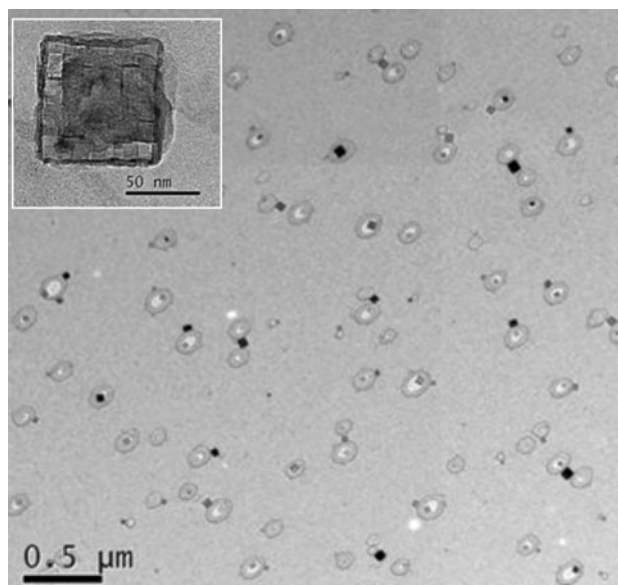
### 3.2 TEM analysis

The morphology of lithium zirconate nanoparticles synthesized by sol–gel method in presence of CTAB and calcined at 900 °C is shown in Fig. 2. The TEM image shows the presence of spherical lithium zirconate nanoparticles in the size range of 8–15 nm with an average particle size was about 12 nm. It is observed that surfactant plays an important role for getting uniform nanoparticle size and morphology, which enhance the property of carbon dioxide sorption.

Figure 3 shows the TEM image of Sodium doped Lithium Zirconate synthesized by sol–gel method in presence of CTAB. The TEM image shows the presence of square-shaped morphology of sodium doped lithium zirconate with the size range of 70–90 nm. These nano squares were found very effective for high temperature carbon dioxide sorption.



**Fig. 2** TEM analysis of lithium zirconate sample prepared in presence of CTAB



**Fig. 3** TEM analysis of sodium doped lithium zirconate sample prepared in presence of CTAB. *Inset* HRTEM of sodium doped lithium zirconate

### 3.3 CO<sub>2</sub> sorption experimental details

Carbon dioxide sorption for lithium zirconate samples were studied using a thermogravimetric instrument (TGA Q5000, TA Instrument). About 10 mg of sample was charged into the sample pan for testing. The sample was dried at the operating temperature before adsorbing the carbon dioxide by passing nitrogen flow until the sample weight becomes stable. The CO<sub>2</sub> flow rate was maintained at 100 mL/min. The sample was equilibrated to the desired temperature and held for 10 min. Then the inlet flow was changed from N<sub>2</sub> to CO<sub>2</sub> for the measurement of the

sample weight gain versus time. Finally the inlet flow was changed from CO<sub>2</sub> to N<sub>2</sub> for the CO<sub>2</sub> desorption by increasing the temperature to 800 °C with the ramp rate of 20 °C/min. The CO<sub>2</sub> sorption study was conducted at different temperatures in order to study the temperature effect on the sorption rate.

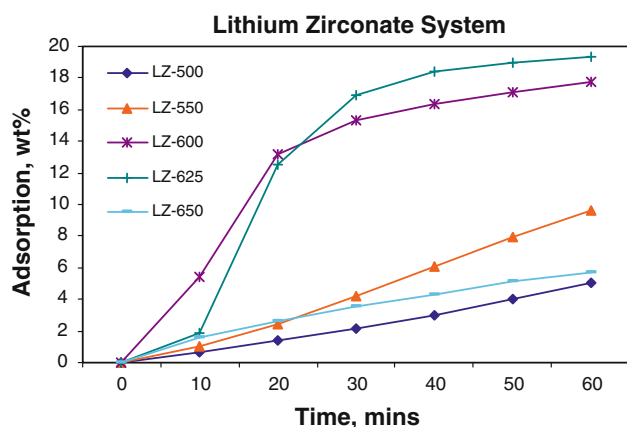
### 3.4 Carbon dioxide sorption study

The carbon dioxide adsorption study for lithium zirconate and sodium doped lithium zirconate are shown in Figs. 4 and 5 respectively. Based on the results of TGA it was found that rate of sorption of sodium doped lithium zirconate was faster at 500 and 550 °C compared to lithium zirconate. Furthermore, with increasing temperature to 600 and 625 °C rate of sorption for lithium zirconate was found to be slightly higher than sodium doped lithium zirconate. Further increasing the temperature to 650 °C rate of sorption for sodium doped lithium zirconate was found to be higher than lithium zirconate i.e. 20 wt% in less than 20 min (sodium doped lithium zirconate) compared to 5 wt% in 60 min (lithium zirconate). The sodium doped lithium zirconate nano squares are giving good sorption capacity for carbon dioxide towards higher temperature. The higher capacity at high temperature (650 °C) make this material most promising candidate for the selective separation of carbon dioxide from combustion gas streams. This is expected to rise with temperature and several researchers have already reported the different mechanisms for the faster rate of carbon dioxide for doped lithium zirconate. Pfeiffer et al. [13] have reported the formation of Li<sub>x</sub>Na<sub>y</sub>ZrO<sub>3</sub> new structure and they explained their results by mixing Na<sub>2</sub>ZrO<sub>3</sub> and Li<sub>2</sub>ZrO<sub>3</sub>. Recently Guzmán-Velderrain et al. [12] have explained the mechanism for formation of “opened” structure of Li<sub>x</sub>Na<sub>y</sub>ZrO<sub>3</sub> for faster rate of carbon dioxide sorption for sodium doped lithium

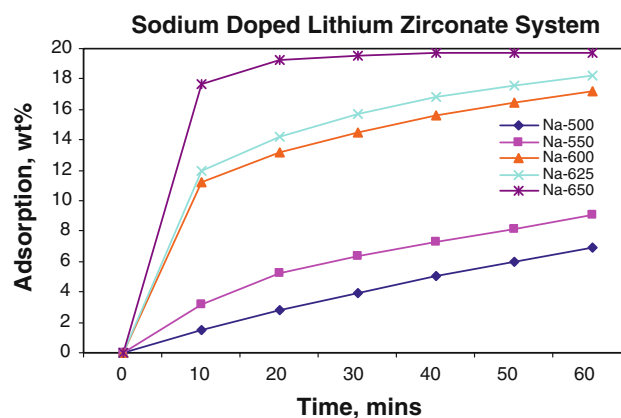
zirconate. The formed “opened” structure it weakens the interaction between Li<sup>+</sup> and Na<sup>+</sup> interaction with ZrO<sub>3</sub><sup>+2</sup> species and to enhance the reactivity of Li<sup>+</sup> with CO<sub>2</sub> which modify the activation energy of the Li<sub>2</sub>ZrO<sub>3</sub> absorption reaction and produces faster CO<sub>2</sub> absorption kinetics.

### 3.5 Adsorption/desorption cycles

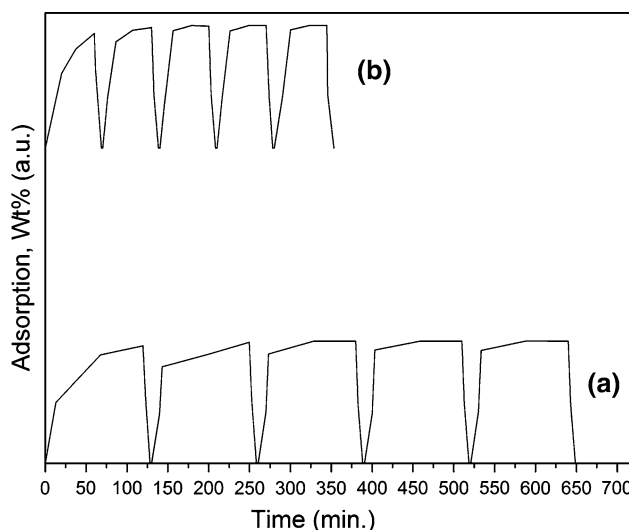
We have carried out five cycles of adsorption and desorption for lithium zirconate and sodium doped lithium zirconate (Fig. 6) to check the regenerability of carbon dioxide sorption capacity. It can be seen from the cycles of both samples that there is no loss of sorption capacity. This proves that both the samples are fully stable at high temperature (650 °C). One more interesting observation is that



**Fig. 4** Carbon dioxide adsorption study for lithium zirconate at different temperature



**Fig. 5** Carbon dioxide adsorption study for sodium doped lithium zirconate at different temperature



**Fig. 6** Carbon dioxide sorption (650 °C) and desorption (800 °C) of lithium zirconate and sodium doped lithium zirconate up to five cycles

the rate of sorption for sodium doped lithium zirconate is very high. This may be due to the possible mechanism for formation of “opened” structure of  $\text{Li}_x\text{Na}_y\text{ZrO}_3$  for faster rate of carbon dioxide sorption for sodium doped lithium zirconate [12]. However, the rate of sorption for lithium zirconate is slow at high temperature.

#### 4 Conclusion

In summary, lithium zirconate nanoparticles and sodium doped lithium zirconate nano squares were synthesized by a novel citrate based sol–gel method in presence of CTAB. Two types of materials were tested for carbon dioxide sorption capacity at different temperatures. The nanoparticles and squares found very effective for the sorption of carbon dioxide at high temperature. The sodium doped lithium zirconate nano squares shows 20 wt% carbon dioxide sorption at 650 °C in less than 20 min. The higher capacity at high temperature make this material most promising candidate for the selective separation of carbon dioxide from combustion gas streams.

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