

Synthesis of Li_2MO_3 ($M = \text{Ti}$ or Zr) by the combustion method

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Abstract

The advantages and disadvantages of the combustion method to prepare Li_2TiO_3 and Li_2ZrO_3 ceramics were studied. Firstly, the ceramic powders were prepared by the combustion process using LiOH , MO_2 (where $M = \text{Ti}$ or Zr) and urea in different molar ratios (from 2 : 1 : 3 to 3 : 1 : 3) at different temperatures for 5 minutes. Li_2TiO_3 and Li_2ZrO_3 were also obtained by the solid-state method, and the results were compared with those obtained by the combustion process. The powders were characterized by X-ray diffraction and scanning electron microscopy. It was found that the combustion process reduces the synthesis time of Li_2TiO_3 (1 minute at 750 °C), but it does not have any advantage on producing Li_2ZrO_3 , due to thermodynamic factors. On the other hand, the combustion process produces carbon contaminants in the solids. It was necessary to add excess of lithium hydroxide, in order to compensate the quantity of Li sublimated during the production of the ceramics. Finally, it seems that both reactions follow the same mechanism, which is determined by the lithium diffusion into the metal oxides.

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1. Introduction

Lithium based oxide ceramics are considered as possible solid breeder materials in the blanket of future nuclear fusion reactors. The role of these breeder materials is to produce tritium, and they have to fulfill the following conditions: produce and release tritium, possess physical and chemical stability at high temperatures, display compatibility with other structural components, and exhibit an adequate irradiation behavior [1–5].

Actually, lithium titanate (Li_2TiO_3) and lithium zirconate (Li_2ZrO_3) are considered by ITER (*International Thermonuclear Experimental Reactor*) as tritium breeding materials in the deuterium–tritium (D–T) fusion reactors [6,7]. Li_2TiO_3 shows good chemical stability in air and acceptable mechanical strength, while Li_2ZrO_3 seems to fulfill the required thermo-physical, chemical and mechanical stability [8–10].

Li_2TiO_3 and Li_2ZrO_3 have been synthesized by different methods such as sol–gel, precipitation, extrusion–spheronisation

process, and solid state reaction [9–12]. However, these reactions are complicated, they require of multi-step reaction routes and/or long processes. Recently, the combustion method has been developed as a new kind of synthesis for the preparation of ceramics. This method is based on the principle of explosive decomposition of nitrate reagents and fuel mixtures, using the instantaneous heat generated by the chemical reaction between the fuel and nitrates to convert the metal ions into the target ceramic material [13–17].

In a previous paper, Chick et al. [17] found out that the fuel in the combustion method (glycine, urea and alanine among others) produces two different effects: First, it produces complexes with metal cations, which increases their solubility and prevent selective precipitation when water is evaporated; and second, it serves as fuel for the combustion reaction.

In order to study further the role of the oxidizers, we were interested on modifying the combustion method to apply it to a rather single system, utilizing non-oxidizer compounds. If we would like to apply the conventional combustion method to prepare lithium titanates or lithium zirconates, we must use titanium or zirconium nitrate compounds. However, the purpose of

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the present paper is to study a “modified” combustion method using lithium hydroxide and metal oxides (ZrO_2 and TiO_2), instead of the metal nitrates. Specifically, the aim of the present paper was to study if the presence of a fuel is essential, or insoluble metal oxides (TiO_2 and ZrO_2) can substitute the metal nitrates to produce Li_2TiO_3 and Li_2ZrO_3 by the combustion method, previously reported for other ceramics [18].

2. Experimental procedure

The combustion syntheses of Li_2TiO_3 and Li_2ZrO_3 were performed using MO_2 ($M = \text{Ti}$ or Zr) and LiOH as precursors, while urea ($\text{CO}(\text{NH}_2)_2$) was used as fuel. The $\text{Li} : M : \text{urea}$ molar ratios, in the precursor mixtures, were 2 : 1 : 3, 2.5 : 1 : 3, 2.75 : 1 : 3 and 3 : 1 : 3. For comparison reasons, some experiments were performed without urea. The resultant powders were heat-treated at different temperatures between 550 and 1300 °C, for 5 minutes [18]. Finally, a set of samples were heat-treated at different times, from 1–30 minutes under the same temperature conditions. Samples are referred in this paper as their $\text{Li} : M : \text{urea}$ molar ratios. For example, sample 2 : Ti : 3 is the name given to the sample prepared with lithium hydroxide, titanium oxide and urea with the corresponding $\text{Li} : \text{Ti} : \text{urea}$ molar ratio of 2 : 1 : 3. The crystalline phases present in the different powders were determined using X-ray diffraction (XRD). A diffractometer Siemens D-5000, coupled to a copper-anode X-ray tube, was used. The relative percentages, of the different compounds present in the samples, were estimated from the total area under the most intense diffraction peak for each phase identified [19–21]. On the other hand, the particle size and morphology of these powders were analyzed by scanning electron microscopy (SEM). In this case, samples were covered with gold to overcome their lack of electrical conductivity and then studied in a Phillips microscope XL30.

3. Results and discussion

3.1. Synthesis of Li_2TiO_3

XRD patterns of the 2 : Ti : 3 samples heat-treated at different temperatures are shown in Fig. 1. At 550 °C, Li_2TiO_3 (JCPDS 33-0831) and TiO_2 (JCPDS 21-1272) were found. Although Li_2TiO_3 was found in 39%, the main product was TiO_2 (61%). It means that the reaction was not completed under these conditions. In the sample heat-treated at 650 °C, Li_2TiO_3 was the main product (72%), and TiO_2 was not formed. However, 28% of a different lithium titanate phase was detected. The XRD data, of this secondary phase, may correspond to two different compounds which have very similar diffraction patterns between them. The first possibility is to consider the formation of LiTiO_2 , which is not stable at high temperatures, because its Ti valence is +3. Hence, some titanium atoms were reduced from +4 (in TiO_2) to +3 (in LiTiO_2), during the combustion process. This effect might be produced as a consequence of

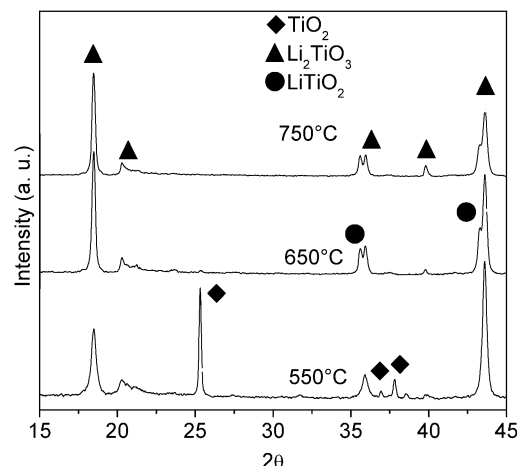
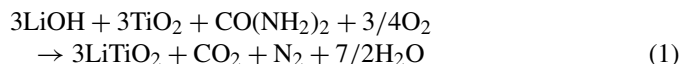
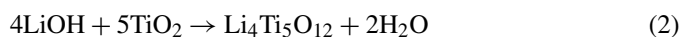


Fig. 1. X-ray diffraction patterns of the 2 : Ti : 3 samples, heat-treated for 5 min at different temperatures.

a reductive environment produced by the urea and the lack of lithium, according to the following reaction.



On the other hand, the second possibility is the formation of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which is a very stable material with a spinel structure. In this case, the titanium is not reduced, and the synthesis is represented in reaction (2). Either LiTiO_2 or $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are lithium poor phases ($\text{Li}/\text{Ti} = 1$ or 0.8, respectively). The presence of any of these materials could be explained by the lithium sublimation during the combustion process because of the high energy produced by the urea combustion.



In order to probe which of the two compounds was produced, the same sample was reheated for 2 h at 800 °C in air. The XRD analysis showed that those peaks, corresponding to the second lithium titanate phase, disappeared (data not shown). This result demonstrated that the second phase present in the samples is LiTiO_2 .

The 2 : Ti : 3 sample heat-treated at 750 °C, showed a similar behavior than that observed for the sample heat-treated at 650 °C. In this case, the composition found out was Li_2TiO_3 (76%) and LiTiO_2 (24%). These results are summarized in Fig. 2a.

A second set of samples, with a higher lithium content ($\text{Li} : \text{Ti} : \text{urea} = 2.5 : 1 : 3$), were heat-treated under the same conditions that the previous samples, the results obtained are shown in Fig. 2b. The results were very similar to those obtained with the 2 : Ti : 3 molar ratio. Here, Li_2TiO_3 was produced in higher quantities, simply because of the lithium excess. It means that lithium excess from 2 to 2.5 was not enough to compensate the lithium sublimation produced during the combustion.

In 2.75 and 3 : Ti : 3 samples (Fig. 2c and d) heat-treated at 550 °C, presented similar behaviours that the previous samples. Increasing the heat-treatment temperature to 650 °C caused a dramatic change in the composition of the powder. It was observed that the samples were formed by Li_2TiO_3 , LiTiO_2 ,

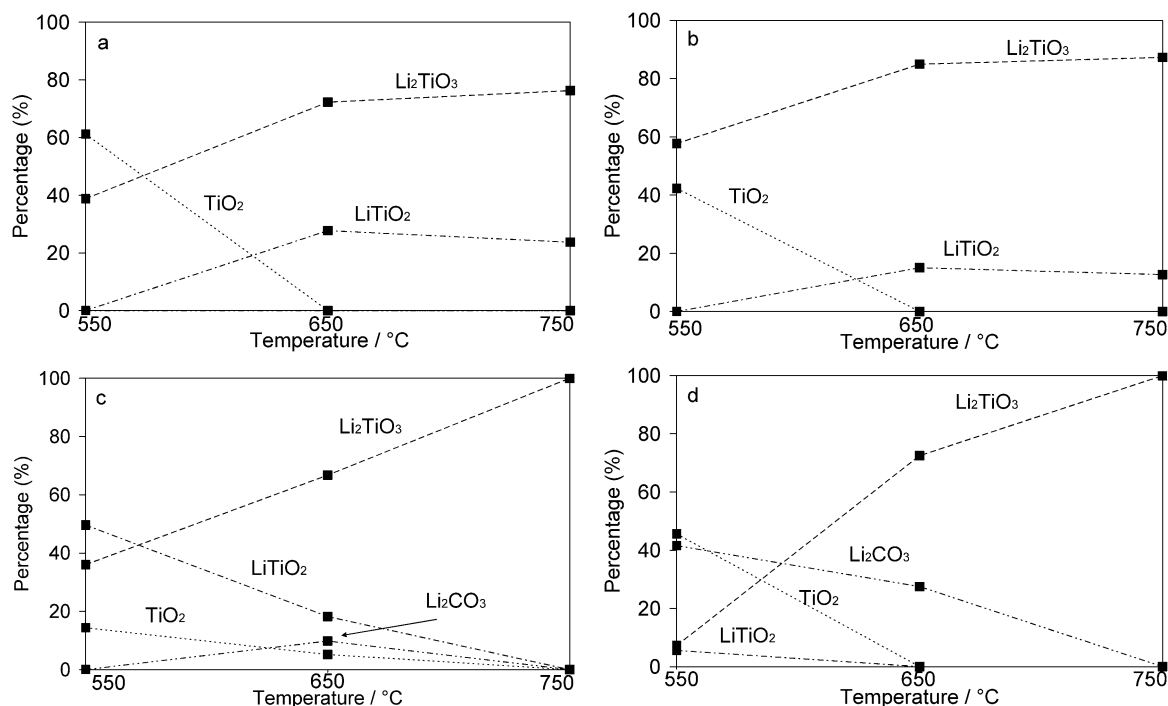


Fig. 2. Curves of the percentages of Li_2TiO_3 , TiO_2 , LiTiO_2 , and Li_2CO_3 as a function of the temperature. The Li : Ti : urea molar ratios are: 2 : 1 : 3 (a), 2.5 : 1 : 3 (b), 2.75 : 1 : 3 (c) and 3 : 1 : 3 (d).

TiO_2 and Li_2CO_3 . The presence of Li_2CO_3 has to be attributed to the lithium excess in the precursor mixture, which induces the CO_2 sorption. It has been reported that some lithium ceramics absorb CO_2 at high temperatures (400–600 °C) producing Li_2CO_3 and the respective metal oxide [21–23]. Finally, in both samples heat-treated at 750 °C TiO_2 declined to zero and Li_2TiO_3 was the only product detected. Hence, the sublimation of lithium was balanced by increasing the lithium amounts from 2.0 to 2.75 or 3. Nevertheless, when the 3 : Ti : 3 sample was left in air-atmosphere, Li_2CO_3 (8%) was produced after sometime. It means, that the lithium excess was higher than that required to balance the quantity of sublimated lithium. Therefore, some lithium must remain in the material without reacting with TiO_2 or sublimating. Later, the excess of lithium reacts with CO_2 of the environment producing Li_2CO_3 .

Once, pure Li_2TiO_3 was obtained, a different set of samples were heat-treated at 750 °C for different times, in order to elucidate the ideal time for the combustion method. The Fig. 3 shows the XRD patterns of the samples heat-treated for 1, 3 and 5 min at 750 °C and another sample, where the combustion was performed without a furnace. In this case, the sample was only left on the hot-plate for 1 hour at 150 °C (Fig. 3a). The products obtained in this sample were Li_2TiO_3 (21%), TiO_2 (63%) and Li_2CO_3 (16%). Evidently, the use of an external thermal energy is needed for the Li_2TiO_3 synthesis, due to the presence of TiO_2 . It was not present if the sample was heat-treated at 750 °C. Furthermore, the presence of Li_2CO_3 indicates that the external thermal energy is required for the total elimination of organic waste material. On the other hand, although TiO_2 was totally eliminated, when the sample was heat-treated for shorter times (1 and 3 min), Li_2CO_3 could not be eliminated (Fig. 3b, c).

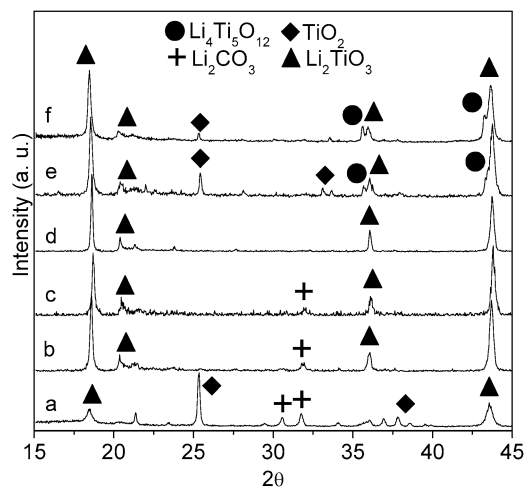


Fig. 3. X-ray diffraction patterns of 3 : Ti : 3 samples heat-treated in (a) air at 150 °C for 1 hour, (b) 750 °C for 1 min, (c) 750 °C for 3 min, (d) 750 °C for 5 min, and samples 3 : Ti : 0 (without urea) heat-treated at (e) 750 °C for 5 min and (f) 750 °C for 30 min.

Finally, in order to compare the combustion method with the solid state method, a mixture of LiOH and TiO_2 with a molar ratio 3 : 1 was treated in the same conditions than that of Li : Ti : urea 3 : 1 : 3 molar ratio for 5 and 30 min. These results are shown in Fig. 3e and f. The XRD patterns show, that both methods produce Li_2TiO_3 . However, the solid-state reaction did not produce pure Li_2TiO_3 , as the combustion method did. In these cases 21 and 10% of TiO_2 were found after 5 and 30 min, respectively. Moreover, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was found as a minor compound, which means that the reaction was not completed. Therefore, the heat produced by the instantaneous combustion of urea must be the principal heat source for the Li_2TiO_3 production.

All the samples were studied by SEM. As expected, the samples presented similar morphology and particle sizes. The particles ranged between 0.5 and 1 μm , and their shape was polygonal (data not shown). The particles were agglomerated, producing a relatively dense material. Jung et al. [13] prepared this material using the conventional combustion method. They got bigger and denser particles by the precipitation of the ceramic and in some cases were contaminated with nitrates. The differences in the morphology and composition of their materials and those obtained in the present work, can be explained by the use of different Ti reagents, TiO_2 ($\approx 1 \mu\text{m}$ of diameter) in this work. Hence, the reaction may be controlled by the lithium incorporation on the TiO_2 particles to produce Li_2TiO_3 , and therefore, the particle size of Li_2TiO_3 was similar to the particle size of TiO_2 .

3.2. Synthesis of Li_2ZrO_3

Fig. 4 shows the XRD pattern of the 3 : Zr : 3 sample synthesized by the combustion method at the same temperature that pure Li_2TiO_3 was produced (750°C). Under these conditions, two different phases of lithium zirconate were identified, m- Li_2ZrO_3 (monoclinic structure, JCPDS 33-843) and t- Li_2ZrO_3 (tetragonal structure, JCPDS 41-324). However, none of the two different zirconates, m- Li_2ZrO_3 (9%) or t- Li_2ZrO_3 (25%) were produced as the main product, ZrO_2 (42%) was the main product and Li_2CO_3 was also found (13%). Moreover, amorphous material was found in 11% as well. Montanaro among others [10,21] have reported that Li_2ZrO_3 converts from tetragonal to monoclinic between 700 and 900°C . All these information indicates that the Li_2ZrO_3 reaction was not completed at 750°C , as Li_2TiO_3 did. The differences, in both syntheses, would be associated to thermodynamical and/or kinetic data. Actually, the formation enthalpy (ΔH°) of Li_2ZrO_3 is $-1762.3 \text{ kJ mol}^{-1}$ while the ΔH° of Li_2TiO_3 is $-1671.7 \text{ kJ mol}^{-1}$ [24]. As the ΔH° of Li_2TiO_3 is 90.6 kJ mol^{-1} lower than that of Li_2ZrO_3 , is evident that Li_2ZrO_3 needs more energy to be produced.

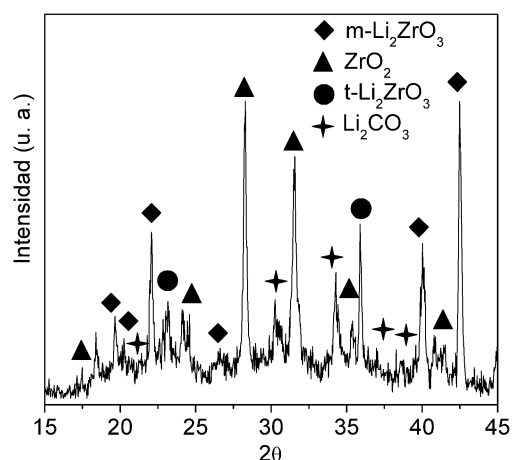


Fig. 4. X-ray diffraction pattern of the 3 : Zr : 3 sample, heat-treated for 5 min at 750°C .

The Li_2ZrO_3 samples were heat-treated at higher temperatures, 900, 1100 and 1300°C , and the results are shown in Fig. 5. The 2 : Zr : 3 sample, heat-treated at 900°C shows that the products were m- Li_2ZrO_3 (61%), t- Li_2ZrO_3 (15%) and ZrO_2 (24%). Hence, the reaction was neither completed. In the sample heat-treated at 1100°C , t- Li_2ZrO_3 was not observed anymore. However, a reduction of m- Li_2ZrO_3 was observed and ZrO_2 increased. Wyers among others [25,26] have reported that m- Li_2ZrO_3 is stable between 800 and 1500°C . However, other studies have demonstrated that m- Li_2ZrO_3 starts to decompose at 900°C , due to lithium sublimation [21]. Therefore, the increment of ZrO_2 composition at 1100°C must be attributed to the lithium sublimation. Finally, at 1300°C the sample showed a similar behavior than that at 1100°C .

The results obtained for 2.5 : Zr : 3 samples are shown in Fig. 5b, as in the previous sample (2 : Zr : 3) the reaction was

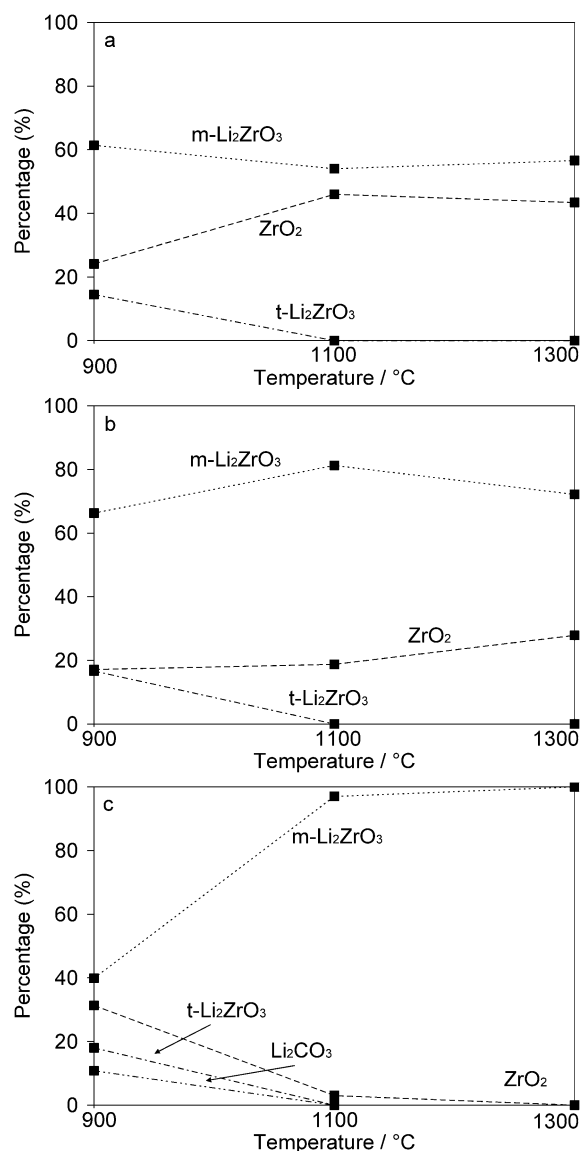


Fig. 5. Curves of the percentages of m- Li_2ZrO_3 , t- Li_2ZrO_3 , ZrO_2 , and Li_2CO_3 as a function of the temperature. The Li : Zr : urea molar ratios are: 2 : 1 : 3 (a), 2.5 : 1 : 3 (b), and 3 : 1 : 3 (c).

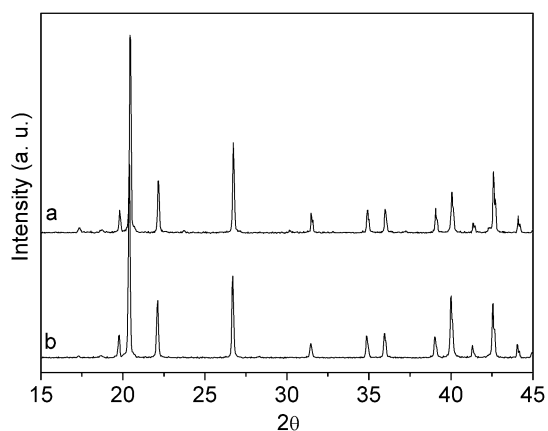


Fig. 6. X-ray diffraction patterns of the 3 : Zr : 3 sample, heat-treated for 5 min at 1300 °C (a) and without urea at the same conditions (b).

not completed at 900 °C. In sample heat-treated at 1100 °C the amount of *m*-Li₂ZrO₃ increased up to 81%, *t*-Li₂ZrO₃ disappeared from the X-ray diffractogram, and ZrO₂ was present in 19%. The final amounts of *m*-Li₂ZrO₃ and ZrO₂ in sample heat-treated at 1300 °C were 72 and 28%. Hence, lithium excess (from 2 to 2.5) was not enough to prevent the lithium sublimation produced during the combustion.

In 3 : Zr : 3 sample heat-treated at 900 °C, the compounds found were *m*-Li₂ZrO₃ (40%), *t*-Li₂ZrO₃ (18%), ZrO₂ (31%) and Li₂CO₃ (11%). In this sample the formation of Li₂CO₃ should be attributed merely to the CO₂ sorption process, as in the titanate cases. The amount of *m*-Li₂ZrO₃ was increased to 97% and the ZrO₂ quantities were decreased to 3% at 1100 °C; *t*-Li₂ZrO₃ and Li₂CO₃ were no longer observed. At 1300 °C the only product found was *m*-Li₂ZrO₃ (Fig. 5c). In addition, a sample of LiOH and ZrO₂ with a 3 : 1 molar ratio, and without urea, was prepared by solid-state method, heating the mixture at 1300 °C for 5 minutes. Fig. 6 shows that in this case there was not any difference between the two methods. *m*-Li₂ZrO₃ was obtained as the only product. Hence at this temperature (1300 °C) the *m*-Li₂ZrO₃ synthesis is produced mainly by the furnace heat and not by the urea combustion. As in the titanium case, the particle size and morphology of the final lithium ceramic depends on the ZrO₂ particle size (≈ 6–10 μm). In this case, the Li₂ZrO₃ presented an average particle size of 9 μm. Thus, the reaction between LiOH and ZrO₂ by the combustion method depends on the lithium incorporation, diffusion and reaction into the ZrO₂ particles, as it happened in the titanium case. Consequently, both reactions may follow the same mechanism.

The reaction model proposed is shown in Fig. 7. First, LiOH, MO₂ (*M* = Ti or Zr) and urea are mixed in water. LiOH and urea are dissolved, while MO₂ is only suspended (Fig. 7A). Then, when the solution is dried at 70 °C the lithium species and urea enclose the MO₂ particles (Fig. 7B). Second, in the combustion process, the lithium atoms diffuse into the MO₂ particles and start reacting with it. Simultaneously, urea decomposes. This phenomenon produces Li₂MO₃, H₂O, CO₂, N₂ and energy because of the urea instantaneous combustion (Figs. 7C and D). Finally, the reaction is completed during the period

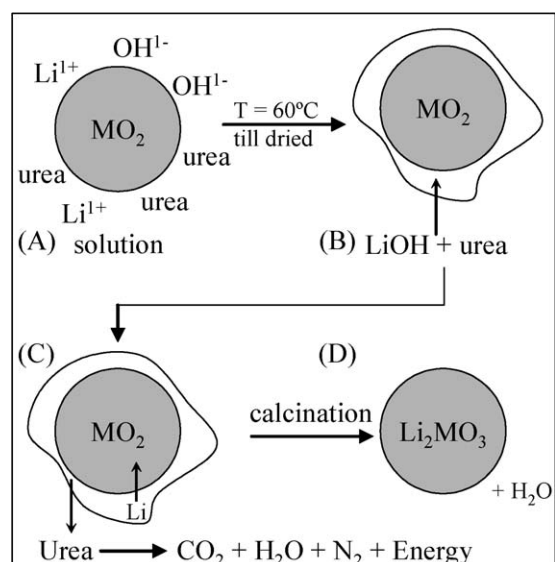


Fig. 7. A reaction model for the Li₂MO₃ (*M* = Ti, Zr) formation, using the combustion method.

that the samples are left at the different temperatures during 5 minutes.

4. Conclusions

The combustion method was used for the production of lithium ceramics, using insoluble compounds as precursors (MO₂ where *M* = Ti or Zr) to prepare Li₂TiO₃ and *m*-Li₂ZrO₃. Li₂TiO₃ was produced by this method by heating the precursors at 750 °C during heating periods as short as 1 minute. However, to prepare *m*-Li₂ZrO₃ it was necessary to increase the temperature up to 1300 °C. In both cases, it was necessary to add lithium in excess, in order to balance the lithium sublimation produced by the high temperatures reached during the urea combustion. On the other hand, in some cases, lithium excess produced the formation of Li₂CO₃. Finally, in the Li₂TiO₃ synthesis, at low temperatures the urea produces a reductive effect on Ti, forming LiTiO₂.

The differences observed in the synthesis of Li₂TiO₃ and *m*-Li₂ZrO₃ were attributed to thermodynamic parameters. Furthermore, the urea combustion showed to be an important inductor factor for the Li₂TiO₃ synthesis. Nevertheless as the Li₂ZrO₃ synthesis has to be performed at 1300 °C, the urea combustion was useless at this temperature.

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