

SYNTHESIS OF $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ APATITE-TYPE BY MECHANICAL ALLOYING

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Abstract. In this work, powders of La_2O_3 and SiO_2 were mechanically alloyed in a planetary ball mill with different rotation speeds (150-350 rpm) for maximum periods of time of 50 h and subsequently compacted at room temperature by cold isostatic pressure (CIP). Finally, the samples were sintering at temperatures up to 1300 °C in air.

The results showed that a higher rotation speed decreases the time required to the formation of the $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ phase. Single phase powders of $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ were obtained with 350 and 250 rpm after 15 and 50 h milling, respectively. No reaction between the La_2O_3 and SiO_2 powders occurred with 150 rpm milling even during 50 h processing. For the milled samples with incomplete reaction the single $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ phase is obtained at temperatures between 900 °C and 1300 °C, depending on the mechanical alloying parameters.

1. INTRODUCTION

Recently, apatite-type lanthanum silicates of general formula $\text{La}_{10-x}(\text{SiO}_4)_6\text{O}_{3-1.5x}$ ($x=0-0,67$) have attracted considerable interest as potential low cost electrolyte materials, with ionic conductivities higher than the conventional yttria-stabilised zirconia (YSZ) electrolyte and lower activation energies at moderate temperatures [1,2]. Conventionally, these materials are synthesized using solid-state methods with intermediate grindings. One key problem is that processing at high temperatures (1700-1800 °C) is necessary to achieve dense materials [3]. The high temperatures present some disadvantages such as poor control of morphology particle size as well as phase and stoichiometric heterogeneities.

The sol-gel route has been proposed to increase reaction rates and/or to decrease reaction temperature of the oxyapatite phase formation. However,

typically, high sintering temperatures (above 1450 °C) are still necessary for consolidation of the final material [4]. On the other hand, this process is time consuming as the resulting amorphous oxides must subsequently be calcinated at elevated temperature (> 800 °C) for several hours, in order to obtain the oxyapatite phase [5]. Moreover, a compaction technique and/or sintering must be subsequently applied for sample consolidation.

In this work, mechanical alloying (MA) is used for the production of the oxyapatite phase. MA is a simple, versatile and, at the same time, an economically viable process with important technical advantages, allowing the production of highly homogeneous nanostructured materials with improved mechanical, physical and chemical properties [6]. During MA, heavy deformation is introduced into the particles. Therefore, the induced high defect density accelerates the diffusion process and

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Table 1. Phase composition of the powder mixtures as a function of rotation speed and milling time.

Milling time (h)	Milling rotation speed (rpm)		
	150	250	350
5	X + O	X + O	X + O + ◆
15	—	—	◆
25	—	X + O + ◆	—
35	X + O	X + O + ◆	◆
50	X + O	◆	◆

◆ = $\text{La}_{9,33}(\text{SiO}_4)_6\text{O}_2$; X = La_2O_3 ; O = SiO_2

Table 2. Phase composition of the powder mixtures milled for 35 h as a function of milling rotation speed and annealing temperature.

Milling rotation speed (rpm)	As-milled	Annealing temperature (°C)			
		800	900	1000	1300
150	X + O	—	—	X + O + ◆	◆
250	X + O + ◆	—	◆	—	—
350	◆	◆	—	—	—

◆ = $\text{La}_{9,33}(\text{SiO}_4)_6\text{O}_2$ - X = La_2O_3 - O = SiO_2

the refined microstructural features decrease the diffusion distances allowing sintering of materials at lower temperatures than required by conventional routes.

The aim of this work is to decrease the synthesis and sintering temperatures necessary for the production of nanometric lanthanum silicate-based apatite phase ($\text{La}_{9,33}(\text{SiO}_4)_6\text{O}_2$) using MA and subsequent compaction and sintering techniques.

2. EXPERIMENTAL

Powders of crystalline La_2O_3 (99.9% purity) and SiO_2 (99.4% purity) were used as starting materials. The mixture, with a 9:7 (SiO_2 : La_2O_3) molar ratio, was placed in 250 ml hardened steel vial together with fifteen 20 mm diameter balls of the same material. About 24.5 g of the powder blend was loaded into the vial, with an approximate ball-to-powder weight ratio of 20:1. The raw materials were dry milled in air in a Fritsch planetary ball mill. The MA process was carried out at 150, 250, and 350 rpm for a maximum time of 50 h. After each 15 min of milling, the process was interrupted for 5 min to cool the vial and to reverse rotation. Small amounts of powder were drawn out at pre-deter-

mined time intervals (5, 15, 25, 35, and 50 hours) and subsequently annealed in air at increasing temperatures up to 1300 °C for 3 hours. The powders produced by MA were also compacted by cold isostatic pressing (CIP) at 330 MPa for 15 min and then sintered in air at temperatures up to 1300 °C. The holding time at the selected temperature was 30 h.

Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) analysis and X-ray diffraction (XRD) with Co $K\alpha$ radiation were used as main characterization techniques.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the powder mixtures obtained after 50 h milling with different rotation speeds and, as a reference, the XRD pattern of the as-blended powders. Besides the characteristic peaks of the raw materials (La_2O_3 and SiO_2), the XRD spectra of the as-blended powder shows several additional diffraction peaks which were indexed as the lanthanum hydroxide ($\text{La}(\text{OH})_3$) phase. According to the literature data [7], the formation of hydroxides and hydroxocarbonates from

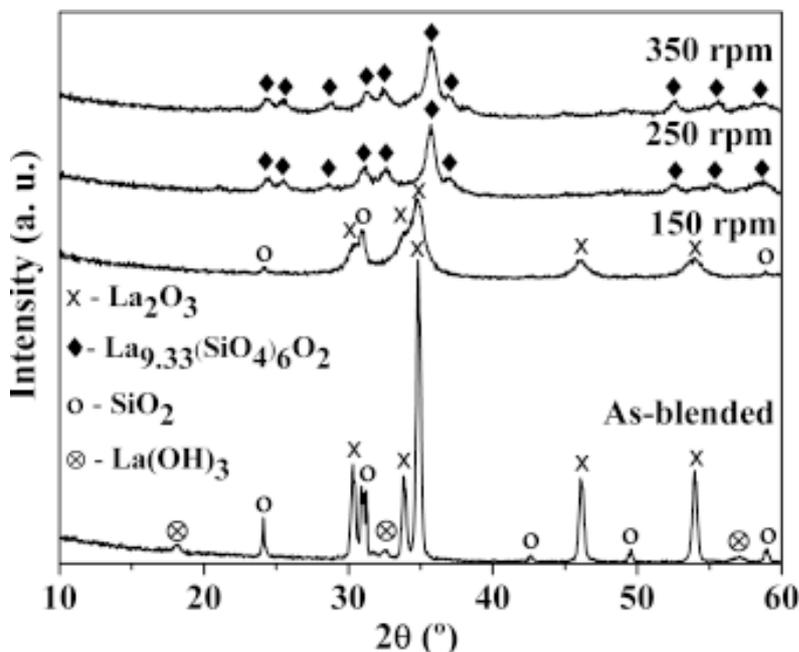


Fig. 1. X-ray diffraction patterns of the mixtures before and after mechanical alloying for 50 h at 150, 250, and 350 rpm.

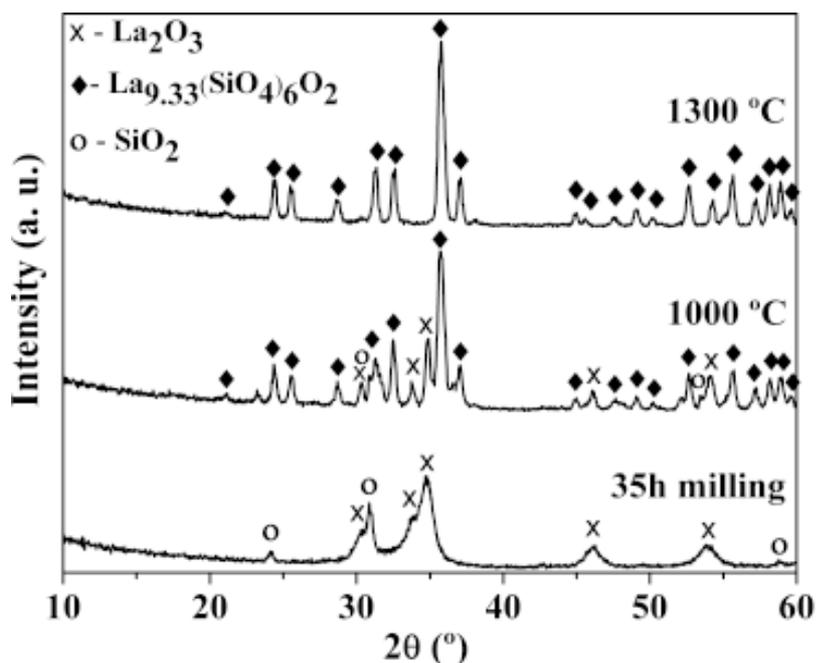


Fig. 2. X-ray diffraction patterns of the powder mixture milled for 35 h at 150 rpm, with and without subsequent annealing at 1000 and 1300 °C for 3 h.

rare earth oxides occur when these materials are exposed to air. However, the hydroxide phase is no longer present in the powder mixture after 50 h milling.

Milling at 150 rpm for 50 h do not facilitate the formation of new phases. Nevertheless, the milling process leads to severe broadening of the La_2O_3 and SiO_2 diffraction peaks, as-compared to the as-

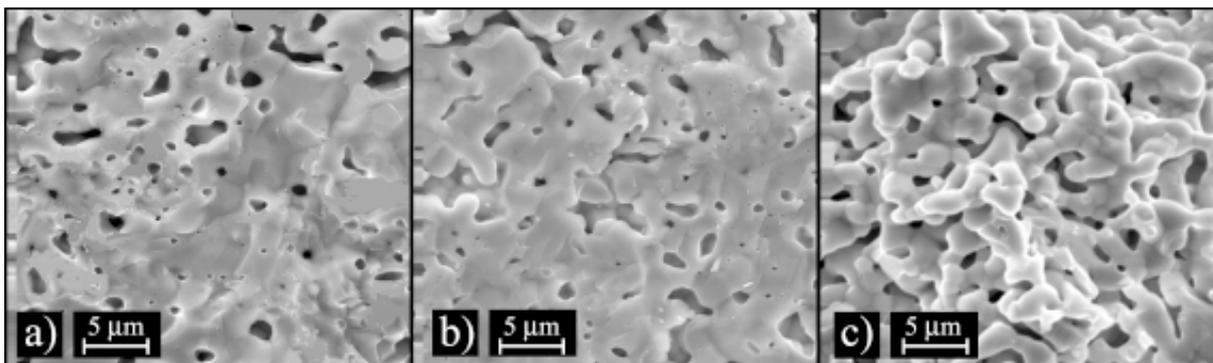


Fig. 3. – Scanning electron micrographs of the samples mechanically alloyed at 350, 250 and 150 rpm for 35 h, compacted by CIP and sintered at 1300 °C for 30 h.

blended mixture, which indicates a decrease in structural range order. It is well known that MA gives rise to a continuous decrease in grain size and destabilisation of the initial crystalline structure(s) by increasing the number of structural defects such as vacancies, dislocations, local stresses and grain boundaries [6]. Milling at 250 and 350 rpm for 50 h leads to complete reaction of the starting materials. The $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ phase is the only phase detected by XRD in the final powder mixture. Once again, broad diffraction peaks, indicating a low structural range order are observed after the MA process. The phase composition of the milled powder mixtures as a function of rotation speed and milling time is given in Table 1. As it was stated above, the $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ phase is never obtained when the powders are milled at 150 rpm. On the contrary, this phase is already formed after 25 h of milling for 250 rpm, although complete consumption of the reactants is only achieved after 50 h. For 350 rpm, single phase $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ powders can be obtained for shorter periods of milling (15 h), meaning that the increase of the rotation speed favours the $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ phase formation. The formation of an amorphous phase during MA referred by G. Tzvetkov *et al.* [8] was not observed in this work. These authors obtained the crystalline $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ phase after thermal treatment of the amorphous precursor phase. In the present work, the $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ phase is formed directly from the milling process at 250 and 350 rpm, without thermal treatment. This is in agreement with the work of Rodríguez-Reyna *et al.* [9], who also observed the formation of apatite-type lanthanum

silicates directly from the reaction products without involving crystallization from an amorphous precursor.

Fig. 2 shows the X-ray diffraction patterns of the powder mixtures milled for 35 h at 150 rpm, with and without subsequent annealing at 1000 and 1300 °C. The as-milled sample is formed by broad peaks of La_2O_3 and SiO_2 . Annealing of this powder mixture at 1000 °C for 3 h leads to the formation of the $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ phase even so traces of the initial reactants are still observed in the corresponding x-ray diffraction pattern. At higher annealing temperature (1300 °C) a complete consumption of the reactant powders occurs with the formation of $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$. The La_2O_3 and SiO_2 phase are no longer detected at this temperature.

Table 2 contains the results of the structural evolution of the powders mechanically alloyed at 150, 250, and 350 rpm for 35h with annealing temperature. The single phase $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ is obtained at 1300, 900, and 800 °C for the powders milled at 150, 250, and 350 rpm, respectively. It should be noted that in this last case (350 rpm / 35 h) the $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ phase already existed as a single phase after 35 h milling. The decrease of the annealing temperature required to the formation of single phase $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ with increasing milling rotation speed can be explained by the refined microstructural features obtained after mechanical alloying which decrease the diffusion distances and promote faster synthesis of new phases.

Fig. 3 shows scanning electron micrographs of the samples mechanically alloyed at 350, 250, and

150 rpm for 35 h, compacted by CIP and sintered at 1300 °C for 30 h. In none case a good compaction was achieved. This is particularly true for the sample mechanically alloyed at 150 rpm and it might be related to the late formation of the $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ phase observed. No significant differences were detected in the consolidation behaviour of both 250 and 350 rpm milled samples, in which the $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ phase is formed at lower temperatures. These results indicate that higher temperature and / or longer time are required to achieve denser samples. Another possibility for a better compaction of this kind of materials is the use of hot isostatic pressure (HIP). In fact, since the $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ phase can be directly obtained by MA from La_2O_3 and SiO_2 powders, no phase transformations would be necessary during sintering and therefore relatively low temperatures could be used in the HIP process.

4. CONCLUSIONS

It is shown that mechanical alloying at high rotation speed is an efficient route for the synthesis of the $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ phase from La_2O_3 and SiO_2 powders. Increasing the rotation speed allows shorter processing times. Single phase materials were formed at sintering temperatures between 900

and 1300 °C, depending on the mechanical alloying parameters: the higher is the MA rotation speed, the lower is the temperature necessary to obtained the $\text{La}_{9.33}(\text{SiO}_4)_6\text{O}_2$ phase.

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