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***Operando* Raman spectroscopic studies of lithium zirconates during CO₂ capture at high temperature**

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Abstract

Li_2ZrO_3 based sorbents were synthesized for CO_2 capture at high temperature between 500 and 700 °C. Monoclinic ZrO_2 , tetragonal Li_2ZrO_3 , Li_2CO_3 , K_2CO_3 and LiKCO_3 phases were detected by XRD and Raman Spectroscopy. The sorbents showed high stability and moderate capture efficiency. The addition of K resulted in the improvement of capture efficiency from 0.052 g CO_2 g mat⁻¹ in materials without K to 0.083 g CO_2 g mat⁻¹ in the doped solid. Here, we report an experimental setup of Raman spectroscopy coupled with online mass spectrometry and a demonstration of its capabilities using lithium zirconates as sorbents for high temperature CO_2 capture.

Operando Raman Spectroscopy allowed us to follow up the phase evolution during the capture process for the first time. The results obtained confirmed the presence of molten K and Li carbonates when the K-doped zirconates were exposed to CO_2 at 500 °C.

Keywords: Raman Spectroscopy, high temperature sorbents, CO_2 , Li_2ZrO_3

1. Introduction

Today, the excess of GHG (Greenhouse Gases) emissions is a critical issue since their accumulation in the atmosphere is directly associated with the increase of the Earth's mean temperature. Among GHG, carbon dioxide (CO₂) plays a leading role because it contributes to 60 percent of the global warming effect, although other gases have much higher warming potential since they absorb more heat per molecule than carbon dioxide¹. According to the IEA² (International Energy Agency), global emissions of carbon dioxide stood at 32.3 billion tons in 2014, unchanged from the preceding year but different projections predict an increase of CO₂ emissions until 2100, approximately³. Power plants, oil refineries, biogas sweetening as well as production of ammonia, ethylene oxide, cement and iron and steel are the main industrial sources of CO₂^{4,5}. Among them, fuel burning in power plants for energy supply greatly contributes to CO₂ emission, and large efforts are being carried out to decrease it. In order to effectively reduce CO₂ emission into the atmosphere, carbon dioxide capture and storage (CCS) processes have been investigated. They include a wide range of technologies that associate capture, transport and storage of CO₂⁶. Three main strategies are generally available for CO₂ capture, namely post-combustion, pre-combustion, and oxyfuel combustion, and their specific application depends on the concentration of CO₂, gas pressure and type of fuel employed⁷. Among current strategies, post-combustion capture offers some advantages, e.g. lower costs by operation at the temperature of flue gases, which avoids additional costs for cooling or higher capture times; easy adaptation in assembled structures, etc. Moreover, it allows the use of materials that react reversibly with CO₂ depending on the operating conditions⁸.

Development of dry-based sorbents for CO₂ post-combustion capture is a promising alternative because they have several advantages with respect to the liquid solvents used at present. They are mostly organic and inorganic compounds and can be classified according to their sorption and desorption temperatures as low-temperature (< 200 °C), intermediate-temperature (200–400 °C), and high-temperature (> 400 °C) sorbents. Low-temperature sorbents include Carbon, Graphite-Graphene, zeolite, Metal Organic Frameworks (MOF), Silica and Polymer based adsorbents. Intermediate-temperature acceptors are mostly layered double hydroxides (LDH) and MgO based sorbents. Finally, high-temperature sorbents are limited to CaO and alkali zirconates and silicate-based materials^{9,10}. The latter capture CO₂ between 450 °C and 650 °C and generate alkali carbonates; then, by increasing temperature, the reversible reaction (decarbonation) could occur^{6,11}. Among them, lithium zirconates and silicates have some advantages like high capture capacity, lower regeneration temperatures (< 750° C) compared to other high-temperature sorbents such as calcium oxide, and elevated stability, thus allowing operating for many cycles without loss of performance. These features make them promising alternatives for the capture process¹². Moreover, Argentina is the second largest producer of lithium compounds and has the third biggest reserves of lithium worldwide, making the use of Li-based compounds very attractive to industry and academic research¹³. Even though lithium zirconates and silicates have low reaction rates, doping with alkaline metals like K or Na improves the kinetics of the capture process through the formation of melting salts at the reaction temperature, thus reducing the diffusive limitations of CO₂¹⁴⁻¹⁷.

Both the synthesis method and the starting reagents are determinants of sorbent capacity and kinetic properties. Ida et al.¹⁴ reported the influence of particle size of

precursors in Li_2ZrO_3 synthesized by the solid state method. Using low particle size starting ZrO_2 , an enhancement in the kinetics of the carbonation reaction was obtained. Moreover, Radafarnia et al.¹⁸ reported that Li_2ZrO_3 -based sorbents synthesized by the ultrasound assisted method showed a higher capture capacity than the sorbents synthesized under the same conditions but without ultrasound. The simplicity of the synthesis method and the attainability of the starting reagents are also important in order to evaluate the scaling of processes for industrial applications. LiNO_3 is a soluble reagent with the advantages of safety, availability, and low melting point (600 °C)⁸. Therefore, in the present study we synthesize Li_2ZrO_3 -based materials by wet impregnation, a simple method which uses ZrO_2 and LiNO_3 as starting reagents and allows decreasing the calcination temperature needed to produce the Li_2ZrO_3 phase. The generated zirconates capture CO_2 over a range of temperatures and pressures through the “carbonation” reaction, which includes the transformation of zirconates into carbonates and zirconia. At temperatures above 650 °C, the reversible reaction can occur releasing the captured CO_2 and regenerating zirconate species. The evolution of the different generated phases could be followed using the *operando* Raman spectroscopy. This is a useful technique that combines the spectroscopic characterization of a material during reaction with the simultaneous measurement of activity. Raman spectroscopy is particularly suited for *in situ* studies because, given the fact that there is negligible interference from the gas phase, the Raman spectra may be acquired over a wide range of sample temperatures and pressures¹⁹.

The aim of this study was to develop lithium zirconates prepared by wet impregnation for CO_2 capture at high temperature. The influence of doping with K was also studied. *Operando* measurements were performed using Laser Raman Spectroscopy

coupled with online mass spectrometry, to simultaneously follow the evolution of the phases and monitor the capture process. Moreover, the solids were characterized by different techniques such as XRD, Laser Raman Spectroscopy, XPS and surface area measurements.

2. Experimental

2.1. Sample synthesis

The samples were synthesized by wet impregnation of Lithium and Potassium soluble salts on a commercial ZrO_2 , which during calcination could form the appropriate oxide. Starting materials were $\text{LiNO}_3 \cdot 2\text{H}_2\text{O}$ (Carlo Erba), ZrO_2 99% (MEL Chemicals) and KNO_3 (Aldrich).

The theoretical Li:Zr molar ratio required to form Li_2ZrO_3 is 2:1, which implies a weight proportion of 20 % of Li_2O and 80 % of ZrO_2 . Then, a solid with 20 wt. % of Li_2O was prepared, denoted $\text{Li}_2\text{O}(20)\text{ZrO}_2$. Specifically, for the preparation of this material, ZrO_2 was added to a $\text{LiNO}_3 \cdot 2\text{H}_2\text{O}$ solution (0.14 g mL^{-1}) keeping it under constant stirring at $70 \text{ }^\circ\text{C}$ until the sample resembled a wet paste. Then, the material was dried at $80 \text{ }^\circ\text{C}$ for 12 hours and calcined in air at $650 \text{ }^\circ\text{C}$ for 6 hours. A fraction of the calcined $\text{Li}_2\text{O}(20)\text{ZrO}_2$ was impregnated with a KNO_3 solution in order to obtain 5 wt. % of K_2O on the previously synthesized material. The solid was denoted K- $\text{Li}_2\text{O}(20)\text{ZrO}_2$.

2.2. Sample characterization

BET measurements

BET measurements were performed in an automatic gas adsorption equipment (Micrometrics Gemini V). Prior to the measurements, samples were outgassed for 1 hour at 150 °C. Then, N₂ isotherms at -196 °C were executed.

XRD measurements

The X-Ray diffraction patterns were recorded using a Shimadzu XD-D1 diffractometer, using Cu K α ($\lambda=1.542$ Å) radiation at 30 kV and 40 mA. The scan rate was 1–2° min⁻¹ in the range $2\theta = 15$ –80°.

CO₂ capture evaluation

The solids were evaluated in a conventional fixed-bed reactor, named “capture/desorption reactor”. They were pretreated at 700 °C for 15 minutes in flowing N₂ to remove the carbonates formed during calcination and those produced under ambient conditions. After that, the capture/desorption cycles were carried out.

One capture/desorption cycle consists of four steps:

- i- Capture step: 60 minutes at 500 °C in 50% CO₂-50% N₂ mixture.
- ii- Desorption step: increasing temperature from 500 °C to 700 °C, 10 °C min⁻¹, in flowing N₂.
- iii-Regeneration step: 15 minutes at 700 °C in N₂ flow.
- iv-Cooling step: from 700 °C to 500 °C, 10 °Cmin⁻¹, in N₂ flow.

The total feed flow was always set at 60 mL min⁻¹. Flue gases (CO₂) and H₂ (35 mL min⁻¹) were fed into a methanation reactor and converted to methane by a Nickel commercial catalyst operated at 400°C. The resultant stream was continuously analyzed in an on-line FID detector (Shimadzu GC-8A Chromatograph)²⁰.

The mass of CO₂ captured per 1 gram of material during each cycle was calculated by the following equation:

$$gCO_2/gmat = \frac{A \times MW_{CO_2}}{F \times SW}$$

where A is the signal area obtained by chromatography, MW CO₂ is the molecular weight of CO₂, F is the calibration factor of the chromatograph and SW is the sample weight in the captured reactor.

Laser Raman Spectroscopy

Raman Spectra were acquired in a LabRam (Horiba- Jobin-Yvon) spectrometer coupled to an Olympus confocal microscope (a 100× objective lens was used for simultaneous illumination and collection), equipped with a CCD detector cooled to about -70°C using the Peltier effect and an 1800 l/mm diffraction grating. In all cases, the excitation wavelength was 532 nm (Spectra Physics diode pump solid state laser). Each Raman spectrum was collected for ~240 s and the laser power was set at 30 mW to avoid extensive laser heating. In all cases, the excitation wavelength was 532 nm (Spectra Physics diode pump solid state laser). The laser power was set at 30 mW. In situ measurements were carried out employing a cell (Linkam) coupled to the Raman system. The Raman

spectra were curve-fitted using Lorentzian peaks after the baseline subtraction in the 400-700 cm^{-1} region.

The material was loaded in powder and the gases flowed through the solids. The feed mixtures were prepared in a flow system built for this purpose. The total flow was always 20 mL min^{-1} .

The following steps were carried out: Pretreatment; at 700 °C for 15 minutes in flowing Ar; i) Capture step: 60 minutes at 500 °C in 30% CO_2 -70% Ar mixture; ii) Desorption step: increasing temperature from 500 °C to 700 °C, 10 °C min^{-1} , in flowing Ar; iii) Regeneration step; 15 minutes at 700 °C in Ar flow and iv) Cooling step; from 700 °C to 500 °C, 10 °C min^{-1} , in Ar flow.

The gases at the outlet of the cell were analyzed by a quadrupole Dymaxion Dycor mass spectrometer from AMETEK. The spectrometer was assembled in our lab and it is equipped with a Pfeiffer HiCubeTM ECO turbo pumping station with a dry diaphragm vacuum pump. The evolution of $m/e= 18$ (H_2O), 30 (NO) and 44 (CO_2) was analyzed during the experiments. A scheme of the *operando* Raman set-up is shown in Figure 1.

XPS measurements

The XPS measurements were carried out using a multi-technique system (SPECS) equipped with a dual Mg/Al X-ray source and a hemispherical PHOIBOS 150 analyzer operating in the fixed analyzer transmission (FAT) mode. The spectra were obtained with a pass energy of 30 eV; a $\text{MgK}\alpha$ X-ray source was operated at 200 W and 12 kV. The working pressure in the analyzing chamber was less than 5.9×10^{-7} Pa. The XPS analyses

were performed on the solids before and after the capture process. The spectral regions corresponding to Li 1s, K 2p, Zr 3d, Zr 3p, Zr 4s, O 1s and C 1s core levels were recorded for each sample. All photoelectron binding energies were referenced to the C 1s peak of adventitious carbon, set at 284.6 eV. The data treatment was performed with the Casa XPS program (Casa Software Ltd, UK). The peak areas were determined by integration employing a Shirley-type background. Peaks were considered to be a mixture of Gaussian and Lorentzian functions in a 70/30 ratio.

3. Results and Discussion

3.1. Material characterization

XRD patterns of samples after calcination and before capture-desorption cycles (fresh) are exhibited in Figure 2. They show tetragonal $t\text{-Li}_2\text{ZrO}_3$ formation after calcination at 650°C (JCPDS-ICDD# 20-643) and the presence of unreacted monoclinic $m\text{-ZrO}_2$ (JCPDS-ICDD# 5-543). In addition to the diffraction peaks assigned to zirconia phases, reflections attributed to LiKCO_3 (JCPDS-ICDD# 34-1148), K_2CO_3 (JCPDS-ICDD# 1-1001) and Li_2CO_3 (JCPDS-ICDD# 1-996) phases were detected. On the other hand, the Raman spectra of $\text{K-Li}_2\text{O}(20)\text{ZrO}_2$, $\text{Li}_2\text{O}(20)\text{ZrO}_2$ and commercial Li_2CO_3 and K_2CO_3 included as reference, are shown in Figure 3. The spectra for both sorbents show several bands corresponding to different vibrational modes of the ZrO_2 lattice²¹. Note that the starting ZrO_2 is in monoclinic phase since no peaks of tetragonal phase appear. Three clear signals corresponding to Li_2ZrO_3 can be visualized. The peak at 578 cm^{-1} corresponds to symmetrical stretching vibrations of Zr-O , lines at 380 cm^{-1} can be attributed to

symmetrical stretching vibrations of Li–O bonds and the peak at 250 cm^{-1} corresponds to both stretching and bending vibrations of Zr–O bonds²². Both the XRD pattern and the Raman spectrum exhibit higher intensity peaks for t-Li₂ZrO₃ than ZrO₂ in the K-Li₂O(20)ZrO₂ sample.

In the case of K-Li₂O(20)ZrO₂, the Raman bands at 1090 cm^{-1} and 1050 cm^{-1} are assigned to a symmetric stretching of the C-O bonds in Li₂CO₃ and LiKCO₃, respectively²³⁻²⁵. Besides, a band corresponding to Li₂CO₃ appears below 200 cm^{-1} . The sharp signal at 126 cm^{-1} can be attributed to the contribution of several phases such as Li₂ZrO₃²², Li₂CO₃^{23,24} and K₂CO₃²³. However, the Li₂O(20)ZrO₂ spectrum only shows a band at 1090 cm^{-1} assigned to Li₂CO₃. The carbonate species are formed by calcination in air atmosphere, which contains CO₂ traces. When the samples were calcined in ultrapure O₂-Ar atmosphere, no carbonate signals were detected (not shown).

The BET analysis shows that the surface areas of Li₂O(20)ZrO₂ and K-Li₂O(20)ZrO₂ are $10\text{ m}^2\text{g}^{-1}$ and $4.5\text{ m}^2\text{g}^{-1}$, respectively. However, the ZrO₂ precursor shows a surface area of $62.4\text{ m}^2\text{g}^{-1}$. This decrease could be associated with ZrO₂ transformation into Li₂ZrO₃ at the calcination temperature employed. However, surface areas are higher than some materials synthesized by different methods such as soft chemistry and solid state reaction^{14,26,27}, which show values no larger than $1\text{ m}^2\text{g}^{-1}$.

3.2. Capture capacity evaluation

Both thermogravimetric analysis (TGA) and capture/desorption reactors are useful tools to investigate CO₂ sorbents at high temperatures. TGA is one of the most commonly used tools to determine the capacity of CO₂ sorption; however, TGA cannot be applied to

accurately measure the absorption capacity of an acceptor because changes in weight may be caused by various factors. Capture/desorption reactors are more accurate systems since they directly measure released CO₂ on sorbents²⁷. Therefore, in this study an assembled system which includes a fixed-bed reactor linked to a methanation reactor and a FID chromatograph was used for the CO₂ capture evaluation of different materials in capture/desorption cycles carried out between 500 and 700 °C.

Each cycle consists of four steps, namely capture (i), desorption (decarbonation) (ii), regeneration (iii) and cooling (iv). The system was fed with a CO₂ stream (50% CO₂-50% N₂ or 100% CO₂) at 500 °C during the capture step. In the other steps, the feed stream was always pure N₂ (Fig 4). The integrated area in Figure 5 allows calculating the mass of desorbed CO₂ during the decarbonation of each cycle.

Both materials showed excellent stability during 15 cycles (Fig. 6), even though a very slight decrease of the capture capacity can be observed in Li₂O(20)ZrO₂. This stability agreed with the Laser Raman phase analysis made before and after the capture/desorption cycles (Figure 2), in which no significant changes were observed.

The average capture capacity of K-Li₂O(20)ZrO₂ was 0.083 g CO₂ g mat⁻¹, while the capture capacity of Li₂O(20)ZrO₂ was 0.052 g CO₂ g mat⁻¹ when a 50% CO₂ mixture was fed. Previous studies concluded that K enhanced the capture kinetics. However, Ochoa et al.²⁷ reported that the addition of K₂O results in lower capacities and poorer stability due to particle coarsening, when Li₂ZrO₃ was prepared by the soft-chemistry route. Iwan et al.²⁹ reported that the reaction rate should be directly proportional to CO₂ pressure and could be expressed by $r = k \cdot p_{\text{CO}_2}^n$, where r is the rate of reaction, k is the rate constant, p_{CO_2} is the

partial pressure of CO₂ in the gaseous phase and n is the order of reaction. In agreement with these results, when Li₂O(20)ZrO₂ was exposed to 100 % CO₂ flow during the capture step, it showed a slight enhancement in capture capacity (0.074 g CO₂ g mat⁻¹). However, no increase was observed in K-Li₂O(20)ZrO₂ under the same conditions (0.082 g CO₂ g mat⁻¹). This fact could indicate that the K-doped material reached the maximum capacity capture with 50% CO₂ mixture, because of its enhanced kinetic reaction⁸.

3.3. Study of phase transformation by *operando* Raman spectroscopy during a CO₂ capture/desorption cycle

Several authors^{11,14,27} have previously reported that Li₂ZrO₃ and molten carbonate species could be involved in the mechanism of the CO₂ capture at high temperature. Consequently, one the aims of this work is to study the presence of molten carbonates upon the reactivity of lithium zirconates during the capture/desorption cycle.

Operando characterization techniques are valuable tools to study the phase transformation of materials under genuine reaction conditions. For the *operando* measurements, a mass spectrometer assembled in our lab was employed. The evolution of $m/e=18$ (H₂O), 30 (NO) and 44 (CO₂) was followed during the experiments.

Figures 7 and 8 show the Raman spectra and gas evolution obtained during one capture/desorption cycle in the temperature range of 500–700°C. The evolution of m-ZrO₂, Li₂CO₃, t-Li₂ZrO₃, K₂CO₃ and LiKCO₃ in Li₂O(20)ZrO₂ and K-Li₂O(20)ZrO₂ is presented. The Raman experiment included the same series of steps as the capture/desorption cycle, namely (i) capture, (ii) desorption, (iii) regeneration and (iv) cooling. Before the *operando* Raman experiment, a spectrum was taken at room temperature. In the case of the Li₂O(20)ZrO₂ material, the Raman spectrum between 200 and 650 cm⁻¹ shows the presence

of ZrO_2 monoclinic and a signal at 578 cm^{-1} assigned to symmetrical stretching vibrations of Zr-O bonds in Li_2ZrO_3 species²¹.

Besides the m- ZrO_2 and Li_2ZrO_3 bands, a signal at 1090 cm^{-1} assigned to Li carbonate could also be observed (Fig. 7.a). In the case of the K- $\text{Li}_2\text{O}(20)\text{ZrO}_2$ material, a signal at 1051 cm^{-1} assigned to LiKCO_3 and/or K_2CO_3 was observed (Fig. 8.a), in addition to the phases previously described. Prior to step (i), the samples were heated in Ar stream from $25\text{ }^\circ\text{C}$ to $700\text{ }^\circ\text{C}$ to decompose CO_3^{2-} species. Figures 7.b and 8.b show the evolution of the mass spectrometer signals during the heating. For both solids, it was observed that the CO_2 signal ($m/e=44$) starts to increase slightly at temperatures above $270\text{ }^\circ\text{C}$, with a desorption peak maximum at $620\text{ }^\circ\text{C}$. This could correspond to decomposition of carbonate species formed during the preparation stage of the material probably due to the presence of CO_2 in the air used for calcination. Note that in addition to the $m/e=44$, a signal corresponding to NO ($m/e=30$) was observed in the K-doped solid due to the decomposition of residues of potassium nitrate.

For both solids (Fig. 7.a and 8.a), when the Raman band at 1090 cm^{-1} disappeared meaning that lithium carbonate decomposed, the main signal assigned to lithium zirconate increased (578 cm^{-1}). This observation is more remarkable for the K-doped solid. In this case, when the temperature reached $700\text{ }^\circ\text{C}$, the signal at 1050 cm^{-1} was still present. The evolution of Raman spectra as a function of time and temperature during the desorption step for the K- $\text{Li}_2\text{O}(20)\text{ZrO}_2$ sample was also included in Figure 1ESI.

After heating, the temperature was decreased to $500\text{ }^\circ\text{C}$ and the solids were subsequently exposed to a CO_2 (30%)/Ar mixture during 60 min (step (i)). Figures 7.a and

8.a show the Raman spectra corresponding to the capture step performed at 500 °C at different exposure times. In the case of the $\text{Li}_2\text{O}(20)\text{ZrO}_2$ material after 15 min of CO_2 capture, the lithium carbonate in the solid phase (at 1090 cm^{-1}) was formed while the bands assigned to lithium zirconate decreased. On the other hand, in the Raman spectrum of the $\text{K-Li}_2\text{O}(20)\text{ZrO}_2$ sample after 5 min of CO_2 capture, there appeared two signals in the region of the CO_3^{2-} , located at 1064 and 1084 cm^{-1} . These signals increased with the exposure time at the same time as the ZrO_2 signals, while those assigned to Li_2ZrO_3 progressively decreased. The carbonate signals could be assigned to a molten Li_2CO_3 - K_2CO_3 mixture and solid Li_2CO_3 ²³, respectively. Note that according to the phase diagram of the Li_2CO_3 - K_2CO_3 system reported by Ida and coworkers¹⁴, it is probable that at the potassium composition (K_2CO_3 molar fraction = 0.071) and temperatures (500 – 700 °C) used in this work, both carbonates are molten and Li_2CO_3 is also present in the solid phase.

Mizuhata et al.³⁰ studied the electrical conductivity and melting behavior of binary molten carbonate, LiKCO_3 , coexisting with several kinds of metal oxide powder. They observed that the CO_3^{2-} stretching band in the Raman spectra was shifted toward a lower wavenumber from 1056 cm^{-1} to 1053 cm^{-1} with the decrease of the liquid phase for the system containing ZrO_2 powder and LiKCO_3 melted at 507°C .

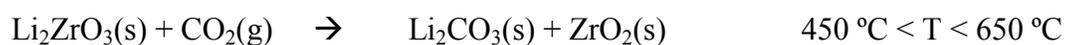
For both materials, during the desorption step (ii), the gas flow was turned to Ar and the temperature was again increased from 500 to 700 °C at a heating rate of $10^\circ/\text{min}$. Li_2CO_3 species, formed in the first stage (i), were decomposed at 700 °C (Fig. 7.b and 8.b) On the other hand, the signal at 1064 cm^{-1} was shifted toward a lower wavenumber at 1048 cm^{-1} , regenerating the solid for a new cycle. Taking into account the results reported by

Mizuhata et al.³⁰ in the LiKCO₃ system containing ZrO₂ powder, this signal could be assigned to the LiKCO₃ molten phase.

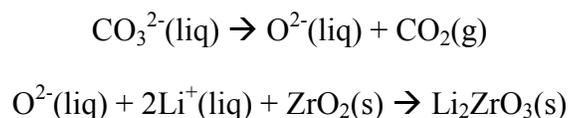
Table 1 summarizes the different conditions and Raman signals present in each experiment. Note that in the Li₂O(20)ZrO₂ material, mainly Li₂ZrO₃ and Li₂CO₃ in the solid phase are present while in the K-Li₂O(20)ZrO₂ sample, carbonate species in the liquid phase are also observed.

In addition, to follow the transformation of Li₂ZrO₃ during the whole process, the Raman spectra were curve-fitted in the 400-700 cm⁻¹ region using three Lorentzian peaks at 470, 578 and 630 cm⁻¹. The peaks at 470 and 630 cm⁻¹ were assigned to ZrO₂ and the band at 578, to Li₂ZrO₃. The intensity ratios of bands at 578 and 470 cm⁻¹ are summarized in Table 2. For the Ar treated K-Li₂O(20)ZrO₂ sample, the I₅₇₈/I₄₇₀ ratio decreased during CO₂ capture, indicating the transformation of Li₂ZrO₃ into ZrO₂ and Li₂CO₃. Besides, the lower value presented for this sample, in comparison with the undoped one, is in agreement with its higher capture capacity. After desorption, the intensity ratio increased for both samples.

In general, for both solids, phase evolution is ruled by the carbonation reversible reaction. The thermodynamic study of this reaction predicts CO₂ capture taking place between 450 and 650 °C and at higher temperatures carbonate decomposition occurs, giving regenerate zirconates^{6,11}.



M. Olivares-Marin et al.³¹ sustained that the introduction or doping of alkaline elements into Li_2ZrO_3 could apparently change the melting points of the system and produce a liquid eutectic mixed-salt molten shell. The molten carbonate shell allows the diffusion and sorption of CO_2 , which changes the viscoelastic properties of the sorbent and improves the effectiveness of the sorbent for the CO_2 uptake. It is generally accepted that doping with potassium favors the diffusion of CO_2 through the Li_2CO_3 layer formed on the surface during the capture reaction^{14,26,27,29}. The layer in a totally or partially liquid phase at the reaction and regeneration conditions facilitates the diffusion of CO_3^{2-} and the mobility of K^+/Li^+ and O^{2-} . The increase in the mobility of the ions could influence the rate of the reactions. Therefore, the presence of liquid carbonate observed by Raman spectroscopy is in agreement with the higher capture capacity of the potassium doped material compared to the undoped sorbent. Then, the reaction mechanism would involve species in the liquid phase according to what was previously reported by Ochoa et al²⁷.



Operando Raman Spectroscopy allowed us to follow up the phase evolution during the capture process for the first time. The results obtained helped us to confirm the reaction mechanism proposed for K-doped zirconates that would involve molten K and Li carbonates.

3.4. XPS analysis

XPS measurements were carried out in order to study surface changes in the materials during the capture process. The K-Li₂O(20)ZrO₂ and Li₂O(20)ZrO₂ samples were analyzed after different treatments: a) pretreated (before the capture step), b) with CO₂ capture (after the capture step and before the desorption step) and c) used (after a whole capture/desorption cycle). The ZrO₂ precursor was also included in the XPS analysis as reference.

Table 3 summarizes the binding energy of the different elements. There were no significant differences in binding energies (BE) of C 1s, O 1s, Li 1s and K 2p regions in K-Li₂O(20)ZrO₂ and Li₂O(20)ZrO₂. However, BE in Zr 3p, 3d and 4s core levels are approximately 0.8 eV higher in ZrO₂ than in K-Li₂O(20)ZrO₂ and Li₂O(20)ZrO₂, which would suggest Li₂ZrO₃ surface phase formation. The Zr 3d_{5/2} core level BEs are shown in Table 3.

Changes in surface species were observed under different treatments. Figure 9 shows the Li 1s-Zr 4s curve fitted XPS spectra for both samples. Signals at 55 eV and 52.6 eV correspond to Li 1s and Zr 4p, respectively. A satellite peak of Zr at lower BE was also included in order to improve the curve fitting of Li 1s and Zr4s peaks. In Li₂O(20)ZrO₂ (Fig. 9.a) the Li/Zr ratio was reversed as the complete capture process occurred, and the peak intensity of Li increased as the signal intensity of Zr 4s decreased. However, no significant changes in Li/Zr ratios were observed in the K-doped material (Fig. 9.b).

The O1s region shows two contributions at 532.0 and 529.8 eV assigned to carbonate oxygen (O_{CO₃}) and lattice oxygen (O_{lattice}), respectively. Differences in the intensities of O_{lattice} and O_{CO₃} contributions are also illustrated in Figure 2 ESI. For both

samples, $\text{Li}_2\text{O}(20)\text{ZrO}_2$ and $\text{K-Li}_2\text{O}(20)\text{ZrO}_2$, the O_{CO_3} peak intensity increased during the capture step and then decreased. However, this behavior was more marked in the K-doped sample. Moreover, no contribution of surface $\text{O}_{\text{lattice}}$ was observed in the latter after the capture step, which would agree with the higher capture capacity of this material. Furthermore, the analysis of the C1s region shows the contribution of different carbon species, among them C_{CO_3} peaks at 289.4 ± 0.2 eV. These signals are in agreement with the results obtained in the O1s region. Table 4 summarizes the surface atomic concentration of each material after the different treatments. For both materials, an increase in intensity of C_{CO_3} signals was observed during the capture step; however, this increase was more pronounced in the K doped- material.

It can be observed that in the K-doped sample with CO_2 capture, both K and Zr atomic percentages decreased while C and O_{CO_3} concentration increased, and returned to the original values after the capture/desorption cycle. However, the Li concentration remained approximately constant. Moreover, in the undoped materials Zr concentration progressively decreased while C, Li and O_{CO_3} atomic percentages gradually increased.

Some trends are more clearly visualized using elemental ratios calculated from surface concentrations. The stoichiometric C/O ratio for CO_3^{2-} species should be equal to 0.33. In samples without K, the C/O ratio remained always near this value; however, in the K-doped materials values not above 0.19 were observed. Moreover, an increase of C/O ratio was noticed after the capture step, from 0.16 to 0.19. This fact would indicate the formation of CO_3^{2-} species during the capture process.

Both Li/Zr and C/Zr ratios were in the same order in K-doped and undoped materials but they showed different trends. In both samples, C/Zr ratios were very similar and increased after the CO₂ capture step. The K-doped sorbent showed a different behavior with respect to the undoped sorbent in the used samples, with a significantly lower C/Zr ratio than the latter. For the K-doped material, it can be observed that the C/Zr ratio increases and then recovers the original value after the “capture-desorption” cycle (0.51, 1.19 and 0.36 in the samples pretreated, with CO₂ capture and used, respectively). However, for the undoped material, the C/Zr ratio remained similar in the used and after CO₂ capture samples (0.54, 1.18 and 1.12). The ability of the K-doped material to recover the low C/Zr values could also be associated with a higher capture capacity, as verified by capture evaluation.

On the other hand, both materials showed a progressive increase of the Li/Zr ratio (pretreated < with CO₂ capture < used). However, this growth was much less pronounced in the K-doped sample than in the undoped material (from 1.46 to 1.88 and from 0.71 to 3.01 in K-doped and undoped samples, respectively). Note that Li/Zr and O_{lattice}/Zr ratios were higher in the K-doped than in the undoped pretreated materials. Furthermore, the Li/Zr ratio was close to the bulk composition (Li/Zr theoretical ratio = 2), which agrees with the high proportion of the Li₂ZrO₃ phase observed in Laser Raman Spectroscopy studies.

A surface lithium segregation was observed in the used Li₂O(20)ZrO₂ sample (Li/Zr ratio = 3.01). The larger surface amount of Li observed in Li_xZrO_y prepared by soft-chemistry²⁸ have been explained by the lower surface free energy of lithium.

4. Conclusions

K-Li₂O(20)ZrO₂ and Li₂O(20)ZrO₂ sorbents were synthesized by wet impregnation using LiNO₃ and monoclinic ZrO₂.

XRD and Laser Raman Spectroscopy characterization confirmed the presence of m-ZrO₂, t-Li₂ZrO₃, KLiCO₃, K₂CO₃ and Li₂CO₃ phases. Both solids showed a moderate capture efficiency, while K-Li₂O(20)ZrO₂ was slightly better than the undoped material. Moreover, they were stable during almost 15 cycles of capture/desorption.

Using *operando* Raman Spectroscopy, we analyzed the phase behavior during the capture process and observed that it agreed well with the reversible carbonation reaction.

In the Li₂O(20)ZrO₂ sorbent, ZrO₂, Li₂CO₃ and Li₂ZrO₃ in the solid phase were present while in K-Li₂O(20)ZrO₂, carbonate species were molten and a fraction of Li₂CO₃ was also present in the solid phase.

The presence of molten KLiCO₃, K₂CO₃ and Li₂CO₃ carbonates during the CO₂ treatment at 500 °C was verified, supporting the role of ion mobility in the reaction rates. In addition, the positive influence of potassium-doping on the reactivity of lithium zirconate to ZrO₂ was confirmed for the first time under *operando* conditions.

The application of Raman spectroscopy in *operando* during the capture/desorption cycle allowed us to clearly follow the changes that occur simultaneously in the course of the different cycle steps and shows a high potential to study other high temperature sorbents under real conditions.

Acknowledgments

The authors wish to acknowledge the financial support received from UNL, CONICET and ANPCyT. Thanks are also given to ANPCyT for the purchase of the Raman instrument (PME 87-PAE 36985) and the UHV Multi Analysis System (PME 8-2003), and to Fernanda Mori for the XPS measurements. The support from Ana Tarditi and Betina Faroldi is also greatly appreciated.

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Figure legends

Figure 1. Scheme of *Operando* Raman system.

Figure 2. DRX patterns of synthesized samples and ZrO₂.

Figure 3. Raman spectra of synthesized samples, m-ZrO₂, Li₂CO₃ and K₂CO₃. Li₂ZrO₃ bands are marked by dotted lines.

Figure 4. Temperature and gases evolution during one capture/desorption cycle. Each cycle consists of four steps: capture (i), desorption (ii), regeneration (iii) and cooling (iv). Total flow: 60 mL min⁻¹. P= 1 atm.

Figure 5. CO₂ signal evolution during the desorption step in the first capture/desorption cycle for K-Li₂O(20)ZrO₂. Total flow: 60 mL min⁻¹. P= 1 atm. Heating rate: 10 °C min⁻¹.

Figure 6. Stability of materials represented by the evolution of capture capacity as a function of cycle number. All cycles were performed under the same conditions. Total flow: 60 mL min⁻¹. P= 1 atm.

Figure 7. *Operando* Raman Spectroscopy of $\text{Li}_2\text{O}(20)\text{ZrO}_2$ during a complete/desorption cycle. (a) Raman spectra at different atmospheres and temperature conditions and (b, c) Mass Spectroscopy during the desorption step and pretreatment.

Figure 8. *Operando* Raman Spectroscopy of $\text{K-Li}_2\text{O}(20)\text{ZrO}_2$ during a complete/desorption cycle. (a) Raman spectra at different atmospheres and temperature conditions and (b, c) Mass Spectroscopy during the desorption step and pretreatment.

Figure 9. XPS spectra of Li 1s and Zr 4p in $\text{Li}_2\text{O}(20)\text{ZrO}_2$ (a) and $\text{K-Li}_2\text{O}(20)\text{ZrO}_2$ (b) under different treatments: before the capture step, after the capture step and before the desorption step and after a complete capture/desorption cycle.

Table 1. Species present in the samples exposed to different conditions, monitored by in situ Raman spectroscopy.

Treatments	Samples	
	Li ₂ O(20)ZrO ₂	KLi ₂ O(20)ZrO ₂
Ar, 25 °C	ZrO ₂ , Li ₂ CO ₃	ZrO ₂ , Li ₂ ZrO ₃ , Li ₂ CO ₃ and LiKCO ₃
Ar, 700 °C	ZrO ₂ , Li ₂ ZrO ₃	ZrO ₂ , Li ₂ ZrO ₃ and molten LiKCO ₃
CO ₂ capture, 500 °C, 5 min	ZrO ₂ , Li ₂ ZrO ₃ , Li ₂ CO ₃	ZrO ₂ , Li ₂ ZrO ₃ , molten Li ₂ CO ₃ -K ₂ CO ₃ mixture and Li ₂ CO ₃ (s)
CO ₂ capture, 500 °C, 15 min	ZrO ₂ , Li ₂ ZrO ₃ , Li ₂ CO ₃	ZrO ₂ , Li ₂ ZrO ₃ , molten Li ₂ CO ₃ -K ₂ CO ₃ mixture and Li ₂ CO ₃ (s)
CO ₂ capture, 500 °C, 40 min	ZrO ₂ , Li ₂ ZrO ₃ , Li ₂ CO ₃	ZrO ₂ , Li ₂ ZrO ₃ , molten Li ₂ CO ₃ -K ₂ CO ₃ mixture and Li ₂ CO ₃ (s)
CO ₂ capture, 500 °C, 60 min	ZrO ₂ , Li ₂ CO ₃	ZrO ₂ , Li ₂ ZrO ₃ , molten Li ₂ CO ₃ -K ₂ CO ₃ mixture and Li ₂ CO ₃ (s)
Ar, 550 °C after CO ₂ capture	ZrO ₂ , Li ₂ CO ₃	ZrO ₂ , Li ₂ ZrO ₃ , molten Li ₂ CO ₃ -K ₂ CO ₃ mixture and Li ₂ CO ₃ (s)
Ar, 600 °C after CO ₂ capture	ZrO ₂ , Li ₂ CO ₃	ZrO ₂ , Li ₂ ZrO ₃ , molten Li ₂ CO ₃ -K ₂ CO ₃ n and Li ₂ CO ₃ (s)
Ar, 700 °C after CO ₂ capture	ZrO ₂ , Li ₂ ZrO ₃	ZrO ₂ , Li ₂ ZrO ₃ and molten LiKCO ₃

Table 2. Evolution of Li_2ZrO_3 intensity during Raman *Operando* measurements.

Treatment	I_{578}/I_{470} ^a	
	K- $\text{Li}_2\text{O}(20)\text{ZrO}_2$	$\text{Li}_2\text{O}(20)\text{ZrO}_2$
Ar, 700 °C	1.30	0.45
CO ₂ , 5 min, 500 °C	1.40	0.48
CO ₂ , 15 min, 500 °C	0.26	0.46
CO ₂ , 40 min, 500 °C	0.20	0.61
CO ₂ , 60 min, 500 °C	0.26	0.56
Ar, 550 °C	0.26	0.64
Ar, 620 °C	0.15	0.87
Ar, 700 °C	1.60	0.70

^a Intensity ratios of bands at 578 and 470 cm^{-1} , assigned to Li_2ZrO_3 and ZrO_2 , respectively.

Table 3. Binding Energies (eV) of all elements in K-doped and undoped samples under different treatments.

	Li 1s	K 2p _{3/2}	Zr 3d _{5/2}	O _{lattice} ^a 1s	O _{CO₃} ^b 1s	C _{CO₃} ^b 1s
Pretrated ^c K-Li ₂ O(20)ZrO ₂	54.9	293.1	181.7	529.8	531.7	288.6
With capture ^d K-Li ₂ O(20)ZrO ₂	54.9	293.0	181.9	-	531.4	288.8
Used ^e K-Li ₂ O(20)ZrO ₂	54.9	293.2	181.7	530.0	532.0	288.8
Pretrated ^c Li ₂ O(20)ZrO ₂	55.3	-	181.8	529.7	531.7	288.9
With ^d capture Li ₂ O(20)ZrO ₂	55.1	-	181.8	529.6	531.7	289.3
Used ^e Li ₂ O(20)ZrO ₂	55.1	-	181.7	529.7	531.9	289.3
ZrO ₂	-	-	182.5	530.6	532.6	288.6
Used ^e Li ₂ O(20)ZrO ₂ ^f	55.0	-	181.7	529.3	531.8	289.4

^a Oxygen corresponding to zirconia and lithium zirconate lattice

^b Oxygen or carbon corresponding to carbonate species

^c Before capture step

^d After capture step and before desorption step

^e Before a complete “capture-desorption” cycle

^f Sample calcined under oxygen atmosphere

Table 4. Elemental composition and atomic ratio of materials under different treatments.

	%Li	%Zr	%K	%O _{CO₃} ^a	%O _{lattice} ^b	%C _{CO₃} ^a	C/O	Li/Zr	C/Zr
Pretrated ^c K-Li ₂ O(20)ZrO ₂	18.5	12.6	4.6	40.0	17.8	6.4	0.16	1.46	0.51
With capture ^d K-Li ₂ O(20)ZrO ₂	17.4	9.6	2.4	59.1	-	11.5	0.19	1.80	1.19
Used ^e K-Li ₂ O(20)ZrO ₂	22.2	11.8	4.9	33.5	23.4	4.2	0.13	1.88	0.36
Pretrated ^c Li ₂ O(20)ZrO ₂	12.7	21.6	-	29.6	30.4	9.6	0.32	0.71	0.54
With capture ^d Li ₂ O(20)ZrO ₂	20.9	11.1	-	43.9	11.1	13.1	0.30	1.89	1.18
Used ^e Li ₂ O(20)ZrO ₂	29.2	9.7	-	37.6	12.7	10.9	0.29	3.01	1.12
ZrO ₂	-	25.6	-	24.5	40.1	9.7	0.40	-	0.38
Used ^e Li ₂ O(20)ZrO ₂ ^f	30.1	6.0	-	47.0	4.6	12.3	0.26	5.03	2.00

^a Oxygen or carbon corresponding to carbonate species

^b Oxygen corresponding to zirconia and lithium zirconate lattice

^c Before capture step

^d After capture step and before desorption step

^e Before a complete “capture-desorption” cycle

^f Sample calcined under oxygen atmosphere

Figure 1

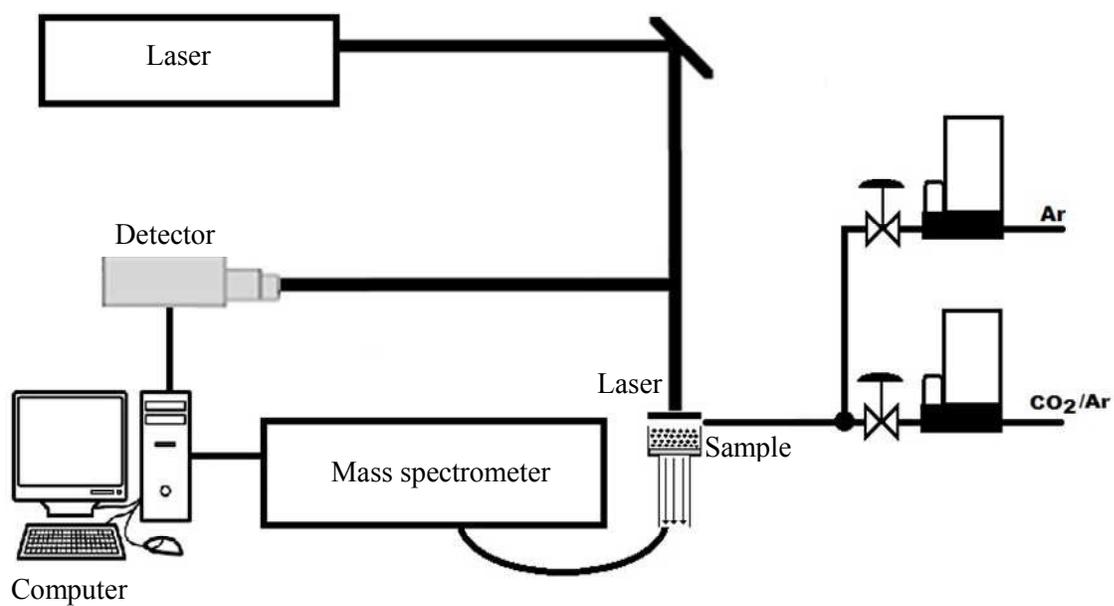


Figure 2

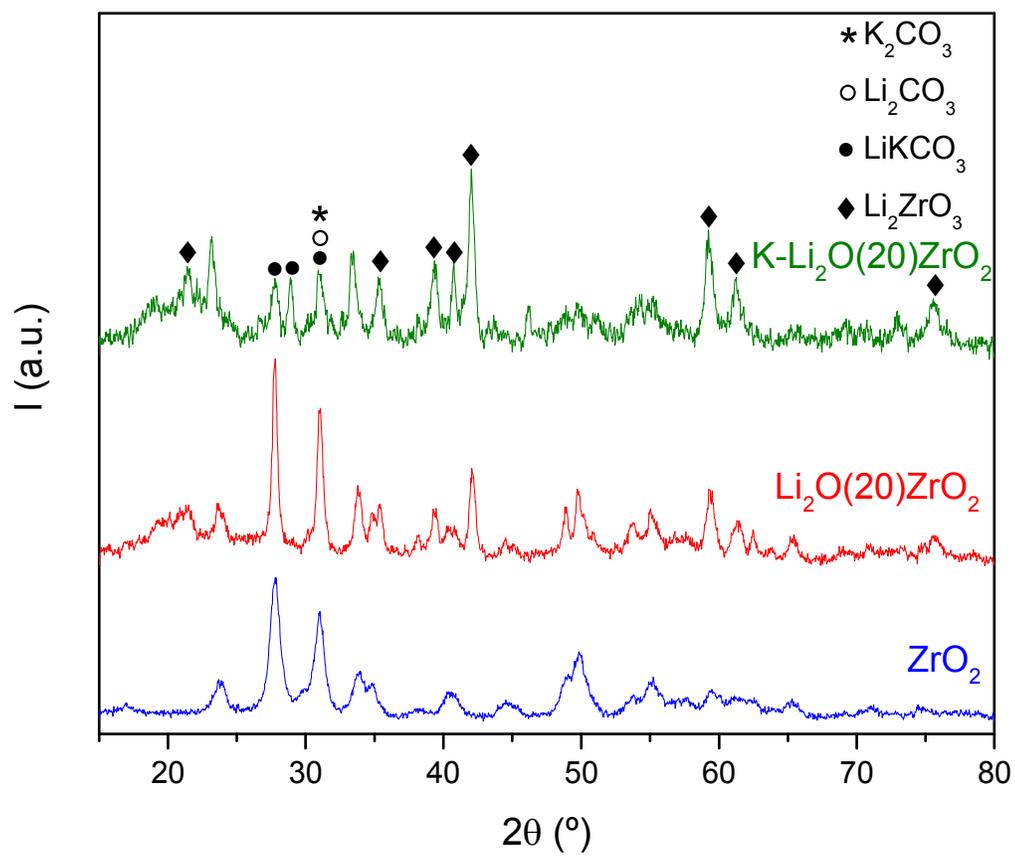


Figure 3

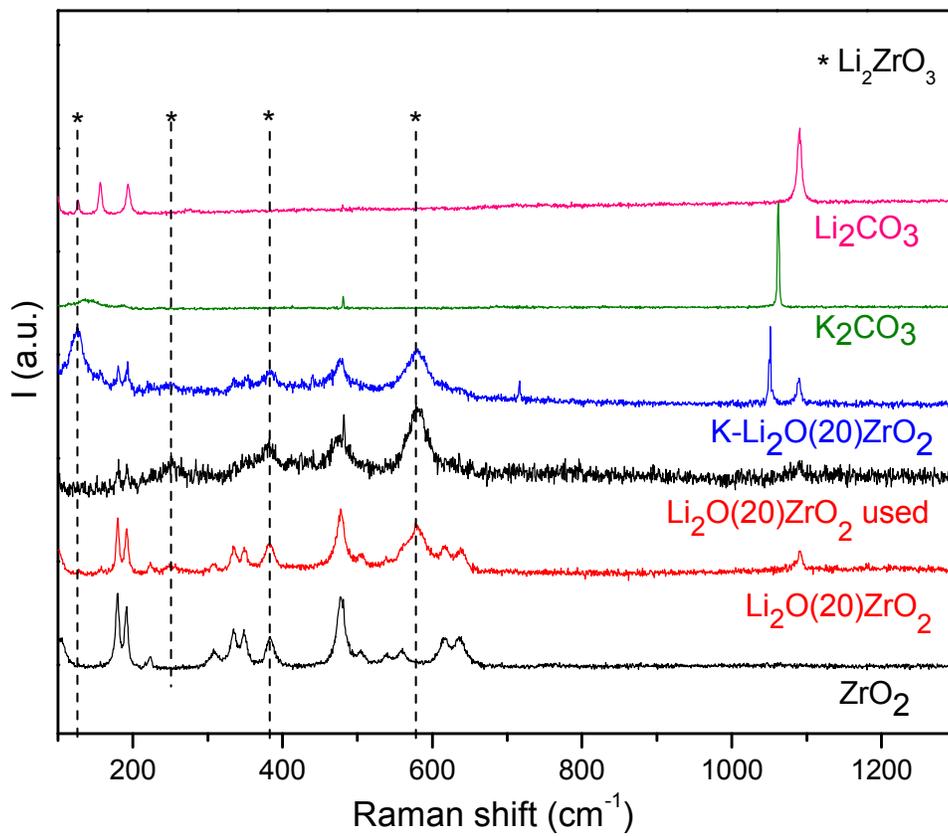


Figure 4

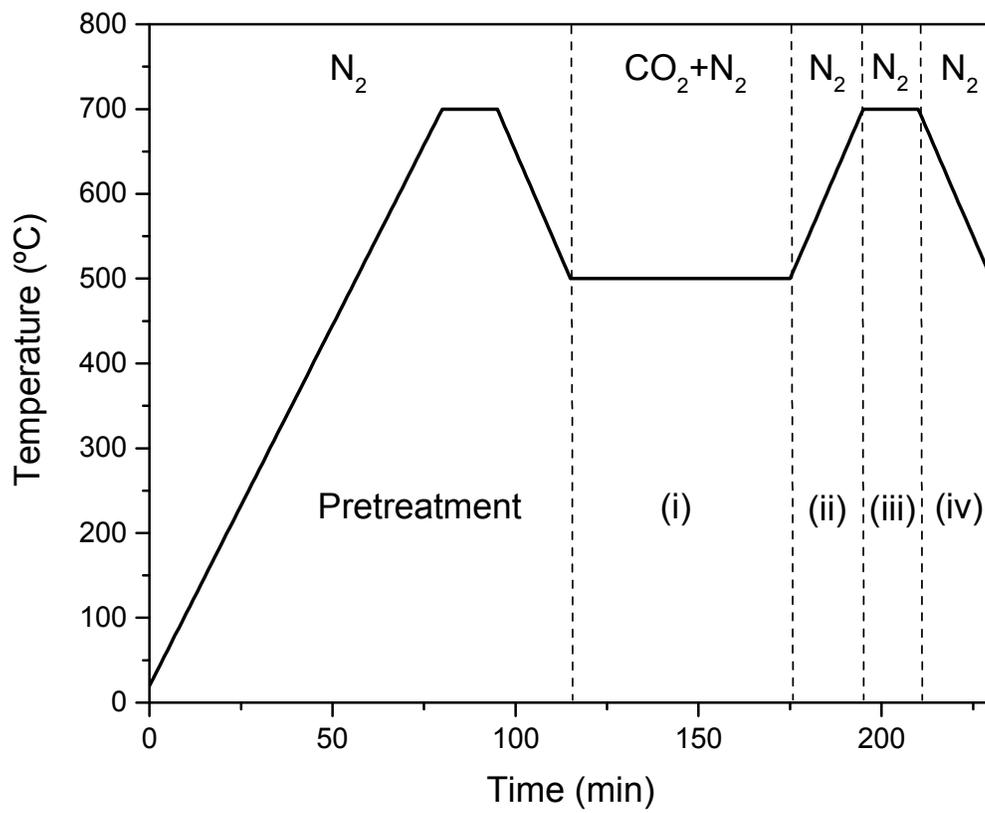


Figure 5

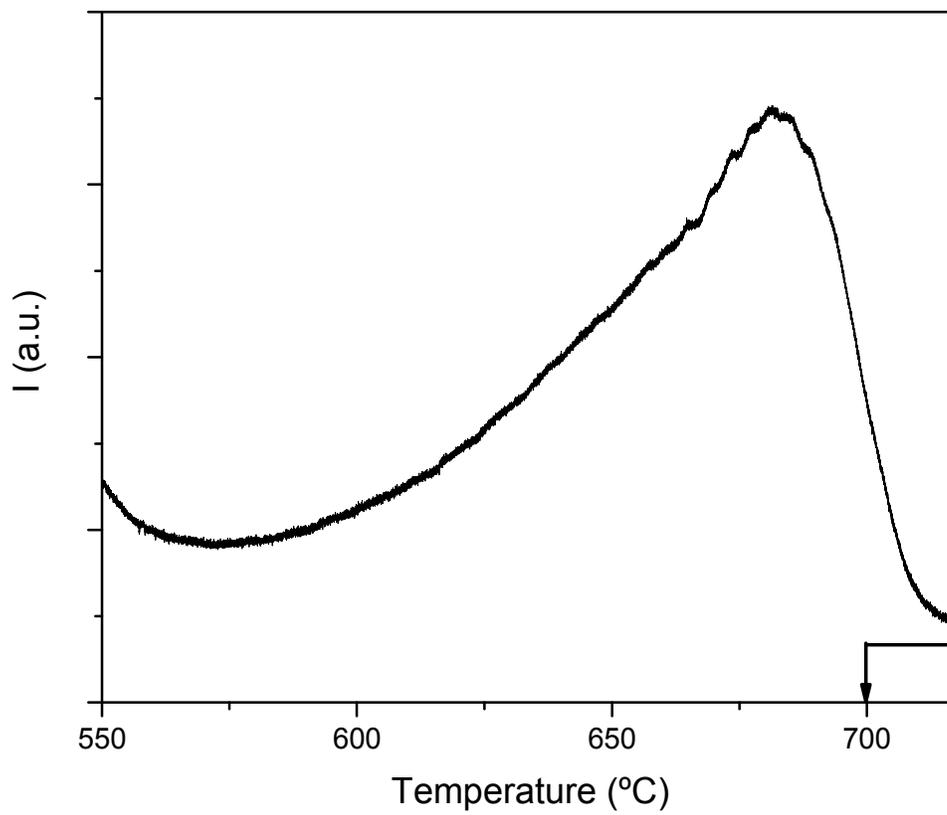


Figure 6

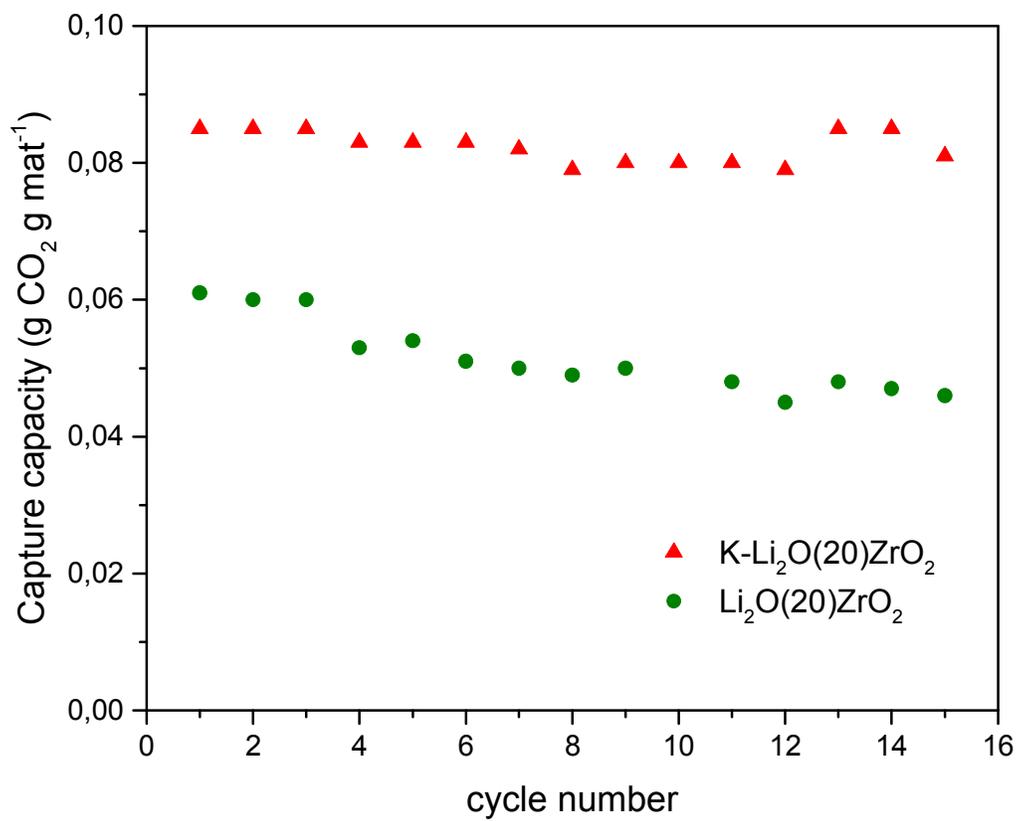


Figure 7

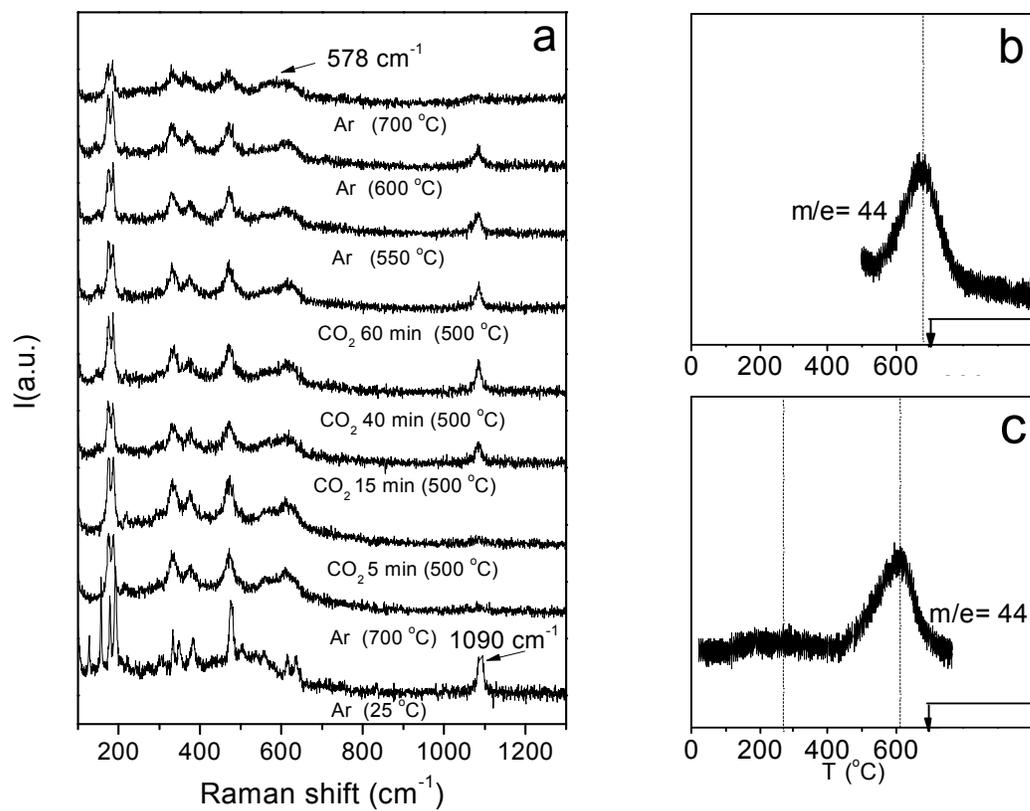


Figure 8

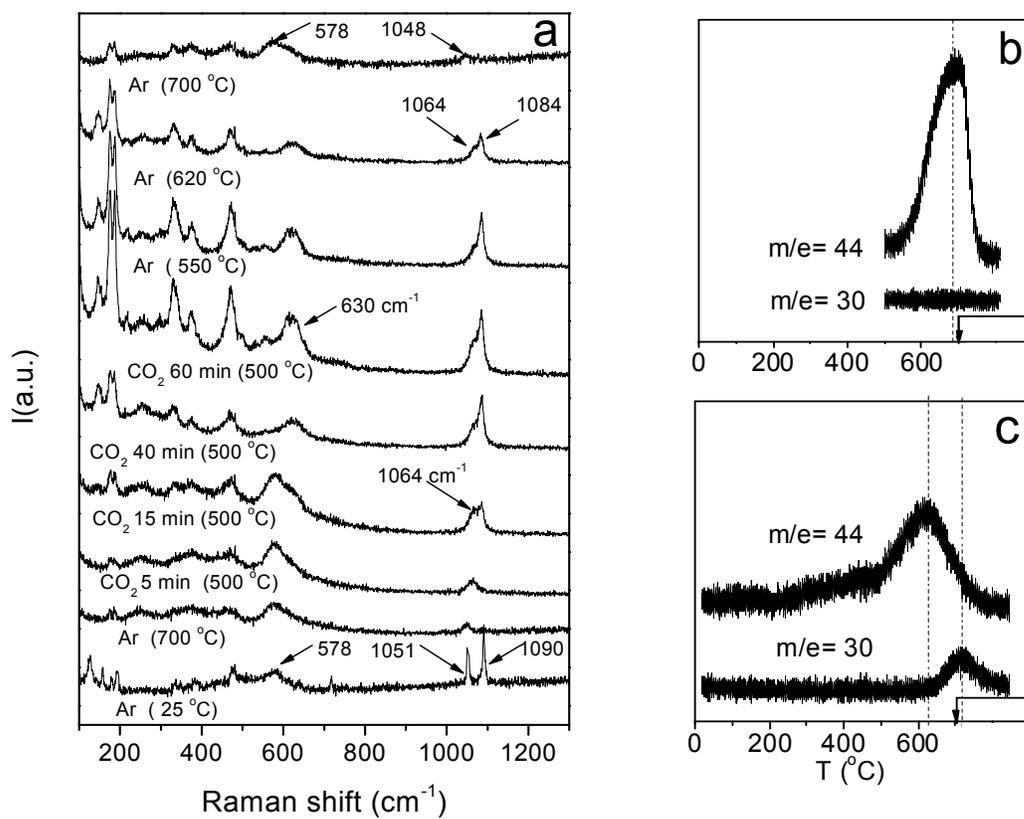
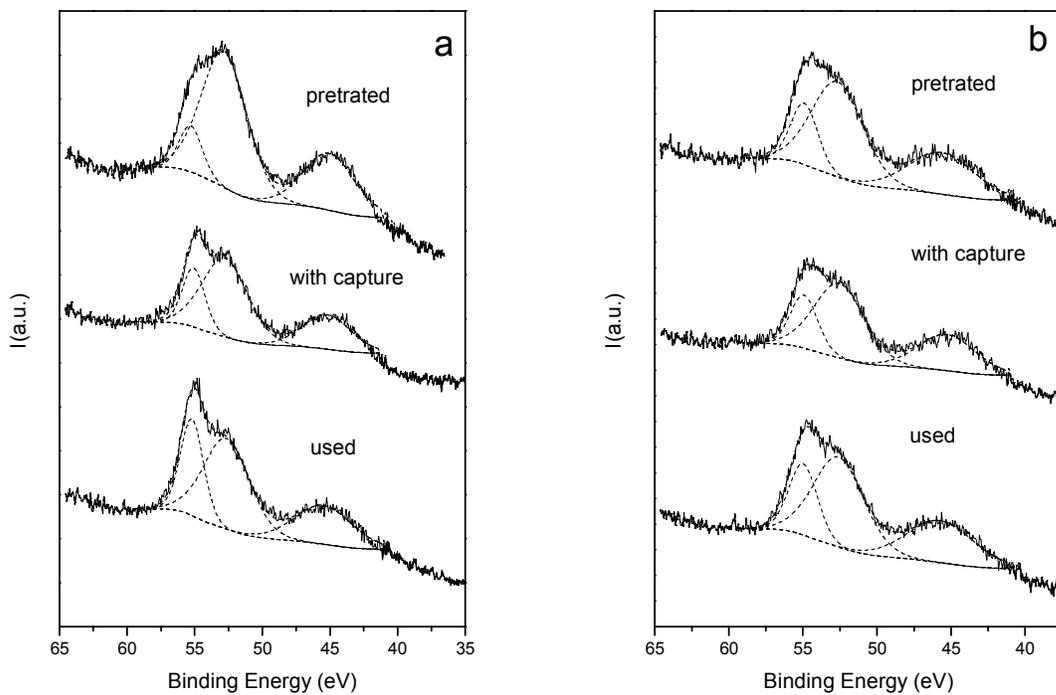


Figure 9



Operando Raman Spectroscopy allowed to follow up the phase evolution for K-doped lithium zirconates during the CO₂ capture process.

