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Research Article

Preparation and Characterization of Lithium Zirconium Silicate for CO_2 Capture

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Abstract

The samples of lithium zirconium silicate were prepared by precipitation, template and sol-gel methods. The samples were prepared with several mol ratios of Li:Zr:Si. The preparation of lithium zirconium silicate samples by precipitation method were carried out by using the lithium nitrate, zirconyl nitrate, zirconium(IV) oxypropoxide and tetramethylorthosilicate (TEOS) as precursors. The samples of lithium zirconium silicate were prepared by using cetyltrimethyl-ammonium bromide (C-TAB) and tetramethyl ammonium hydroxide (TMAOH) by template method. The samples of lithium zirconium silicate were characterized by XRD, TEM, SEM, ^{29}Si-MAS NMR and FTIR. The surface area, alkalinity / acidity of the samples of lithium zirconium silicate were measured. The TGA analysis of lithium zirconium silicate samples was done. The CO_2 captured by the samples of lithium zirconium silicate was estimated. The captured CO_2 by the samples of lithium zirconium silicate was found to be in the range 3.3 to 8.6 wt%. © 2014 BCREC UNDIP. All rights reserved

Keywords: Lithium zirconium silicate; Preparation method; sol gel method; template method; characterization; CO_2 capture

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1. Introduction

The increased concentration of anthropogenic greenhouses gases (GHGs) in the atmosphere particularly CO_2 is causing major contribution to climate change and ocean acidification. The 60 to 70% of the current CO_2 emissions come from power plant, fossil fuel and industry sector such as oil refineries, aluminum iron and steel production plants, etc For controlling the emission of CO_2 in the atmosphere, recently, the capturing of CO_2 and sequestration have been emerging technology techniques. The potential processes for CO_2 capture include the physical and chemical adsorption. The work concerned based on CO_2 capture by gas- solid adsorption at higher temperature (900 °C) [1-9]. The lithium based sorbents have been considered as promising material for CO_2 capture.

The lithium zirconate (Li_2ZrO_3) was proposed for CO_2 capturing [1-13]. The porous nano-material of lithium zirconate was prepared by using surfactant template method. The lithium zirconate showed the CO_2 captured 22 wt% at higher temperature. Zirconium is a transition metal. Li_2O is a basic in nature so it's helps to maintain the alkalinity of adsorbent. Lithium reacts with silicate and gives

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polyatomic anion and three dimension cage structures. The Li_4SiO_4 sorbent was reported for CO_2 capture [11].

The lithium reacts with zirconium and silicon in presence of oxygen with different mole ratios. The captured CO_2 by the Li_2ZrO_3, Li_4SiO_4 and $Li_2ZrSi_6O_{15}$, can be given by following mechanisms:

$$Li_4SiO_4 + 2CO_2 \rightleftarrows 2Li_2CO_3 + SiO_2 \quad (1)$$

$$Li_2ZrO_3 + CO_2 \rightleftarrows Li_2CO_3 + ZrO_2 \quad (2)$$

$$Li_2ZrSi_6O_{15} + CO_2 \rightleftarrows Li_2CO_3 + ZrSiO_4 + 5\ SiO_2 \quad (3)$$

From the above reactions (1, 2, 3), it can be seen that lithium carbonate and other metal oxide are formed. In this paper, the samples of lithium zirconium silicate were prepared by precipitation, template [14-16] and sol-gel method [5-13]. The prepared samples of the lithium zirconium silicate were characterized by using scanning electron microscopy (SEM), EDX, X-ray diffraction (XRD), transmission electron microscope (TEM) [15-32], Fourier transform infrared spectroscopy (FTIR) [15-33], solid state MAS ^{29}Si NMR [17-20], acidity / alkalinity and surface area.

2. Materials and Methods

2.1. Chemical and Apparatus

The chemical zirconyl nitrate (Loba Chemie), lithium nitrate (Loba chemie), tetramethylsiliane (Lancaster), zirconium (IV) oxypropoxide (Aldrich), ammonium carbonate (Merck) were used to prepared lithium zirconium silicate. All chemicals of analytical grade were used without any further purification. Carbon dioxide and helium of high purity gases were used (Deluxe India, Ltd). The oven (Innovative PTS-72) was used to dry the solid mass of samples. The furnace (Thermax Co-Ltd) was used to calcine the lithium zirconium silicate samples. The IKA-RCT hot plate was used for heating and stirring. The samples of lithium zirconium silicate were screened for the TGA (Mettaler – TGA / SDTA-851).

2.2. The Preparation of the Samples of the Lithium Zirconium Silicate

The several samples of lithium zirconium silicate were prepared by different methods such as precipitation, sol-gel and template methods. The samples were prepared with different mol ratio by varying the composition of lithium from 1 to 6 mol ratio with respect to constant composition of zirconium and silicon.

2.2.1. The preparation of the sample of the lithium zirconium silicate by precipitation method

The several samples of lithium zirconium silicate were prepared with different mol ratios like 1:1:1, 2:1:1, 4:1:1, 6:1:1 by precipitation method. The lithium zirconium silicate Li:Zr:Si samples were prepared by using the ammonium carbonate as a precipitation agent. The other precursors used were $LiNO_3$, $ZrO\ (NO_3)_2$, xH_2O and TEOS (tetraethylorthosiliane). The lithium nitrate and TEOS were dissolved in ethanol then after adding ammonium carbonate solution the precipitate was formed. The precipitate was filtered and then solid mass was dried under 150 ^{0}C for one day. Further, the calcination of this solid mass was done at 900 ^{0}C for 3 h. Then solid mas was particled to -22 to -30 mesh size.

2.2.2. The preparation of the sample of the lithium zirconium silicate by template method

The several samples of lithium zirconium silicate were prepared with different mol ratios of varying the lithium, zirconium and silicon. The CTAB (cetyl tri methyl ammonium bromide) was used as a template. The CTAB was taken 0.02, 0.04 and 0.06 moles depending on the mol ratios of lithium, zirconium and silicon. The precursor lithium nitrate, TEOS and zirconium(IV) oxy propoxide were used to prepare the samples. The CTAB and TMAOH (tetra methyl ammonium hydroxide) were used to make the precipitation and size orientation molecules. The precipitate was dried at 80 ^{0}C for 8 h and then at 150 ^{0}C for two days under a vacuum (400 mm Hg). The solid mass was calcined at 900 ^{0}C for 3 h. Then particle was prepared of to -22 to -30 mesh size.

2.2.3. The preparation of the sample of the lithium zirconium silicate by sol-gel method

The lithium zirconium silicate samples were prepared of different mol ratios by sol-gel method. The tetraethylorthosilicate TEOS ($Si(OC_2H_5)_4$ zirconium(IV) oxypropoxide and lithium nitrate were used as precursors. The sol was prepared by hydrolyzing the precursors by the slow addition of a dilute solution of nitric acid of pH 2. The mixture was refluxed for 12 h to complete the gelation. The obtained gel was dried at 80 ^{0}C for 8 h then at 150 ^{0}C for one day. The solid mass was calcined at 900 ^{0}C for 3 h. The particles were prepared of -22 to -30 mesh size. The samples of mol ratios of Li:Zr:Si such as 6:1:1 was indicated by LZSP611 (precipitation method), LZSS411 (sol-gel method with 4:1:1 mol ratio), LZST 211 (template method with 2:1:1 mol ratio), etc.

2.3. The Characterization of the Samples of Lithium Zirconium Silicate

The samples of the lithium zirconium silicate were characterized by X-ray diffraction (XRD) for the identification of the crystal phases. The surface areas were obtained by using the instrument Quanta-chrome Instrument Autosorb-I. The morphology of the prepared samples was studied by using the images obtained by FEI Quanta 200 3D, Dual beam scanning electron microscopy (SEM) and FEI Tecnai-G^2 (200 KV) Transmission electron microscopy (TEM). The TGA of the samples were obtained by using the Perkin Elmer (STA-6000) TGA. The FTIR was obtained by an Agilent Cary 660 FTIR spectrometer. The acidity/ alkalinity were measured by acid-base titration. ^{29}Si NMR was obtained by a JEOL ECX 400 MHz spectrometer at room temperature.

2.4. The Procedure for CO_2 Capture

The capture of CO_2 was performed by using the thermo-grametric analysis (Mettler – TGA/ SDTA-851). The CO_2 capture was done in the temperature range 40 ^{0}C to 900 ^{0}C under atmospheric pressure with the CO_2 feed flow 50 ml min^{-1} through the sample with respect to heating rate 10 ^{0}C min^{-1}. A sample mass was used 0 to 15 mg in platinum pan in the TG unit.

3. Results and Discussion

3.1. The Characterization of the Samples of Lithium Zirconium Silicate

3.1.1 The characterization by XRD Phases

In Figures 1-3, the XRD patterns of the samples of lithium zirconium silicate were shown. The different phases were observed for

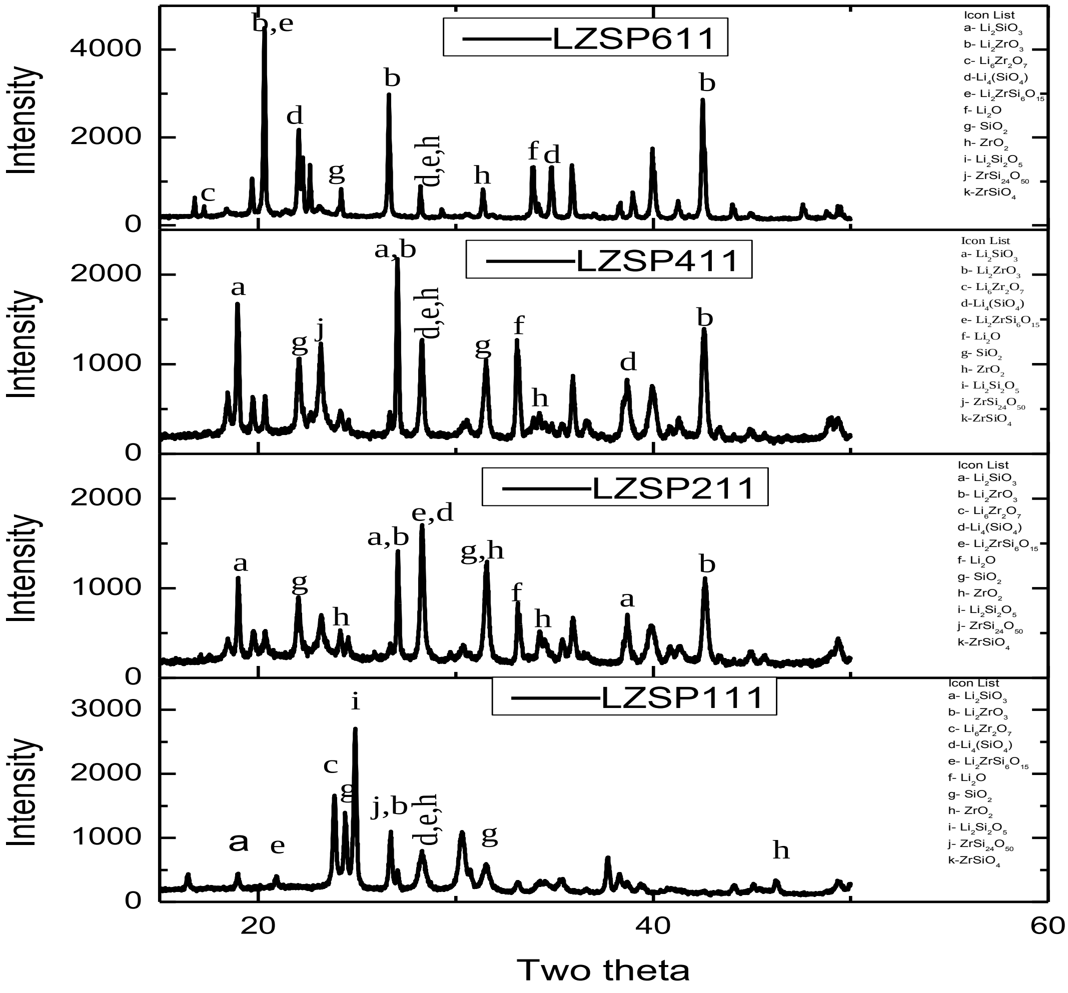


Figure 1. The XRD patterns of prepared the samples by precipitation method of lithium zirconium silicate, a) LZSP111, b) LZSP211, c) LZSP411, d) LZSP611.

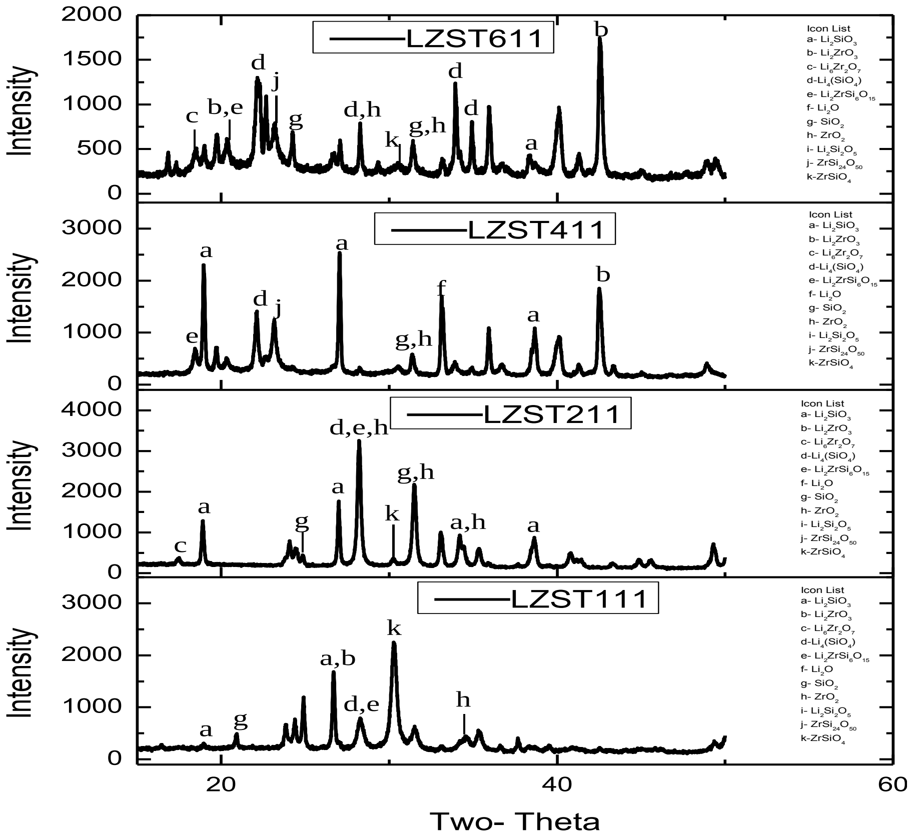


Figure 2. The XRD patterns of prepared the samples by template method of lithium zirconium silicate, a) LZST111, b) LZST211, c) LZST411, d) LZST611.

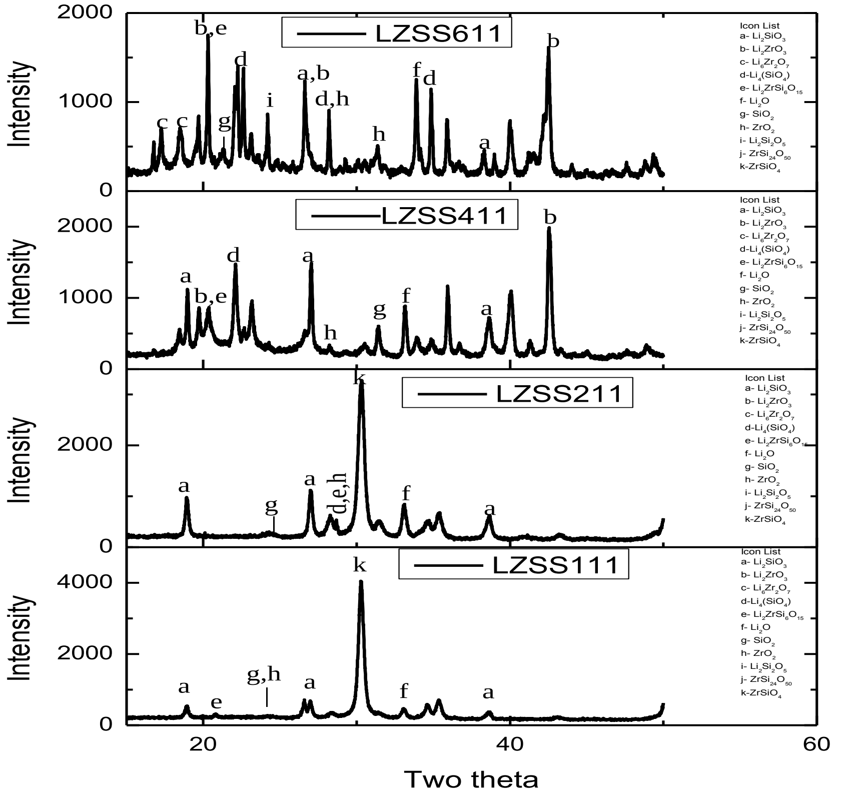


Figure 3. The XRD patterns of prepared the samples by the sol-gel method of lithium zirconium silicate, a) LZSS111, b) LZSS211, c) LZSS411, d) LZSS611.

the samples of prepared by different methods. In Figure 1, the XRD patterns are shown of the samples LZSP611, LZSP411, LZSP211 and LZSP111by prepared by precipitation method. The ZrO_2, SiO_2 [27], Li_2SiO_3 [25], Li_2ZrO_3, $Li_6Zr_2O_7$ [26], Li_4SiO_4 [24], $ZrSi_{24}O_{50}$ [23], Li_2O [21], $ZrSiO_4$ [31] and $Li_2ZrSi_6O_{15}$ phases were observed. In Figures 2, the XRD patterns are shown of the samples LZST611, LZST411, LZST211 and LZST111 by prepared by template method. The ZrO_2, SiO_2 [27], Li_2SiO_3 [25], Li_2ZrO_3, $Li_6Zr_2O_7$ [26], Li_4SiO_4 [24], $ZrSi_{24}O_{50}$ [23], Li_2O [21], $ZrSiO_4$ [31] and $Li_2ZrSi_6O_{15}$ phases were observed. In Figure 3, the XRD patterns are shown of the samples LZSS611, LZSS411, LZSS211 and LZSS111 by prepared by sol gel method. The ZrO_2, SiO_2 [27], Li_2SiO_3 [25], Li_2ZrO_3, $Li_6Zr_2O_7$ [26], Li_4SiO_4 [24], $ZrSi_{24}O_{50}$ [23], Li_2O [21], $ZrSiO_4$ [31] and $Li_2ZrSi_6O_{15}$ phases were observed. The similar phases were observed except $ZrSiO_4$ phase which was not observed in the samples prepared by precipitation method. However, this phase was disappeared with the increasing the mol ratio of lithium. The $ZrSiO_4$ phase is tetragonal and other phases are monoclinic. The phases formation $Li_2ZrSi_6O_{15}$ [29], ZrO_2 [28] and Li_2ZrO_3 [22] improve CO_2 capture.

3.1.2. The characterization of the samples by TEM and SEM

In Figure 4a, the TEM images of the samples LZSP111 of lithium zirconium silicate were prepared by precipitation method. The round, oval and hexagonal shaped particles were observed. In Figures 4b, 5 and 6, the SEM images of the samples of lithium zirconium silicate were shown which were prepared by precipitation, template and sol-gel methods. The samples of the lithium zirconium silicate showed the different particle morphology. It was clearly showed that the particle have uniform sizes. The particles have no indication of cracks or agglomeration.

3.1.3. The characterization of the samples by ^{29}Si-MAS NMR

In Figures 7, 8 and 9, the ^{29}Si NMRs were shown of the samples prepared by precipitation, template and sol-gel method. In the samples of lithium zirconium silicate which were prepared by precipitation method, chemical shifts were observed at -89.63, -71.09, -70.78

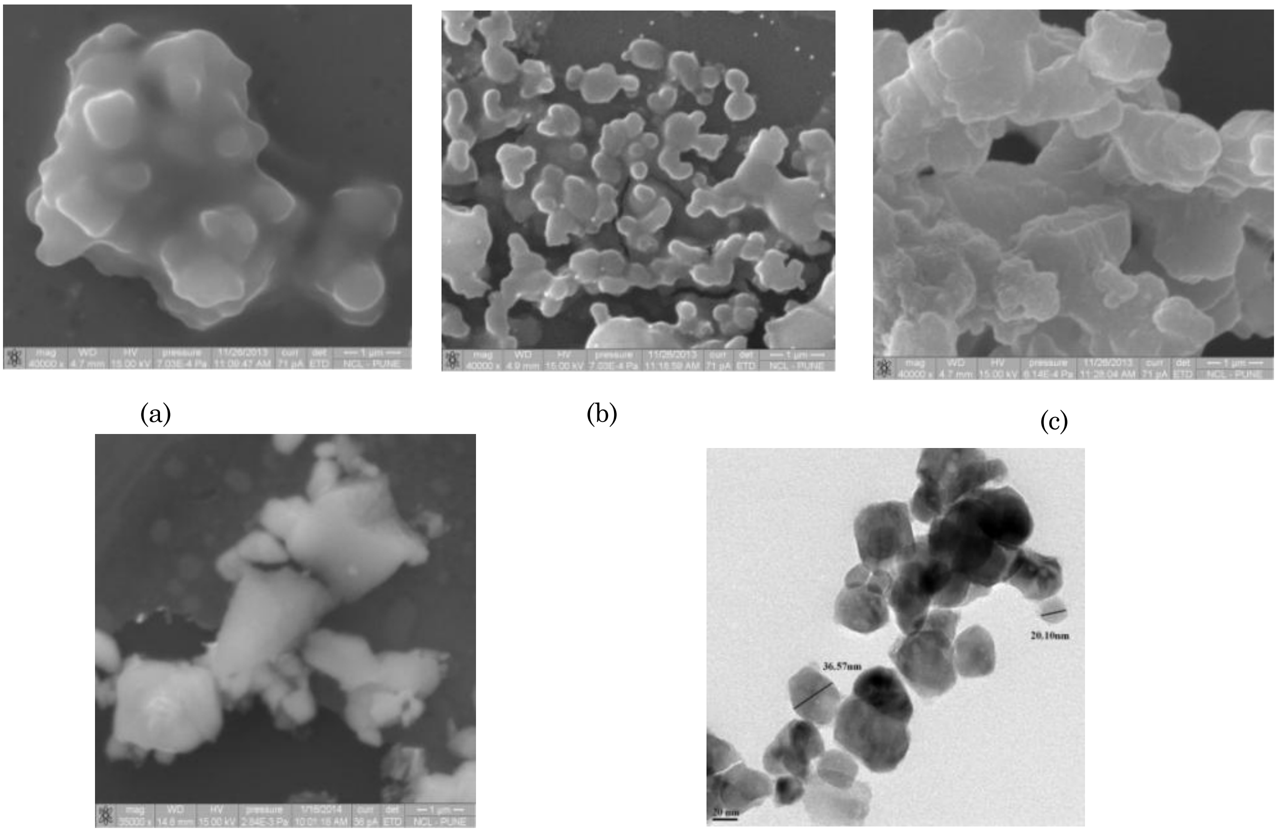
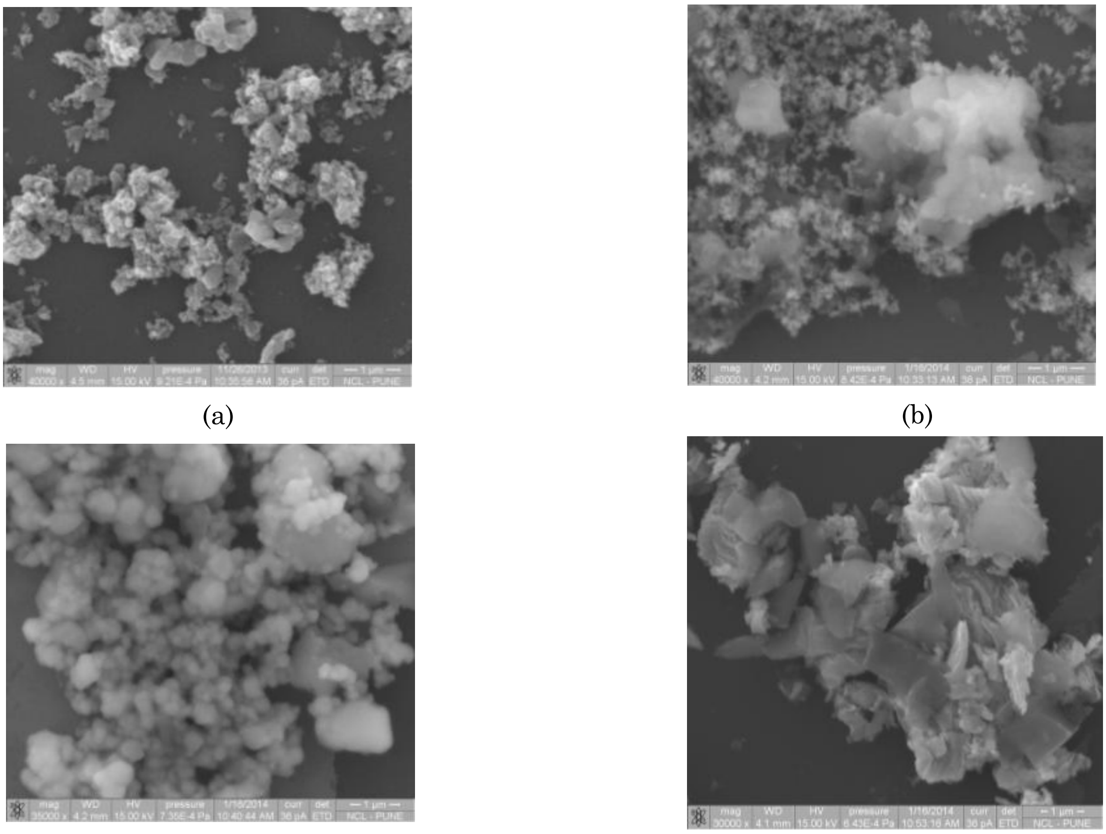


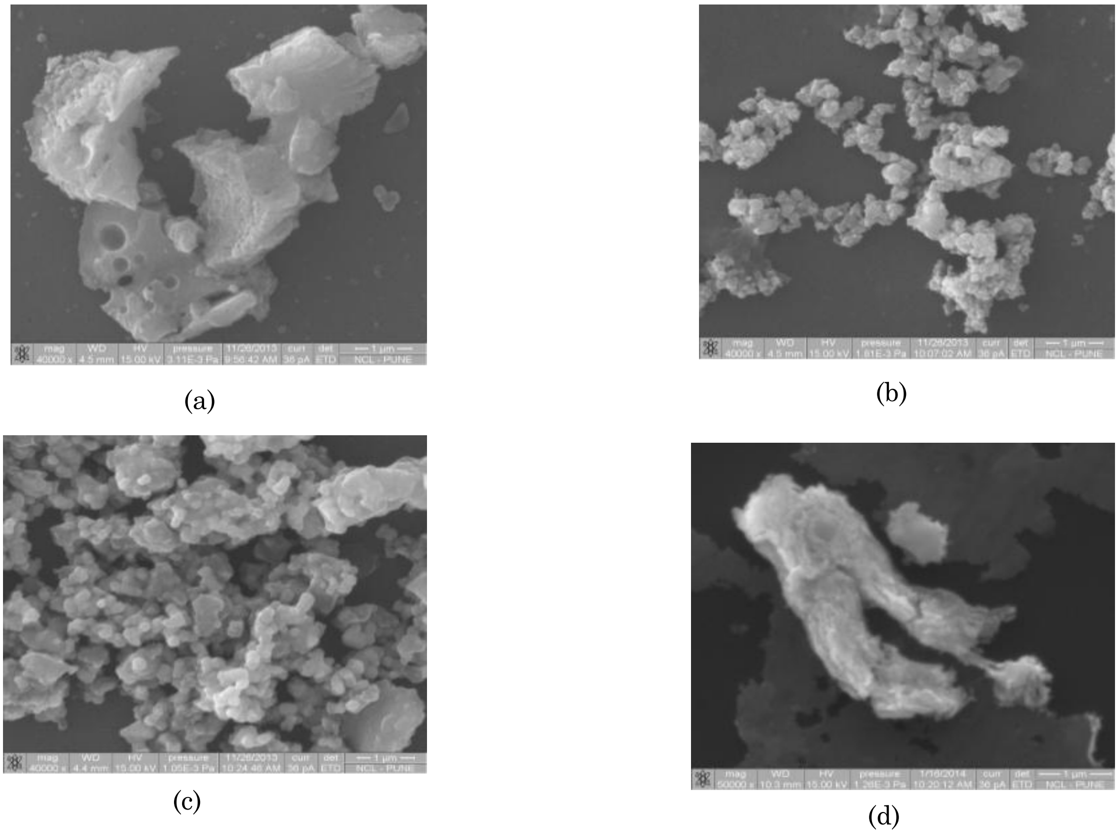
Figure 4. The TEM and SEM Images of some prepared the samples by precipitation method of lithium zirconium silicate, (a) LZSP111, (b) LZSP211, (c) LZSP411, (d) LZSP611, (e) LZSP111.



(a) (b)

(c) (d)

Figure 5. The SEM Images of prepared the samples by template method of lithium zirconium silicate , a) LZST111, b) LZST211, c) LZST411, d) LZST611.



(a) (b)

(c) (d)

Figure 6. The SEM Images of prepared the samples by sol-gel method of lithium zirconium silicate, a) LZSS111, b) LZSS211, c) LZSS411, d) LZSS611.

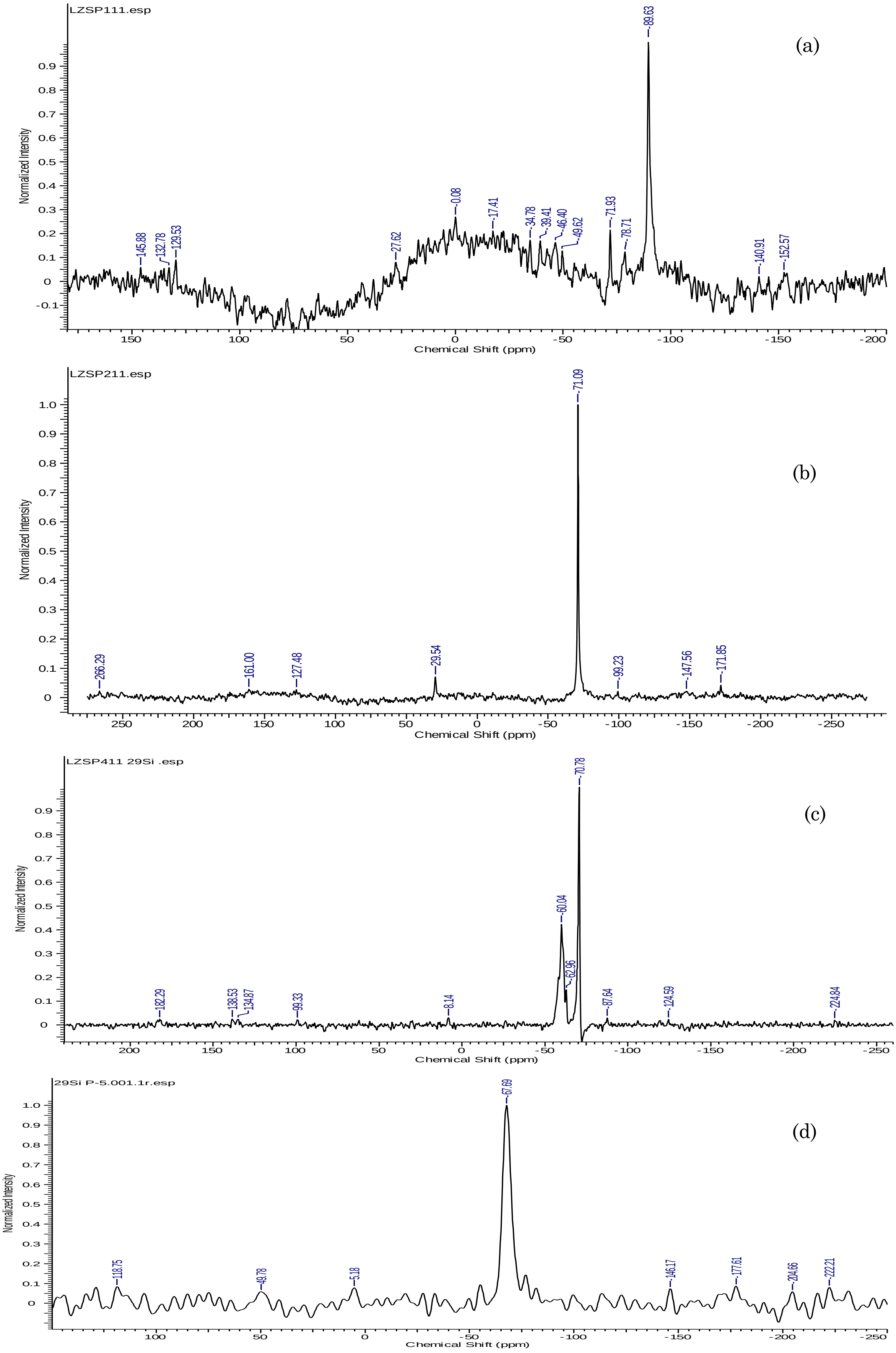


Figure 7. The ^{29}Si NMR of prepared the samples by precipitation method of lithium zirconium silicate, a) LZSP111, b) LZSP211, c) LZSP411, d) LZSP611.

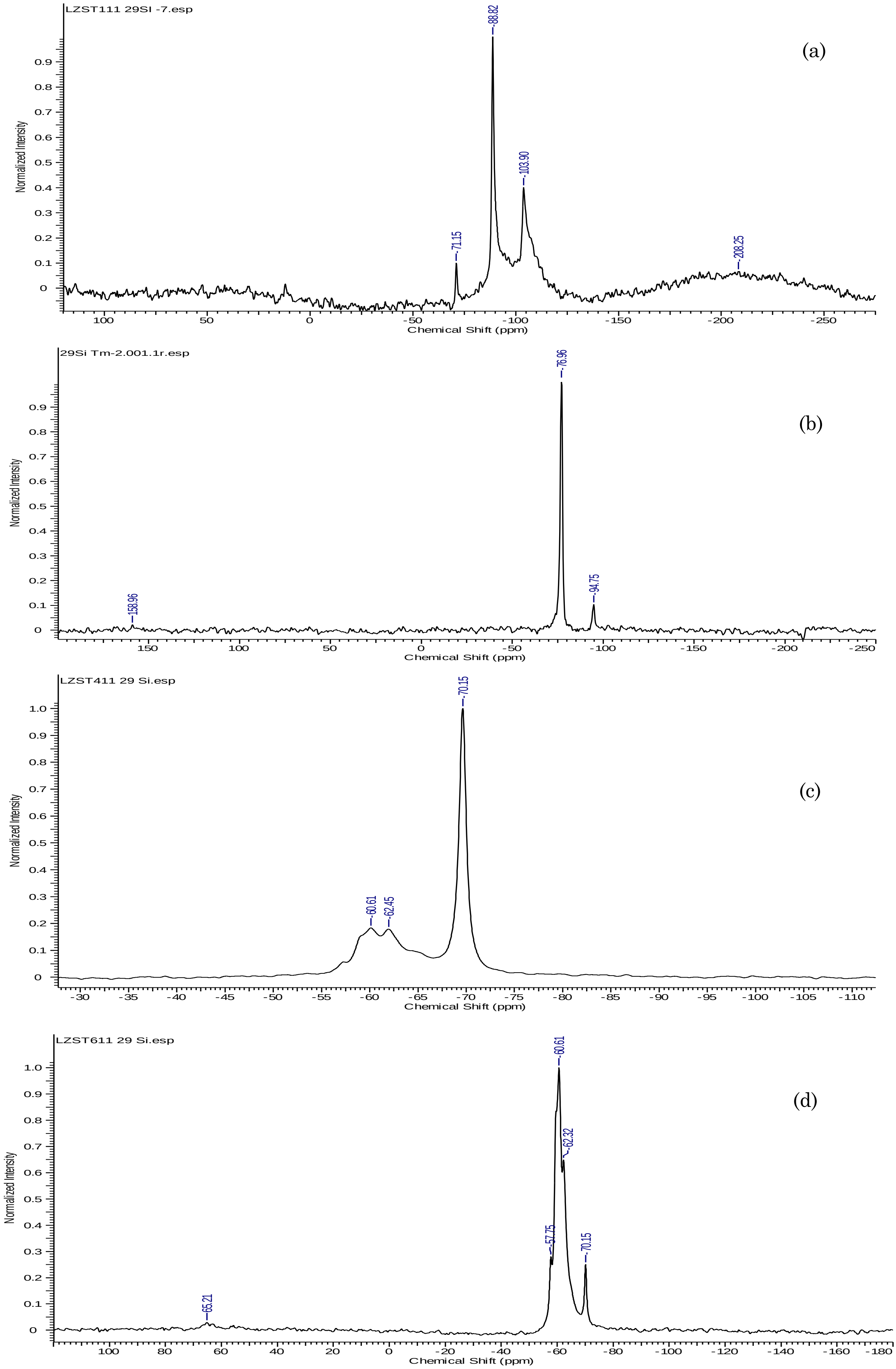


Figure 8. The ^{29}Si NMR of prepared the samples by template method of lithium zirconium silicate , a) LZST111, b) LZST211, c) LZST411, d) LZST611.

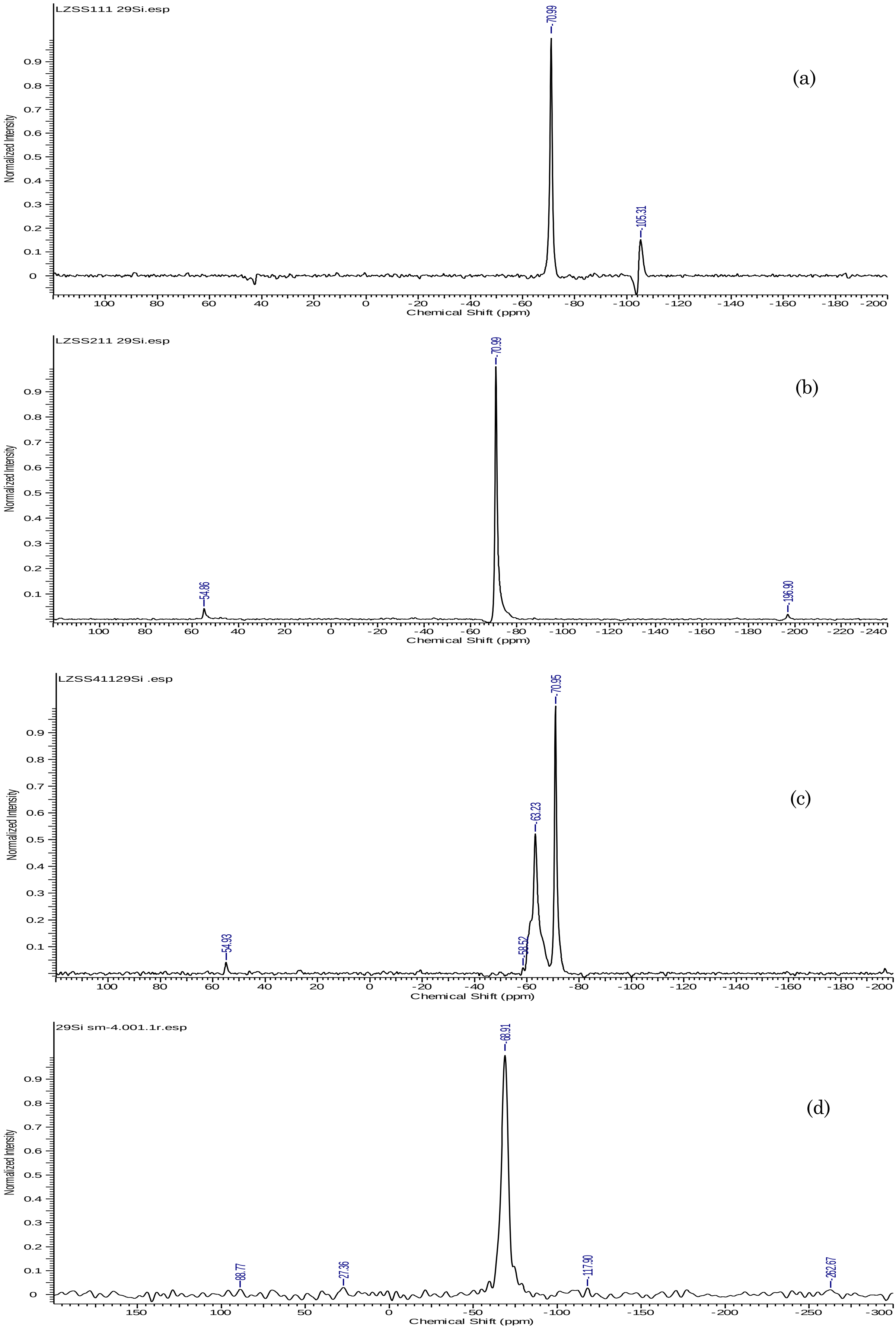


Figure 9. The ^{29}Si NMR of prepared the samples by sol-gel method of lithium zirconium silicate, a) LZSS111, b) LZSS211, c) LZSS411, d) LZSS611.

and -67.69 ppm. In the samples of lithium zirconium silicate prepared by template and sol-gel methods, the chemical shifts at -88.82, -70.15, -76.96, -60.61,-70.99, -70.99,-70.95 and -68.91 ppm were observed. These peaks indicate that there is more than one crystallographic site for silicon. The ^{29}Si chemical shift of silicate found at high field of SiO_4 tetrahedral position. In the sample LZSP111, the chemical shift was observed at -89.63 ppm. The phase was observed with $ZrSiO_4$ octahedral. In the sample LZST111, the chemical shift was observed at -88.82 ppm. The silicon is coordinated with zirconium, i.e. tetrahedral to octahedral. However, in the samples LZSS, LZSP and LZST, the chemical shifts were in the range -70 to -71 ppm. The low chemical shift was found in the phase Li_2SiO_3. The smaller Si−O−Si bond angel chemical shift was in SiO_4 tetrahedra chain. In the sample LZSP411, showed small second shoulder chemical shift was at -60.04 ppm. In the sample LZST611, the shoulder chemical shift was observed at -60.61 ppm showing Q^0 amorphous lithium silicate impurity.

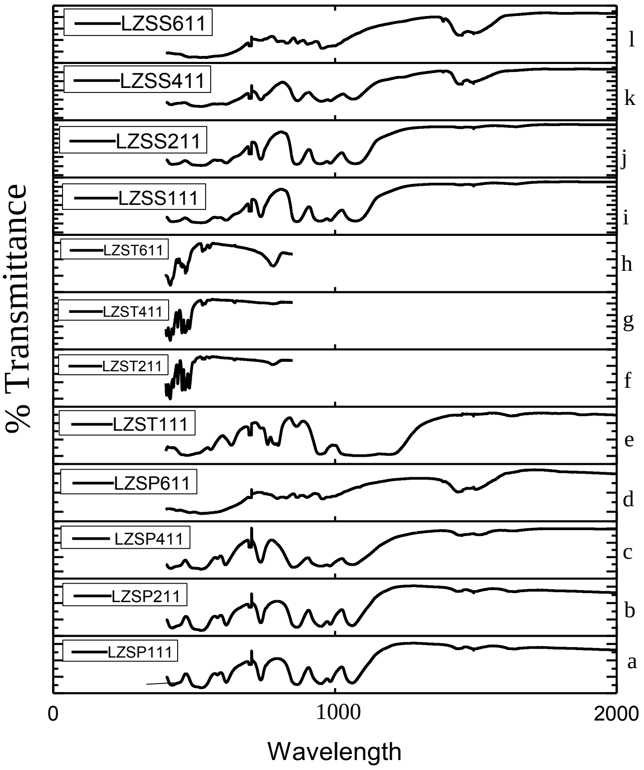


Figure 10. The FTIR of prepared the samples by precipitation, template and sol-gel method of lithium zirconium silicate: (a) LZSP111, (b) LZSP211, (c) LZSP411, (d) LZSP611, (e) LZST111, (f) LZST211, (g) LZST411, (h) LZST611, (i) LZSS111, (j) LZSS211, (k) LZSS411, (l) LZSS611.

3.1.4. The characterization of the samples by FTIR

The FT-IR spectrum of the samples with Li:Zr:Si different molar ratios were shown in the Figure 10. The first peak was observed at 500 cm^{-1} to 533 cm^{-1} of Li−O vibration. The other peak was observed at 502 cm^{-1} of Zr−O vibration. The peak at 620 cm^{-1} and 730 cm^{-1} was observed of Si−O and Si−O−Si vibrations. The peak at 730 cm^{-1} was observed of O−Li−O (υ_3 bending). The deformation of Si−O−Si tetrahedral geometry of SiO_4 is shifted to octahedral site by showing the peaks at 986 cm^{-1} and 868 cm^{-1}. The Si−O stretching in Si−O−Zr was noticed. At higher mol ratios of lithium in the samples, the small peak at 986 to 998 cm^{-1} was observed of Li−O−Si (υ_3 stretching). The peaks were observed at 1100-1040 cm^{-1} may be attributed to a Si−O−Si vibration. The observed peak at 986 cm^{-1} is due to Si−O vibration in $(Si_2O_5)^{2-}$ of minimum formula of $(Si_6O_{15})^{6-}$. The three oxygen form each tetrahedral group are shared to other two radical from the samples. It can be formed sheet silicate structure. In the XRD pattern, the phase $Li_2ZrSi_6O_{15}$ is observed. There is no peak at 3300 cm^{-1} of O−H vibration. There is no any free water molecule but hydroxyl groups are bonded.

3.1.5. The characterization of the sample by TGA

In Figure 11, the results of thermogravemetic analysis were shown of weight loss with respect to temperature. The observed was 1.00, 2.52 and 2.07 % weight loss in the samples LZP111, LZST111 and LZSS111, respectively up to 900 ^{0}C. This indicates that the prepared samples of the lithium zirconium silicate were highly stable.

3.1.6. The characterization of samples for alkalinity/acidity and surface area

The alkalinity/acidity and surface area of the samples were given in the Table 1. The estimated alkalinity of the sample LZSP611, LZST611 and LZSS611 were given 12.1, 12.4 and 14.1 mmol g^{-1}, respectively (Table 1). The surface area 7.76 m^2 g^{-1} was observed of the LZST611 sample.

3.2. The Captured CO_2 by TGA Method

In Figure 12, the TGA of CO_2 capture by the samples of the lithium zirconium silicate was given. The TGA of captured CO_2 showed different nature. There is low capture of CO_2 under 300 ^{0}C. However, the sample LZSP611 showed

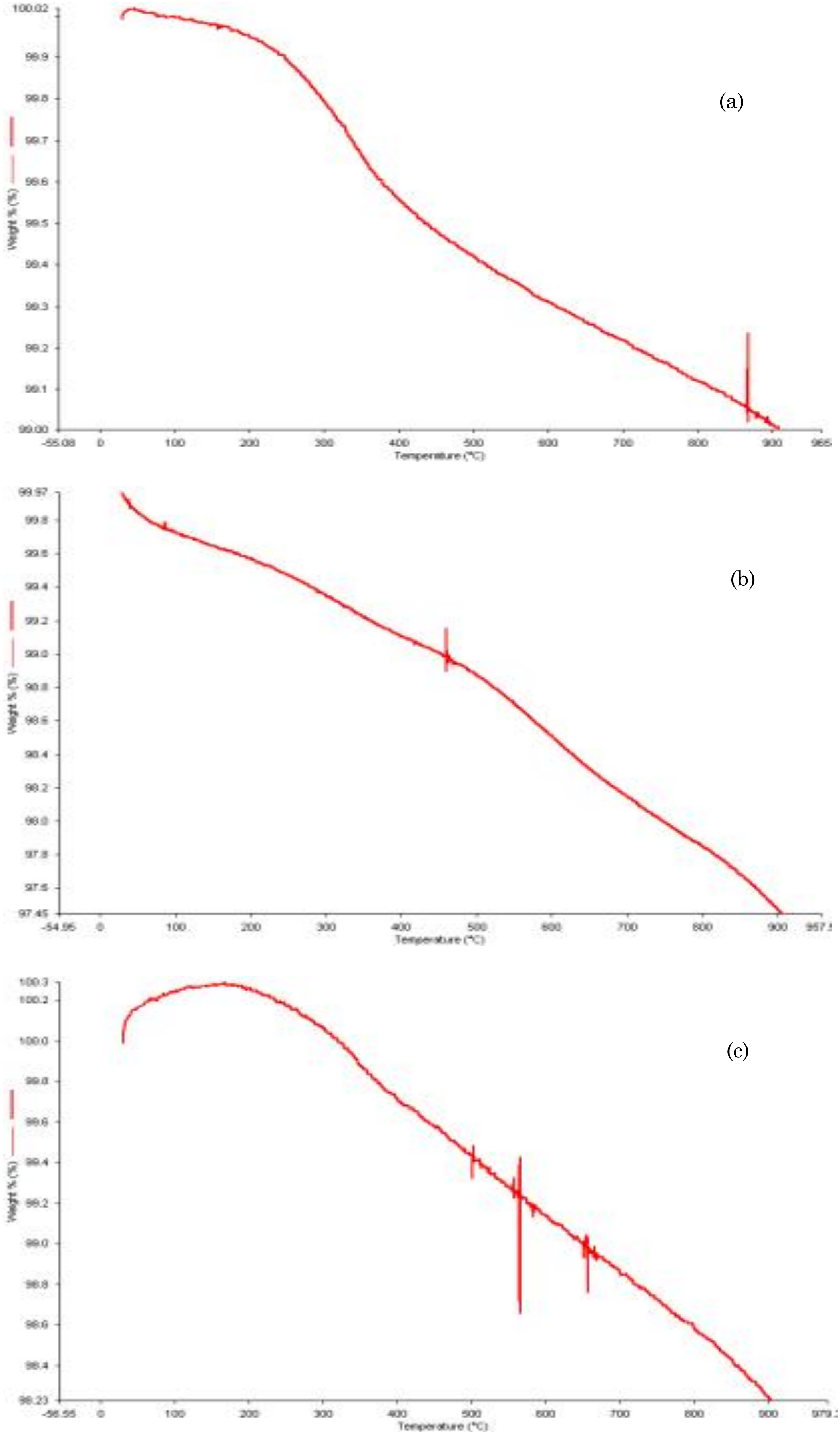


Figure 11. The TGA of prepared samples by precipitation, template and sol-gel method of lithium zirconium silicate , a) LZSP111, b) LZST111, c) LZSS111.

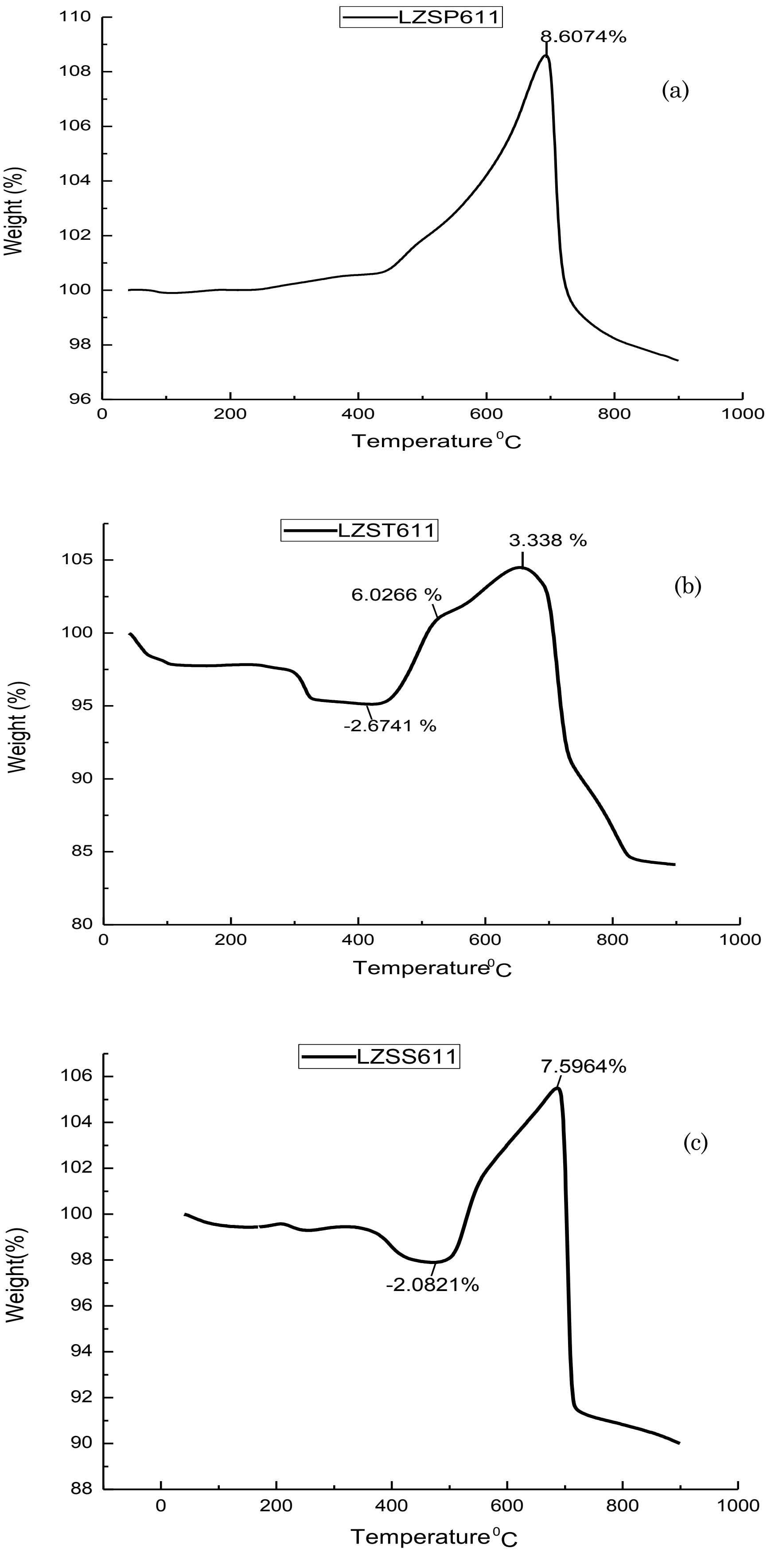


Figure 12. The TGA of prepared samples of lithium zirconium silicate for CO_2 adsorption, a) LZSP611, b) LZST611, c) LZSS611.

higher capture of CO_2 above 350 ^{0}C. The samples LZST611 and LZSS611 showed higher capture of CO_2 above 450 ^{0}C. The sample LZSP611 captured CO_2 8.6 wt.% at 700 ^{0}C. The sample LZSP611 showed the lowered capture of CO_2 above the temperature 720 ^{0}C. The captured CO_2 by the sample LZST611 was 6 wt.% at 700 ^{0}C. The sample LZSS611 showed the captured CO_2 7.6 wt.% at 700 ^{0}C.

4. Conclusions

The samples of lithium zirconium silicate were prepared by using the precipitation, template and sol gel methods with variable mol ratio. The samples of lithium zirconium silicate were characterized by XRD, SEM, TGA, NMR, alkalinity, surface area, etc. The samples of the lithium zirconium silicate were screened for CO_2 capture. The captured CO_2 at 700 ^{0}C was observed 8.6 wt.%. The samples were reusable for CO_2 capture.

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Table 1. The alkalinity and surface area of the samples of lithium zirconium silicate

Sr. No	Sample	Alkalinity (mmol g^{-1})	Surface area (m^2 g^{-1})	Captured CO_2 (wt. %)
	Precipitation method			
1	LZSP111	1.76	6.47	7.89
2	LZSP211	4.45	6.39	7.99
3	LZSP411	8.46	6.30	8.24
4	LZSP611	12.05	6.19	8.61
	Template method			
5	LZST111	1.23	8.79	3.19
6	LZST211	5.91	7.76	3.28
7	LZST411	11.54	7.58	3.31
8	LZST611	12.39	7.76	3.34
	Sol-gel method			
9	LZSS111	3.20	0.44	7.20
10	LZSS211	6.81	2.11	7.31
11	LZSS411	11.17	2.56	7.51
12	LZSS611	14.06	2.98	7.60

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