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Trans. Nonferrous Met. Soc. China 28(2018) 1793−1800

Transactions of
Nonferrous Metals
Society of China

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Modified combustion synthesis of γ-$LiAlO_2$ using metal oxides

Daniel CRUZ[1], H. B. ORTIZ-OLIVEROS[2], L. M. PÉREZ-DÍAZ[1],
R. M. FLORES-ESPINOSA[2], G. ROSANO-ORTEGA[3]

1. Facultad de Ingeniería Química, Benemérita Universidad Autónoma de Puebla,
14 Sur y San Claudio, Ciudad Universitaria, C.P. 72570, Cd. Puebla, México;
2. Instituto Nacional de Investigaciones Nucleares, Dirección de Investigación Tecnológica,
Apartado Postal 18-1027, 11801 México, DF, México;
3. Universidad Popular Autónoma del Estado de Puebla, 21 Sur no. 1103, Colonia Santiago, C.P. 72410, Puebla, México

Received 2 November 2017; accepted 10 May 2018

Abstract: An alternative solution for the direct formation of γ-$LiAlO_2$ was presented by a modified combustion method, to apply it to rather simple systems, utilizing non-oxidizer compounds such as Al_2O_3 and LiOH, and urea as fuel. $LiAlO_2$ was prepared via non-stoichiometric 1:1, 1.5:1 and 2:1 of Li/Al molar ratios at 900 and 1000 °C for 5 min. Textural and structural characterization of γ-$LiAlO_2$ was performed. Also, the effect of different Li/Al molar ratios on material morphology and its stability before high gamma radiation gradients was evaluated. The results showed that the crystal structures of the obtained powders were γ-$LiAlO_2$ and α-$LiAlO_2$, depending on the Li/Al molar ratio. The results obtained demonstrate that γ-$LiAlO_2$ microbricks, polyhedral and laminar shapes can be successfully synthesized with the proposed method and without any subsequent process. Additionally, gamma irradiation showed that the γ-$LiAlO_2$ obtained does not decompose, forming only small amounts of Li_2CO_3. It can be established that the irradiation produces consolidation, which is not favourable for an efficient extraction of tritium. Finally, it could be demonstrated that nitrate precursors are not necessary in the combustion method to produce γ-$LiAlO_2$ with high purity.

Key words: urea; oxide; combustion; lithium aluminate; ceramic

1 Introduction

It is well documented that economic development and consumption of energy resources in the last 200 years have caused the deterioration of environment, as evidenced by phenomena such as the degradation of water resources, deforestation, loss of biodiversity and global warming due to the emission of greenhouse gases [1,2]. Global warming is an alarming symptom that shows the unsustainability of the form of energy production and consumption [3−5]. Total energy consumption at the end of 2014 was 12.928 million tons of oil equivalent barrels [6]. According to the International Energy Agency, in the same year around 32190 million tons of CO_2 were emitted [7].

In this context, nuclear energy has a fundamental role to meet the growing energy demand, as it is considered by many countries as an energy base of operation, contributing to the reduction of greenhouse gases [5,8].

Currently nuclear energy production was carried out by nuclear fission, having the disadvantage of generating a significant amount of radioactive waste. Projects with the International Thermonuclear Experimental Reactor, work on the development of nuclear fusion reactors, as well as large-scale and carbon-free source [9,10]. Fission reactors use lithium ceramics such as tritium breeders. A variety of breeding blanket concepts have been considered, ranging from more conservative concepts to higher-risk higher-payoff concepts for future fusion reactors. The major candidates for breeding materials consist of liquid breeders, mainly liquid metals although recently some attention has been given to FLiBe, and lithium ceramic breeders. Candidate breeder materials are mainly lithium oxide (Li_2O), lithium orthosilicate (Li_4SiO_4), lithium metatitanate (Li_2TiO_3), lithium metazirconate (Li_2ZrO_3) and lithium aluminate ($LiAlO_2$) [11−13]. $LiAlO_2$ is one of the most promising ceramics for excellent chemical, structural and mechanical stability against intense fields of thermal and gamma radiation, as well as mixed fields (gamma-neutron) [14].

Corresponding author: H. B. ORTIZ-OLIVEROS; Tel: +52-5553297200-13460; E-mail: huemantzin.ortiz@inin.gob.mx

DOI: 10.1016/S1003-6326(18)64823-X

Additionally, it is used in polymeric composites, matrix of molten carbonate fuel cells (MCFC), electrolyte tiles in MCFC, among other applications such as electrical pumped ultraviolet-blue, light emitting diodes, laser, biosensors and photon detectors, due to its thermal conductivity [15−18].

The lithium aluminate crystal structure exhibits four allotropic forms depending on thermodynamic states and chemical environmental conditions, namely, α-$LiAlO_2$ (hexagonal), β-$LiAlO_2$ (orthorhombic), γ-$LiAlO_2$ (tetragonal) and δ-$LiAlO_2$ (tetragonal) [11,19]. Among all polymorph modifications of $LiAlO_2$, γ-$LiAlO_2$ is the most stable one, so that at elevated temperature (above 750 °C, and present lattice parameters a=(5.1687± 0.0005) Å and c=(6.2679±0.0006) Å [18].

The γ-$LiAlO_2$ has been obtained by several conventional powder synthesis techniques, including solid-state synthesis, co-precipitation and sol−gel process [20−23]. Although these methods have advantages, elevated temperatures and long heat treatment time are required to ensure the formation of pure γ-$LiAlO_2$. The situation is even more complicated due to many sophisticated techniques and time-consuming procedures that are required, which are not cost effective and represent obstacles to reproducibility and reliability of the final powder [15,24−26].

Combustion synthesis is an innovative and promising powder preparation method, it is a very rapid chemical process based on the principle of explosive decomposition of nitrate reagents and fuel mixtures, using the instantaneous heat generated by the chemical reaction between the desired metal nitrates (the oxidizing agent) and a reducing agent, which is called as the fuel [27−30]. The advantages of this method have been demonstrated as it needs little heating to start a rapid reaction and it permits considerable savings of time and energy compared with other techniques [31,32]. The fuel (glycine, urea, alanine, carbohidrazide) produces two different effects: first, it produces complexes with metal cations, which increases their solubility and prevents selective precipitation when water is evaporated; and second, it serves as fuel for the combustion reaction [33−36]. It was proved that combustion synthesis allowed the direct formation of the desired oxide compound with and without any subsequent calcination. For instance, starting from a stoichiometric mixture of lithium nitrate/aluminium as starting materials and urea/carbohidrazide as fuels, IANOS et al [29] and LI et al [33] reported the formation of pure γ-$LiAlO_2$ by the combustion synthesis only after thermal treatment at 900 and at 450 °C, respectively.

In this work, the aim is to present an alternative solution for the direct formation of γ-$LiAlO_2$ by a modified combustion method, to apply it to rather simple systems, utilizing non-oxidizers compounds such as aluminium oxide (Al_2O_3), lithium hydroxide (LiOH) and, urea as fuel.

2 Experimental

2.1 Synthesis of γ-$LiAlO_2$

γ-$LiAlO_2$ powder was prepared, as starting materials, analytical grade reagents without further purification: aluminium oxide (Al_2O_3 powder, J. T. Baker, 99.0%), lithium hydroxide (LiOH powder, Merck, 98.0%) and urea (CH_4N_2O powder, Merck, 99.5%). The required mass of each reactant was calculated from the desired mass of the products, according to the chemical reactions. In this work, the main parameters studied were: lithium hydroxide molar ratio and calcination temperature (900−1000 °C). Different molar ratios of LiOH to Al_2O_3 (1:1, 1.5:1 and 2:1) were prepared and were placed in distilled water with urea at a molar ratio of 3:1 [37,38]. The mixture was dried at 60 °C until most of the water was evaporated resulting in a humid integrated solid; this mixture was transferred into 30 mL crucible which was introduced during 5 min into a High Temperature Muffle Furnace Barnstead Thermolyne Corporation at different heat treatment temperatures (900−1000 °C).

Samples were referred in this work as their $LiOH:Al_2O_3:CH_4N_2O$ molar ratios. For example, sample (1:1:3) is the name given to the sample prepared with lithium hydroxide, aluminium oxide and urea with the corresponding $LiOH:Al_2O_3:CH_4N_2O$ molar ratio of 1:1:3 at the study temperatures (900 °C or 1000 °C).

2.2 Textural and structural characterization of γ-$LiAlO_2$

Powder XRD patterns were recorded on a Siemens D−5000 diffractometer using Cu $K_{\alpha 1}$ radiation. The relative percentages of the various compounds present in the pellets were estimated semi-quantitatively from the total area under the most intense diffraction peak for each phase identified, with the simplifying assumption this was proportional to the volume fraction of each compound. In this way, the amounts of the crystalline compounds present in the samples were obtained within an estimated experimental error of 5% [39,40].

Since no internal standard was introduced, the X-ray absorption for each compound was assumed to be the same. Standard deviations of the measured samples were around 3.0%. A Philips XL−30 scanning electron microscopy (SEM), equipped with an energy dispersive X-ray spectroscopy (EDS) detector was used to study morphology of the samples. Powders were covered with gold to prevent the lack of conductivity. The thermogravimetric analyses (TGA) were performed with a heating rate of 10 °C/min up to 800 °C, flowing N_2 (TGA 51, Thermogravimetric Analyzer, T.A. Instruments) to determine the mass loss at high temperatures.

2.3 Gamma irradiation of γ-$LiAlO_2$

The gamma irradiation of γ-$LiAlO_2$ synthesized by the proposed method was performed in order to determine structural changes due to gamma radiation. Exposure to gamma radiation was performed in an industrial irradiator JS−6500 equipped with a ^{60}Co source of 28971.56 TBq (1 July 2016). The solid was placed in aluminium containers (in duplicate) and subjected to a dose of 12000 kGy, applying a calculated dose rate of 14.09 kGy/h (8 September 2016).

3 Results and discussion

3.1 Synthesis and structural characterization of γ-$LiAlO_2$

Synthesis of lithium aluminate ceramics by a modified combustion method was investigated using insoluble metal oxide. Most samples obtained utilizing different $LiOH$:Al_2O_3:CH_4N_2O molar ratios and different heating temperatures were white opaque powders.

Figure 1 compares the diffraction patterns of samples with $n(LiOH)$:$n(Al_2O_3)$:$n(CH_4N_2O)$=1:1:3, 1.5:1:3, 2:1:3 heat treated in a muffle furnace at 900 and 1000 °C. It was found in sample $(1:1:3)_{900}$ that γ-$LiAlO_2$ is a main compound (72%), but α-$LiAlO_2$ and Al_2O_3 were also present (14% in both samples) showing that the reaction was not completed under these working conditions (Fig. 1(a) and Fig. 2(a)). Although $LiAlO_2$ exists in three forms, only α and γ phases were observed, it can be explained due to that β phase form only exists at high pressures [41].

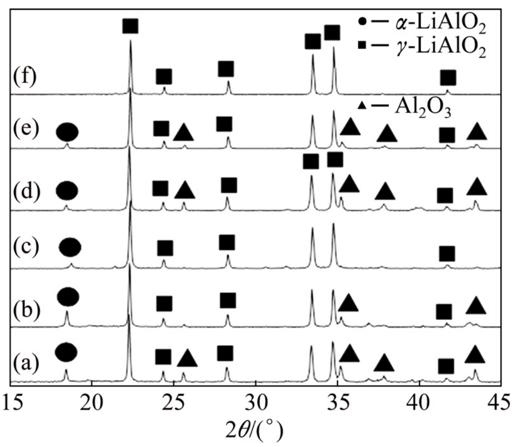

Fig. 1 XRD patterns of samples prepared by modified combustion method: (a) $(1:1:3)_{900}$; (b) $(1.5:1:3)_{900}$; (c) $(2:1:3)_{900}$; (d) $(1:1:3)_{1000}$; (e) $(1.5:1:3)_{1000}$; (f) $(2:1:3)_{1000}$

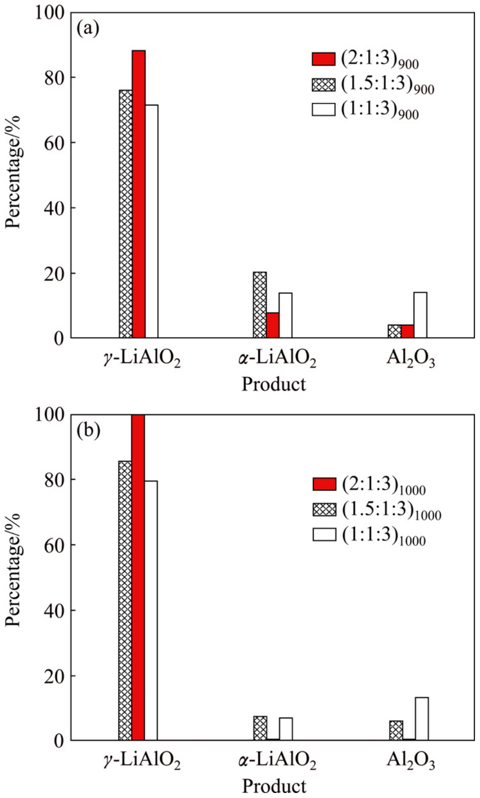

Fig. 2 Percentage of products obtained by modified combustion method as function of temperature and lithium concentration according to XRD: (a) 900 °C; (b) 1000 °C

In this work, the synthesis of $LiAlO_2$ was carried out to atmospheric pressure. The low-temperature α tetragonal structure transforms to the high-temperature γ structure irreversibly by sintering the α phase at 1350 °C [40,42]; however, in this work samples were heated in the presence of urea (fuel) at 900 °C. Although combustion temperature was not measured directly, we can predict that the combustion of the urea reached a temperature of at least 1200 °C, to carry out the transformation of α tetragonal structure to γ structure of high-temperature. In the present work, the maximum combustion temperature during reaction was inferred due to the fact that:

1) The Li_2O−Al_2O_3 phase diagram reported by NAKAGAWA et al [43] allows us to predict that the combustion of the urea reached a temperature of at least 1200 °C, to carry out the transformation of α tetragonal structure to γ structure of high-temperature.

2) CHICK et al [34] have reported that fuel combustion can be achieved at one peak flame temperature of about 1450 °C. Then, following reactions will occur:

$$\begin{aligned}&LiOH+Al_2O_3+CH_4N_2O \xrightarrow{\Delta} \alpha\text{-}LiAlO_2 \xrightarrow{\Delta}\\&\quad \gamma\text{-}LiAlO_2+H_2O+CO_2+N_2\end{aligned} \tag{1}$$

Heat due to combustion urea:

$$\alpha\text{-}LiAlO_2+CO_2 \longrightarrow Li_2CO_3+Al_2O_3 \tag{2}$$

$$LiOH+CO_2 \longrightarrow Li_2CO_3+H_2O \tag{3}$$

3) Finally, ZU et al [44] have reported that the combustion process can be divided into three stages: a slowly heating zone (Stage I), a rapidly reaction zone (Stage II), and a cooling zone (Stage III). In Stage I, the oxidation reaction is essentially absent at the beginning due to the low temperature. As the sample is heated, the temperature continues to increase (about 1397 °C). The obtained high heating rate indicates that the combustion reaction is violent with a large amount of heat released.

The presence of Al_2O_3 can be attributed to incomplete reaction with LiOH, probably due to Li sublimation at 900 °C [40,41]. Although the XRD analyses did not show the presence of Li_2CO_3, the thermal analyses demonstrated that materials contained some minor impurities. Note that the lower limit detection by XRD technique depends on the scattering properties of the components of the materials.

In order to obtain γ-$LiAlO_2$, LiOH molar ratio was increased to 1.5, to compensate Li_2O sublimation (Fig. 1(b)). Under these conditions in sample $(1.5{:}1{:}3)_{900}$, it was observed that Al_2O_3 decreased from 14% to 4% probably because it was able to react with the LiOH in excess. The main product found was γ-$LiAlO_2$ (76%); however, α-$LiAlO_2$ increased up to 20% (Fig. 2(a)). High concentration Li reacts with Al_2O_3 to produce α-$LiAlO_2$ first, and subsequently, due to the combustion of urea, it produces γ-$LiAlO_2$ (Reaction 1). BECKERMAN et al [45] reported that γ-$LiAlO_2$ is produced by α-$LiAlO_2$ at temperatures between 650 and 1350 °C. In order to obtain pure γ-$LiAlO_2$, LiOH molar ratio was increased from 1.5 to 2. Figure 1(c) shows that γ-$LiAlO_2$ increased considerably (88%) and α-$LiAlO_2$ decreased (8%); however, Al_2O_3 was still present (4%), probably due to decomposition of α-$LiAlO_2$ to Al_2O_3 according to reaction 2. It is well known that α and β phases of $LiAlO_2$ are unstable at high temperatures and are transformed into γ-$LiAlO_2$ when heat treated at temperatures of 650−1350 °C for 4 h [45]. Therefore, in order to eliminate the α-phase, samples were heat treated at 1000 °C.

Increase of the muffle furnace temperature to 1000 °C caused a considerable change in the percentage of the powders. Figures 1(d), (e) and (f) compare the diffraction patterns of samples with mole ratios of 1:1:3, 1.5:1:3 and 2:1:3 heat treated at 1000 °C. γ-$LiAlO_2$ (Fig. 1(d)) was found as main compound (80%) in sample $(1{:}1{:}3)_{1000}$, but α-$LiAlO_2$ and Al_2O_3 were also present (7% and 13% respectively, Fig. 2(b)) showing that the reaction is not completed under these working conditions. As at 1000 °C Li_2O sublimates in high proportion, LiOH molar ratio was increased to 1.5 to compensate Li_2O sublimation. Under these conditions Al_2O_3 was present in 6% (Fig. 1(e) and Fig. 2(b)). The main product found was γ-$LiAlO_2$ (86%), and α-$LiAlO_2$ was still present in the sample (8%). By increasing the LiOH molar ratio to 2 (Fig. 1(f)), the only product obtained was γ-$LiAlO_2$ (100%) showing that molar ratio $(2{:}1{:}3)_{1000}$ was the best condition to obtain pure γ-$LiAlO_2$ (Fig. 2(b)). Although Li_2CO_3 was not observed in XRD, TG analysis showed a mass loss attributed to carbonates present in the sample. Comparing the products obtained by the modified combustion method and the conventional combustion method [33], it was found that the conventional combustion method produces nitrogen contaminants. While in this work, due to the use of metal oxide instead metal nitrate, it was not observed contamination due to nitrate compounds. LI et al [33] have reported that γ-$LiAlO_2$ could be synthesized using lithium nitrate/aluminium nitrate as starting materials and urea as fuel by the combustion process. In this study, the pure γ-$LiAlO_2$ could be easily synthesized using lithium oxide/aluminium oxide and urea as fuel by the similar combustion process.

Representative scanning electron microscope (SEM) images of the reaction products are shown in Fig. 3 (1:1:3, 1.5:1:3 and 2:1:3 samples heat-treated at 900 °C). As shown in Fig. 3(a), the product obtained by the modified combustion method with $(1{:}1{:}3)_{900}$ molar ratio clearly reveals a brick-like morphology with one cross-section rectangular; hence they could be called "microbricks". Length of microbricks was 2−3.5 μm. In this case, growth of bricks is not template-directed, or surfactant assisted, because no additional template or surfactants were introduced into the reaction. X-ray diffraction patterns in Fig. 1(a) showed that microbricks are composed mainly of crystalline tetragonal γ-$LiAlO_2$ structures. Previous work reported the synthesis of Li_2TiO_3 by the modified combustion method, where reaction between LiOH and TiO_2 depends on the lithium incorporation, diffusion and reaction into the TiO_2 particles, in the present work, reaction between lithium and Al_2O_3 should be taking a similar mechanism as in the case of titanium [46]. Increasing LiOH concentration from 1 to 1.5 (Fig. 3(b)), polygonal particles were observed between 0.4 and 4.5 μm and agglomerates of about 5 μm. Finally, $(2{:}1{:}3)_{900}$ sample (Fig. 3(c)) showed smaller particles of about 0.5−2 μm with laminar shapes ranging between which form considerably bigger agglomerates than the previous ones, of about 25 μm. The formation of the different structures can be attributed to the lithium volatilization during the calcination process. Due to easy volatilization of Li element, the excess Li element existing in the powder easily migrates to the surface of particles and turns into liquid phase. The local existence of liquid phase is conducive to the formation of new $LiAlO_2$ particles at the site and also encourages the formation of networks between the particles [47,48].

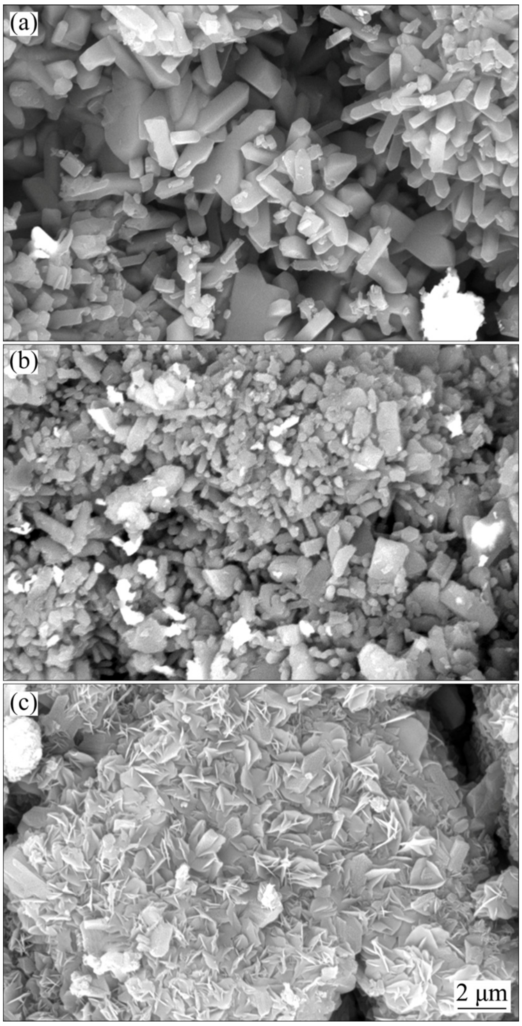

Fig. 3 SEM images of $LiAlO_2$ synthesized at 900 °C with different molar ratios: (a) 1:1:3; (b) 1.5:1:3; (c) 2:1:3

Figure 4 shows micrographs of 1:1:3, 1.5:1:3 and 2:1:3 samples heat-treated at 1000 °C. The morphology is denser than that discussed previously, mainly due to the sinterization effect produced by the high temperature. The particle size in sample $(1:1:3)_{1000}$, ranges between 0.4 and 2 μm (Fig. 4(a)), with agglomerates of about 5 μm. $(1.5:1:3)_{1000}$ sample (Fig. 4(b)) shows particles between 0.4 and 4.1 μm. Finally, $(2:1:3)_{1000}$ sample (Fig. 4(c)) shows particles between 1 and 2 μm with a laminar shape and agglomerates considerably bigger ones (about 20 μm). Therefore, the morphology of the resulting γ-$LiAlO_2$ crystals also seems to depend upon the lithium concentration and temperature. It is well known that one of the major parameters that determine the phase formation of the ceramics is the Li/metal molar ratio and temperature [25,46]. In this study, the effects of Li/metal molar ratio and temperature on the characteristics of the synthesized powder were investigated in a precursor solution consisting of urea as a fuel and a mixed oxide of lithium and aluminium. Finally, morphology has been reported which affected product parameters such as surface reaction on the grain, diffusion through pores of sintered particles and diffusion through the boundary layer formed on the particle surface must be considered, and therefore tritium production can be altered [49].

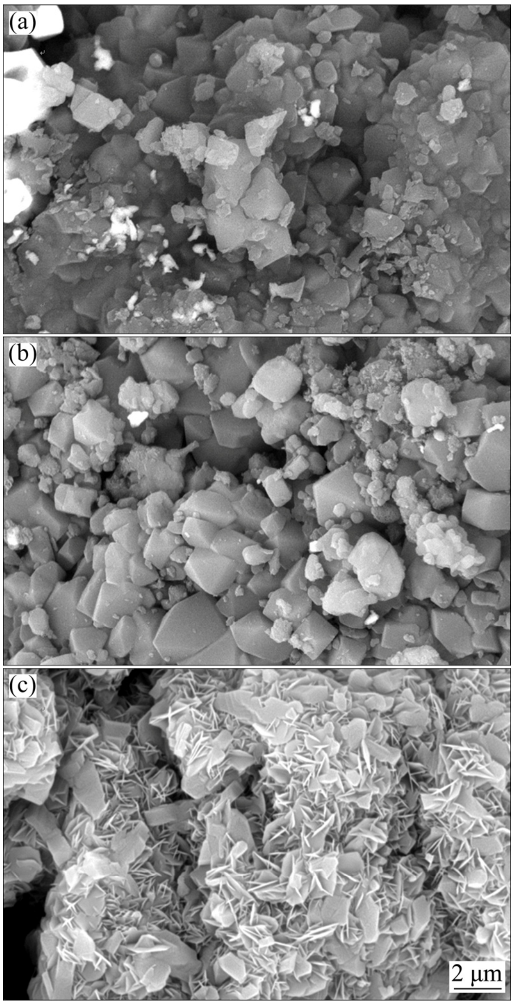

Fig. 4 SEM images of $LiAlO_2$ synthesized at 1000 °C with different molar ratios: (a) 1:1:3; (b) 1.5:1:3; (c) 2:1:3

Figure 5 shows the thermogravimetric curves of samples with molar ratios $(1:1:3)_{900}$ and $(1.5:1:3)_{900}$ (Figs. 5(a) and (b)), no significant mass loss was observed (<1%). The mass loss observed throughout the analysis can be attributed to the evaporation of Li element due to its low melting temperature [48].

Samples $(2:1:3)_{900}$ and $(2:1:3)_{1000}$, presented total mass loss of about 10% (Fig. 5(c)). The first mass loss of about 3%, in both samples, occurs at 25−250 °C. This process is associated to the dehydration of the samples, which were hydrated after the combustion during the cooling by two processes [14]; one at T<573 K (physic-sorption) and second one at T>573 K (chemisorption). At temperatures between 580 and 650 °C, a mass increase of ~1% could be observed, probably due to one of the

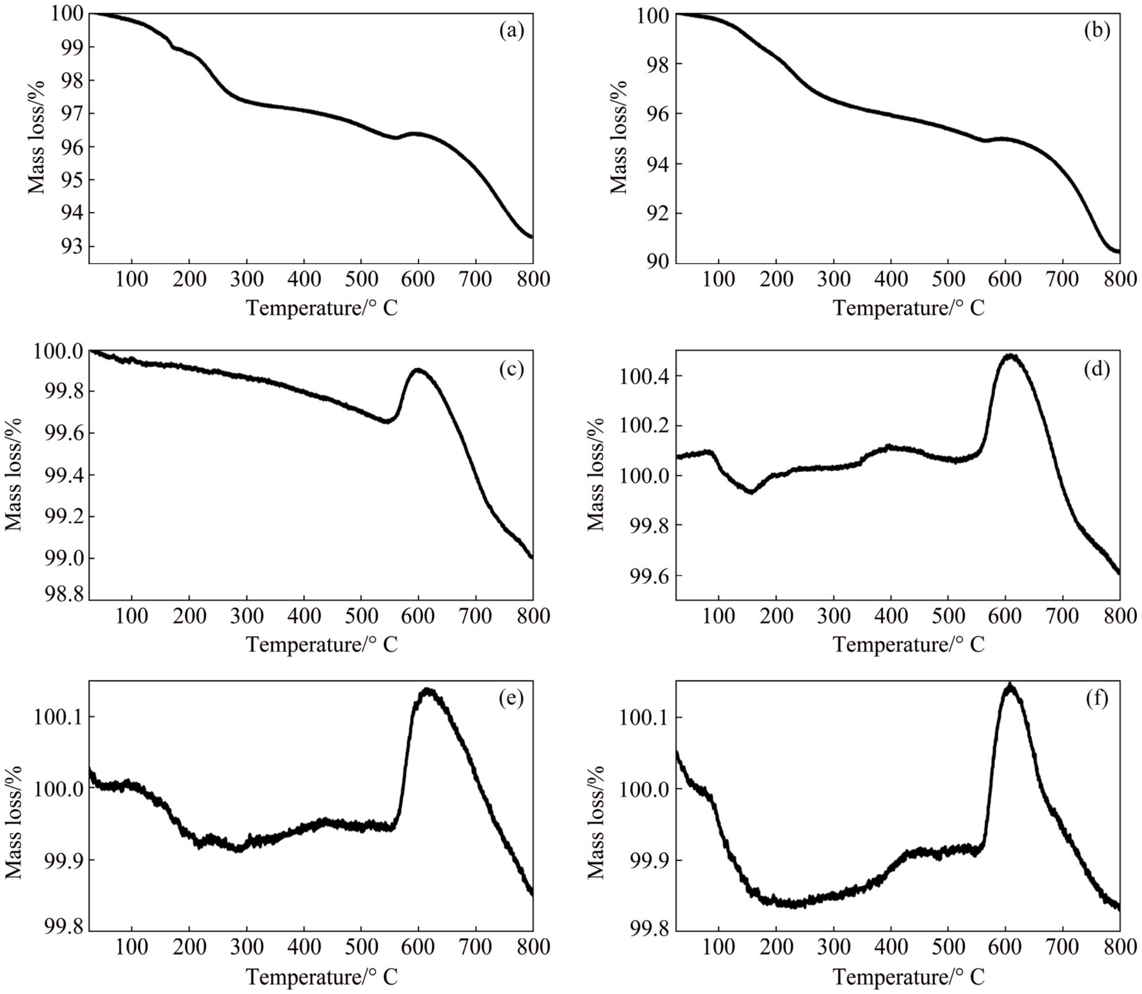

Fig. 5 TGA analyses of samples with different molar ratios prepared by modified combustion method at 900 (a, c, e) and 1000 °C (b, d, f): (a, b) 2:1:3; (c, d) 1.5:1:3; (e, f) 1:1:3

following two processes: 1) chemical reactions with the components of the purge gas, N_2, in the present case, forming non-volatile or less volatile compounds, and 2) physical transformations, as adsorption of gaseous products in the sample. Finally, the second mass loss of about 5%, between 600 and 800 °C, is attributed to decarbonation process. The presence of carbonates in samples can be attributed to capturing process of CO_2 over lithium aluminate [50].

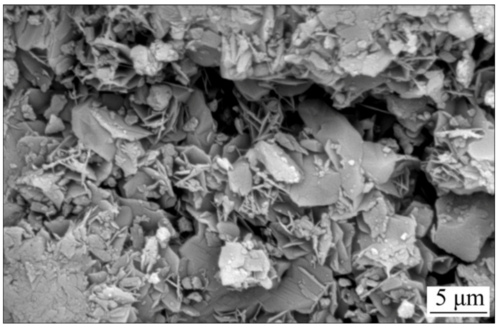

Fig. 6 SEM image of γ-$LiAlO_2$ irradiated at 12000 kGy

3.2 Gamma irradiation of γ-$LiAlO_2$

The results obtained from the gamma irradiation of γ-$LiAlO_2$ showed that the material synthesized changed from white to grey colour as a consequence of gamma dose received. The XRD spectra obtained (not shown) of the γ-$LiAlO_2$ allowed to observe that the γ-$LiAlO_2$ decreases from 97% to 89% with the formation of Al_2O_3 and Li_2CO_3. Li_2CO_3 formation could be explained by the reaction of excess carbon and lithium present in the sample. Figure 6 shows the micrograph of γ-$LiAlO_2$ irradiated. It is observed that the gamma radiation causes changes in the morphology and particle size of the material. The radiation caused the formation of agglomerates of polyhedral particles of a size of approximately 170 μm.

However, γ-$LiAlO_2$ does not decompose, forming only small amounts of Li_2CO_3. It can be established that the irradiation produces consolidation, which is not favourable for an efficient extraction of tritium. The extraction efficiency is increased by decreasing the particle size.

4 Conclusions

1) The present study demonstrates that γ-$LiAlO_2$ microbricks, polyhedral and laminar shapes can be successfully synthesized from Al_2O_3 and LiOH by simple modified combustion method in 5 min without any subsequent process. A critical effect of Li/Al molar ratio and synthesis temperature was clearly demonstrated on the morphology of the products, at 900 °C, $n(\mathrm{Li})/n(\mathrm{Al})=1:1$ ratio gives microbricks, whereas $n(\mathrm{Li})/n(\mathrm{Al})=2:1$ ratio gives laminar shapes. However, at 1000 °C microbricks structures were not observed, instead polyhedral structures were observed in $(1:1:3)_{1000}$ and $(1.5:1:3)_{1000}$ samples. Sample $(2:1:3)_{1000}$ presented laminar shapes. γ-$LiAlO_2$ was obtained with a yield of 100%.

2) The complexion effect of the fuel with Al_2O_3 was not possible; however, it was demonstrated that insoluble metal oxides can substitute the metal nitrates to produce $LiAlO_2$ by a modified combustion method with high purity.

3) It can be established that the irradiation produces consolidation, which is not favourable for an efficient extraction of tritium. Finally, the modified combustion process described for the synthesis of γ-$LiAlO_2$ seems to have a great potential in the preparation of ceramic materials.

Acknowledgments

This work was supported by National Institute of Nuclear Research (ININ), Autonomous University of Puebla (BUAP) and co-financed by National Council of Science and Technology (CONACYT, México). Furthermore, the authors thank to M. Espinosa, L. Baños, C. Rodríguez an L. Carapia for the analysis.

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以金属氧化物为原料改进燃烧法合成 γ-$LiAlO_2$

Daniel CRUZ[1], H. B. ORTIZ-OLIVEROS[2], L. M. PÉREZ-DÍAZ[1],
R. M. FLORES-ESPINOSA[2], G. ROSANO-ORTEGA[3]

1. Facultad de Ingeniería Química, Benemérita Universidad Autónoma de Puebla,
14 Sur y San Claudio, Ciudad Universitaria, C.P. 72570, Cd. Puebla, México;
2. Instituto Nacional de Investigaciones Nucleares, Dirección de Investigación Tecnológica,
Apartado Postal 18-1027, 11801 México, DF, México;
3. Universidad Popular Autónoma del Estado de Puebla, 21 Sur no. 1103, Colonia Santiago, C.P. 72410, Puebla, México

摘　要：提出一种合成 γ-$LiAlO_2$ 的替代解决方案—改进燃烧法直接合成 γ-$LiAlO_2$，并将其用于相对简单的反应体系中，原料为非氧化性化合物如 Al_2O_3 和 LiOH，燃料为尿素。采用 1:1、1.5:1 和 2:1 的非化学计量 Li/Al 摩尔比，在 900 和 1000 °C 下反应 5 min，制备 $LiAlO_2$，并对其组织和结构进行表征。考察 Li/Al 摩尔比对材料形貌和高 γ 射线辐照下材料稳定性的影响。结果表明，所得粉体的晶体结构为γ-$LiAlO_2$ 和α-$LiAlO_2$，其取决于 Li/Al 摩尔比。因此，用该方法可以成功合成微砖状、多面体状和层状γ-$LiAlO_2$，而无需任何后续处理。γ 辐照结果表明，所得到的γ-$LiAlO_2$ 不分解，只形成少量的 Li_2CO_3；由此可以确定，辐照会导致固结，不利于氚的有效提取；结果证明，用燃烧法生产高纯度γ-$LiAlO_2$ 不需要硝酸盐前驱体。

关键词：尿素；氧化物；燃烧；铝酸锂；陶瓷

(Edited by Xiang-qun LI)