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Mixed Si/Ge Apatite-Type Phase Produced by Mechanical Alloying

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Abstract. The aim of the present work is to study the influence of the partial substitution of Si by Ge on the formation of the apatite-type $La_{9.33}Si_2Ge_4O_{26}$ phase by mechanical alloying and subsequent annealing. Powders of La_2O_3, GeO_2 and SiO_2 were dry milled in a planetary ball milling at increasing rotation speeds of 150, 250 and 350 rpm and milling times up to 50 h. The resulting mixtures were subsequently annealed at increasing temperatures up to 1100 ºC. Single phase apatite-like $La_{9.33}Si_2Ge_4O_{26}$ was obtained during mechanical alloying at high rotation speed. The higher the rotation speed the lower was the time required for the lanthanum germanosilicate phase formation. For the samples in which complete reaction between initial phases did not occur during milling, $La_{9.33}Si_2Ge_4O_{26}$ was always obtained during the annealing process. The more severe was the mechanical alloying process the lower was the annealing temperature required for the apatite phase formation. The formation of apatite phase during mechanical alloying did not provoke significant changes in densification behavior of the milled samples. The addition of GeO_2 as raw material promotes a faster formation of the apatite phase as compared to the results obtained using only La_2O_3 and SiO_2.

Introduction

Solid Oxide Fuel Cells (SOFCs) are among the most efficient fuel cell electricity generators currently being developed word-wide [1]. In last years, intensive research has been made to develop new fast oxide ion conductors for application as solid electrolytes of intermediate temperature solid oxide fuel cells (IT-SOFCs). Apatite-type lanthanum silicates and germanates of general formula $La_{9.33}(RO_4)_6O_2$ (R= Ge, Si) exhibit higher ionic conductivities and lower activation energies at moderate temperatures (600–800ºC) than the conventional yttria-stabilised zirconia (YSZ) electrolyte [2,3]. These materials have been produced by solid-state methods consisting of several firing cycles with intermediate grindings. One key problem is the high processing temperature necessary to prepare them [4,5]. The sol-gel process has been proposed to decrease the temperature of the apatite-type phase formation. However, this process is time consuming as the resulting amorphous oxides must be subsequently calcinated for several hours in order to obtain the apatite phase. However, high sintering temperatures are still necessary for achieving good consolidation [6]. Mechanical Alloying, conceived initially to synthesize nanocrystalline metal-based materials and powder alloys, has been recently used for the synthesis of ceramics. In a previous work, the $La_{9.33}Si_6O_{26}$ apatite-type ionic conductor was synthesised using mechanical alloying as processing technique [7]. The aim of the present work is to study the influence of the partial substitution of Si by Ge on the formation of the apatite-type $La_{9.33}Si_2Ge_4O_{26}$ phase by mechanical alloying (MA) and subsequent annealing.

Experimental

Crystalline La_2O_3 (99.9% purity), GeO_2 (99.9% purity) and SiO_2 (99.4% purity) powders were mixed in a 7:3:6 (La_2O_3:SiO_2:GeO_2) molar ratio and mechanically alloyed in a Fritsch planetary ball mill for a maximum time of 50 h. A 250 ml hardened steel vial and fifteen balls with 20 mm diameter of the same material were used in the process. 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 MA process was carried out at 150, 250 and 350 rpm. After each 15 min of milling, MA was interrupted for 5 min to cool the vial and to reverse rotation. Small amounts of powder were drawn out at pre-determined time intervals (5, 15, 25, 35 and 50 hours) and subsequently annealed in air at increasing temperatures up to 1100ºC for 3 hours. X-ray diffraction (XRD) with Co Kα radiation was used as main characterization technique.

Results and Discussion

Fig. 1 shows the XRD patterns of the as-blended powder mixture and after milling for 50 h at different rotation speeds: 150, 250 and 350 rpm. The XRD pattern of the as-blended mixture shows the characteristic reflections of the raw materials (La_2O_3, SiO_2 and GeO_2) as well as less intense peaks ascribed to lanthanum hydroxide ($La(OH)_3$). Formation of hydroxides and hydroxocarbonates from rare earth oxides frequently occurs when these materials are exposed to air [8].

No structural changes were detected after milling at 150 rpm. However, the X-ray diffraction peaks are less intense and broader which indicates a loss of crystallinity. It is well known that MA processing leads to a continuous decrease in grain size and to an increase of the number of structural defects, local stresses and grain boundaries [9]. Concerning the higher rotation speeds (250 and 350 rpm), a complete reaction of starting materials occurred during milling resulting in the formation of the $La_{9.33}Si_2Ge_4O_{26}$ phase. The XRD peaks of the lanthanum germanosilicate phase are shifted to lower diffraction angles when compared with the ICDD card of the $La_{9.33}Si_6O_{26}$ phase [10].

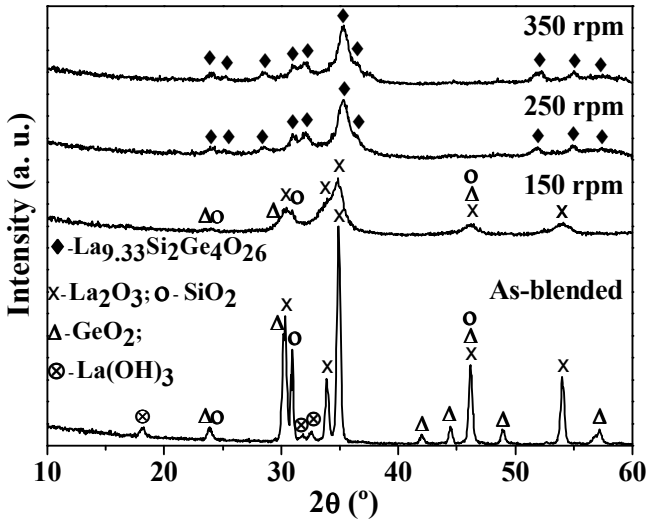

Figure 1 - XRD patterns of the mixture before and after mechanical alloying for 50 h at 150, 250 and 350 rpm.

This is an indication of Si substitution by Ge in the apatite-type lattice since the ionic radius of Ge is higher than the ionic radius of Si (53 pm against 40 pm, respectively). The shape of the lanthanum germanosilicate peaks (broad and with low intensity) indicates a low degree of crystallinity.

Table I compiles the results of phase identification by XRD of the mixtures milled with different conditions (time and rotation speed). The $La_{9.33}Si_2Ge_4O_{26}$ phase is never formed when a rotation speed of 150 rpm is used. In spite of the decrease in grain size reported above, the raw materials do not react to form the apatite-like phase. Increasing the rotation speed to 250 rpm, i.e., increasing the amount of energy involved in the milling process, allows the formation of lanthanum germanosilicate phase after 15 hours of milling. Single phase $La_{9.33}Si_2Ge_4O_{26}$ is obtained after 25 hours. Further increasing the rotation speed to 350 rpm allows the formation of the apatite-type phase after only 5 hours of milling while complete consumption of the reagents is achieved after 15

hours. As was observed in a previous work on the La-Si-O system [10], the higher the rotation speed the lower is the time required for the apatite-like phase formation. However, the addition of GeO_2 as raw material promotes a faster formation of the apatite phase.

For instance, at 250 rpm, 50 h of milling were necessary for the formation of the single apatite-like phase in the La-Si-O system whilst in the system with Ge this phase is produced after only 25 h were enough. An interesting observation to point out is that previous work on milling of crystalline La_2O_3 and amorphous SiO_2 [11] referred the formation of an amorphous precursor phase. The authors claim the formation of crystalline lanthanum silicate after thermal treatment of the amorphous precursor phase.

Table I – Phases formed after mechanical alloying using different conditions (rotation speed and time).

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

◆ = $La_{9.33}Si_2Ge_4O_{26}$; **X** = La_2O_3 ; **O** = SiO_2 ; Δ = GeO_2

As refereed above, in the present work, the crystalline $La_{9.33}Si_2Ge_4O_{26}$ phase is formed directly during mechanical alloying at 250 and 350 rpm, with no need of subsequent annealing. A similar result was obtained by the authors for the La-Si-O system [7] in agreement with the work of Rodrígues-Reyna et al. [12, 13], which also observed the formation of apatite-type lanthanum silicates [12] and germanates [13] by mechanical milling.

The formation of the $La_{9.33}Si_2Ge_4O_{26}$ phase with temperature was studied by annealing the samples for which this phase was not obtained during the milling process. Fig. 2 shows the structural evolution of the sample milled at 150 rpm for 25 h as a function of annealing temperature. As was observed for the sample milled for 50 h (see Fig. 1), the powder obtained after milling for 25 h is characterized by broad diffraction peaks of La_2O_3, GeO_2 and SiO_2. After annealing at 900 ºC the apatite-type phase is already detected coexisting with starting materials. After annealing at 1100 ºC, $La_{9.33}Si_2Ge_4O_{26}$ is the only phase detected by XRD. The steep decrease in the diffraction peaks width shows that a higher crystalline degree is achieved with increasing temperature.

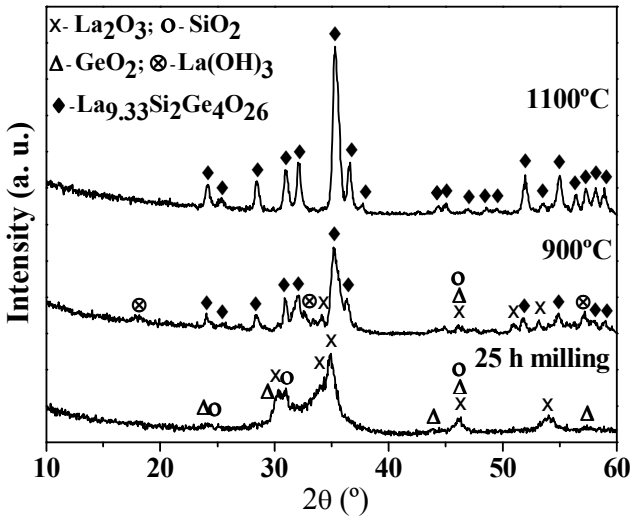

Fig. 2 – XRD patterns of the powder mixture after milling for 25 h at 150 rpm and after subsequent annealing at 900 and 1100 ºC for 3 h.

The phase composition of the powder mixtures for which complete consumption of the starting materials did not occur during the mechanical alloying process are summarized in Table II for the as-milled state and after thermal annealing at different temperatures. In spite of the lanthanum germanosilicate phase being formed in all the annealed samples, different thermal behaviours were observed depending on the milling rotation speed and time. Complete consumption of the reagents was not achieved only for the samples milled at 150 rpm for 5 hours, even after annealing at 110 ºC.

Single phase $La_{9.33}Si_2Ge_4O_{26}$ was obtained after annealing at 1100 and 1000 ºC for the samples milled at 150 rpm for 25 and 50 hours, respectively. At last, annealing at 900 and 1000 ºC for 3 hours was enough to produce single phase $La_{9.33}Si_2Ge_4O_{26}$ for the samples milled for 5 hours at 350 and 250 rpm, respectively. In accordance with a previous work [7], the higher the milling rotation speed and/or time the lower is the temperature required for the apatite phase formation. This results shows that the energy necessary to achieved complete consumption of the reagents and single phase $La_{9.33}Si_2Ge_4O_{26}$ production may be delivered to the La_2O_3, SiO_2 and GeO_2 powder mixture either by mechanical alloying or by thermal annealing. If more energy is delivered during the MA process, either by increasing the rotation speed or the milling time, less energy will be necessary during the annealing process. This conclusion shows that the MA process is an efficient route to lower the temperature of production of the $La_{9.33}Si_2Ge_4O_{26}$ phase.

Table II - Phase composition of the powder mixtures for which complete consumption of the starting materials did not occur during the mechanical alloying process in the as-milled state and after thermal annealing at different temperatures.

Milling [rotation speed (rpm), time (h)]	As-milled	Annealing temperature (ºC)		
		900	1000	1100
[150, 5]	**X O** Δ	**X O** ⊗ Δ ◆	**X O** ⊗ Δ ◆	**X O** Δ ◆
[150,25]	**X O** Δ	**X O** ⊗ Δ ◆	**X O** Δ ◆	◆
[150,50]	**X O** Δ	**X O** Δ ◆	◆	---------
[250, 5]	**X O** Δ	**X O** ⊗ Δ ◆	◆	---------
[350, 5]	**X O** Δ ◆	◆	---------	---------

◆ = $La_{9.33}Si_2Ge_4O_{26}$; X = La_2O_3; **O** = SiO_2; Δ = GeO_2; ⊗ = $La(OH)_3$

Summary

Powders of La_2O_3, GeO_2 and SiO_2 were dry milled in a planetary ball milling at rotation speeds of 150, 250 and 350 rpm and milling times up to 50 h. Formation of single phase $La_{9.33}Si_2Ge_4O_{26}$ was achieved during mechanical alloying, at room temperature, when high rotation speed and/or long periods of time are used. Subsequently annealing of samples in which complete reaction between initial phases did not occur during milling also lead to the formation of single phase $La_{9.33}Si_2Ge_4O_{26}$ at temperatures between 900 and 1100 ºC, depending on the milling conditions. The energy necessary to achieved complete consumption of the reagents and single phase $La_{9.33}Si_2Ge_4O_{26}$ production may be delivered to the La_2O_3, SiO_2 and GeO_2 powder mixture either by mechanical alloying or by thermal annealing. If more energy is delivered during the MA process, either by increasing the rotation speed or the milling time, less energy will be necessary during the annealing process. This conclusion shows that the MA process is an efficient route to lower the temperature of production of the $La_{9.33}Si_2Ge_4O_{26}$ phase.

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