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Mechanochemically induced formation of La_2SiO_5

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A mechanochemical technique was applied to prepare La_2SiO_5 under conditions where the conventional solid-state synthesis shows unsatisfactory results. The effects of the mechanochemical treatment of a mixture of lanthana and silica gel (in molar ratio $La_2O_3/SiO_2 = 4:3$) has been studied by X-ray diffractometry (XRD), infrared spectroscopy (IR) and using a scanning electron microscope (SEM). Differential thermal analysis (DTA) and thermogravimetry (TG) have been used to follow the thermal behaviour of initial and milled samples. It was found that the amorphous silicate precursor of $La_{4.67}(SiO_4)_3O$ is formed as a result of a mechanochemical solid-state reaction. The crystallization of the latter silicate occurs at 880 °C during the subsequent heat treatment of the milled samples. The formation of La_2SiO_5 without any XRD—detectable traces of $La_{4.67}(SiO_4)_3O$ takes place after heating at 1100 °C for 2 h. The rate of conversion increases with increasing the milling time, reaching 96% after mechanochemical treatment for 3 h and subsequent heating at 1100 °C.

1. Introduction

Mechanochemical synthesis of precursors and its subsequent heat treatment has become a useful method for obtaining complex oxide materials [1, 2]. Recently it has been shown that the use of hydrated oxides or hydroxides accelerates the incipient solid-state reaction during the milling [2–6]. It was also found that in these systems variations in acid-base properties of oxides are quite important for the efficiency of the mechanochemical process [2, 3, 7]. This new technique of inorganic synthesis that is known as a "soft" mechanochemistry [1] was used for the formation of different compounds, such as alkaline-earth silicates [2, 5], titanates [3], vanadates [6] and aluminosilicates [4, 8].

According to the phase diagram of the La_2O_3-SiO_2 system [9], the silicates which can be formed are $La_{4.67}(SiO_4)_3O$, $La_2Si_2O_7$ (low- and high-temperature polymorphs) and La_2SiO_5. In our previous reports it has been shown that the mechanochemical technique is an effective method for the stimulation of $La_{4.67}(SiO_4)_3O$ and $La_2Si_2O_7$ synthesis [10, 11].

Lanthanum oxyorthosilicate (La_2SiO_5) is a material which has received attention because of its application as a component of high-temperature resistant composites, dielectric materials and abrasives [12–14]. La_2SiO_5 (monoclinic, $P2_1/c$) is traditionally prepared by solid-state reaction between La_2O_3 and SiO_2 in molar ratio 1 : 1. The reaction is slow and high temperatures are needed (∼1700 °C) to get a full conversion in a reasonable time [15]. Besides, the solid-state reaction is completed only when the amount of La_2O_3 is in stoichiometric excess [16]. It has to be noted that when the reaction proceeds at lower temperatures, $La_{4.67}(SiO_4)_3O$ is formed as an impurity phase.

The present work aims at studying the effect of mechanochemical treatment on the mixture of La_2O_3 and silica gel in order to find the possibilities for obtaining La_2SiO_5 under milder conditions in comparison to the classical method.

2. Experimental details

The starting materials are La_2O_3 (Fluka, 99.98%) and amorphous SiO_2 (silica gel, Merck). $La(OH)_3$ is present at a significant level in the commercially available lanthana, but we used that material without any pretreatment in order to investigate the system under the concept of soft mechanochemistry. According to the TG analysis the total loss of weight for lanthana and silica gel is, respectively, 12.4 and 8.9%. The starting mixture of lanthana and silica gel in molar ratio $La_2O_3/SiO_2 = 4:3$ was prepared after short-time homogenization in an agate mortar. La_2O_3 is present in a stoichiometric excess in the initial mixture in order to eliminate the influence of impurity SiO_2 from the machinery parts (see below) on the phase composition of the product.

The experiments were carried out in a planetary ball mill Pulverisette 5 (Fritsch, Germany) in 80 cm^3 agate vessels with agate balls 20 mm in diameter and 40 g overall mass. The ball-to-powder mass ratio was 7 : 1. The samples (denoted as LS-t) were treated for 1, 2 and 3 hours (t) in air at 256 rpm. X-ray diffraction patterns (XRD) were obtained on an automatic powder

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diffractometer TUR-62M (Germany) using Co K_α radiation in the 8–68° (2θ) angular range. The phase identification was done according to JCPDS cards 5-602 for La_2O_3, 36-1481 for $La(OH)_3$, 40-0234 for La_2SiO_5 and according to Refs. [11, 17] for $La_{4.67}(SiO_4)_3O$. IR spectra (4000–400 cm^{-1}) were recorded with a Specord 75 spectrometer (Carl Zeiss, Germany) in KBr-pellets or in Nujol mulls. Differential thermal analysis (DTA) and thermogravimetry (TG) were carried out with a MOM Derivatograph (Paulik-Paulik-Erdey System, Hungary). Samples of $\sim$0.3 g were heated in synthetic corundum crucibles (10 °C/min) up to 1000 °C in static air. Al_2O_3 was used as a reference. The particle morphology was monitored on a JEOL JSM-5300 (Japan) scanning electron microscope (SEM). In order to investigate the changes in phase composition, the treated samples were heated at different temperatures for 2 h.

The rate of conversion was quantitatively estimated by chemical analysis of the heated samples of LS-0 and LS-t. The method, based on the complexometrical determination of the free La_2O_3 content, after its dissolving in a NH_4NO_3 solution, was used. The details of this procedure were given elsewhere [16, 18].

The amount of impurity agate after 3 h milling was determined by chemical analysis of the heated at 1100 °C LS-3 sample. The procedure was described in Ref. [18].

3. Results and discussion

The XRD pattern of the initial mixture (LS-0) is shown in Fig. 1a. The dominant presence of $La(OH)_3$ is not surprising, taking into account the great reactivity of La_2O_3 with respect to the atmospheric moisture and carbon dioxide [19, 20]. XRD patterns of LS-1, LS-2 and LS-3 are also shown in Fig. 1. The broadening of diffraction peaks of both La_2O_3 and $La(OH)_3$ with increasing milling times is seen. A fully amorphous state is achieved after 3 h milling. Diffraction peaks of a new crystalline phase are not observed. Such a gradual amorphization of the ingredients indicates a reduction in crystallite size, an increased number of defects and, probably, the formation of an amorphous intermediate product.

LS-0 and LS-3 were examined using SEM to observe the microstructural morphology, as shown in Figs 2 and 3. It is evident that the milling causes fracturing of the irregularly shaped particles of the initial mixture. Most of the produced rounded particles are brought into intimate contact with each other, and new aggregates are formed. The process of agglomeration is a typical phenomenon for the mixtures, where mechanochemically induced reactions take place. Urakaev *et al.* [21] have found that such a type of aggregates contains mixed species of all reactants and final products. The structural changes caused by milling are also indicated by IR measurments, shown in Fig. 4. The IR spectrum of LS-0, presented in Fig. 4a, confirms the presence of $La(OH)_3$. The absorption bands at 3600 cm^{-1} and 640 cm^{-1} can, respectively, be interpreted as associated with OH-stretching and with La–OH bending modes in $La(OH)_3$ [19, 22]. The bands at 1450 cm^{-1} and 1385 cm^{-1} are explained by a process of carbonization of the initial lanthana [23]. These bands, along with the band at 1620 cm^{-1}, due to the bending mode of water, and the broad mode at 3430 cm^{-1}, assignable to the stretching mode of water, suggest the existence of an amorphous hydroxycarbonate-like phase $La_2(OH)_{2(3-x)}(CO_3)_x \cdot nH_2O$, where x is *ca.* 1 [19, 20, 23]. The other bands in the spectrum of LS-0 are typical for the pure silica gel. As one can see, the IR spectra of the treated samples demonstrate a gradual change in the chemical composition with milling

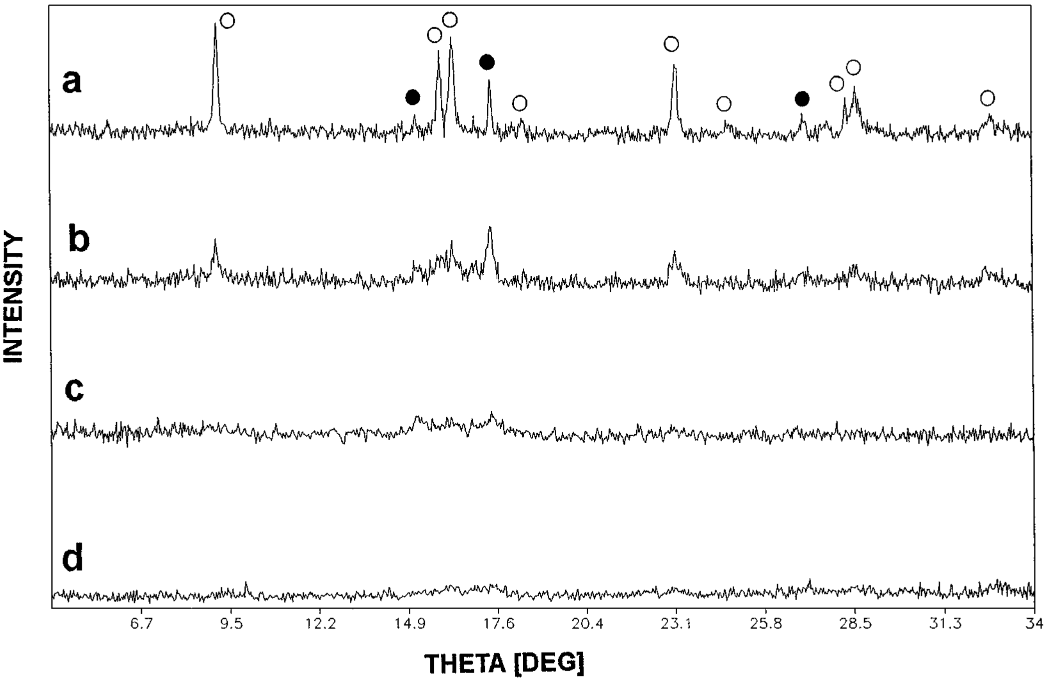

Figure 1 XRD patterns of (a) LS-0, (b) LS-1, (c) LS-2 and (d) LS-3. Key: (○) $La(OH)_3$; (●) La_2O_3.

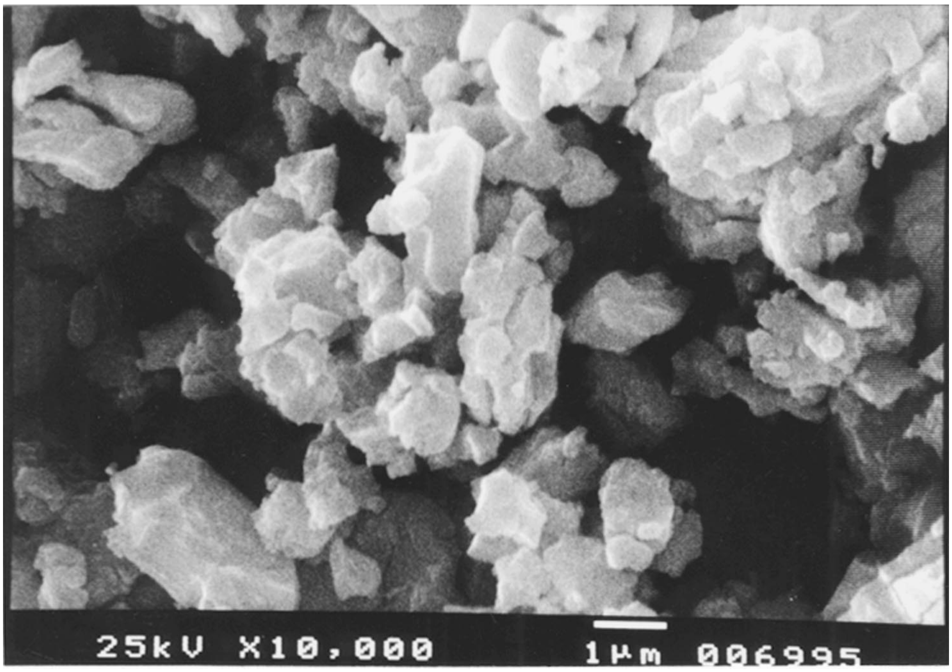

Figure 2 SEM micrograph of LS-0.

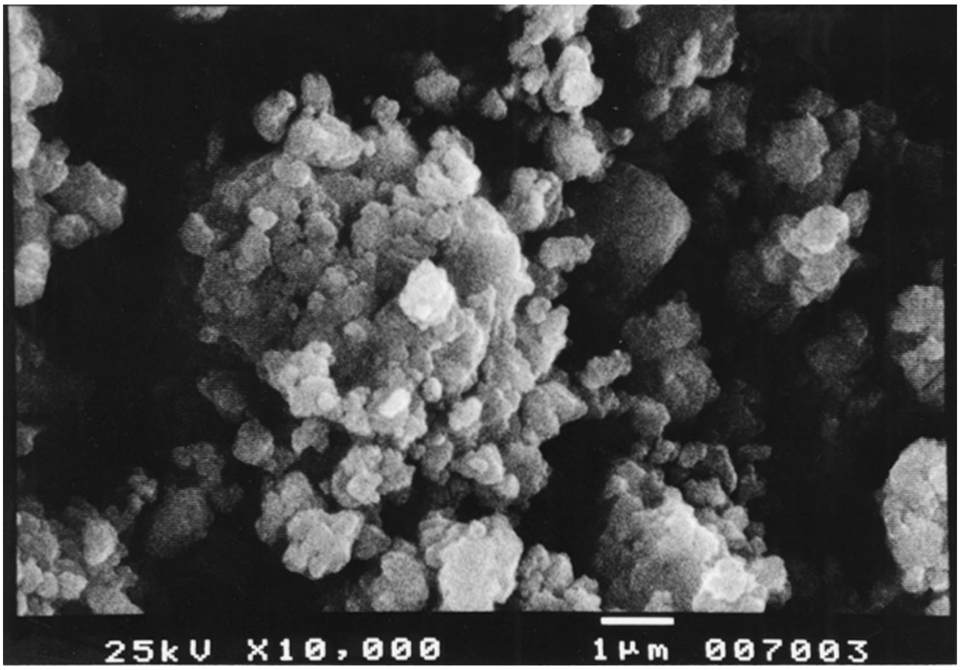

Figure 3 SEM micrograph of LS-3.

time. The 790 cm^{-1} absorption band, assigned to the Si–O–Si symmetric stretching vibration [7], practically disappears in the spectra of the milled samples. This effect is explained in terms of disappearance of the three-dimensionally bonded SiO_4 tetrahedra to less connected tetrahedra [7]. The disappearance of this band was observed by other authors when milling various metal hydroxides with SiO_2 [2, 7]. They found that amorphous precursors of the respective silicates are formed due to mechanochemical solid-state reaction. Another more explicit evidence of the formation of a silicate precursor in the present system is the observation of new absorption bands at 895 cm^{-1} and 920 cm^{-1} in the spectrum of LS-3. These bands may be associated with the asymmetric stretching vibrations in the SiO_4 tetrahedra of the mechanochemically formed silicate structure [10, 24]. The disappearance of the absorption band at 950 cm^{-1}, due to stretching vibration of silanol groups (Si–OH) [25] in the initial silica gel, along with the decreasing of the band at 3600 cm^{-1}, suggest that in the course of milling a condensation reaction between the reactants occurs.

With increasing the milling time, the bands at 1450 cm^{-1} and 1385 cm^{-1} become better defined, which means that a gradual process of carbonation of lanthana takes place.

The DTA-TG traces of LS-0, LS-1, LS-2 and LS-3 are compared in Fig. 5. The DTA-TG traces of LS-0

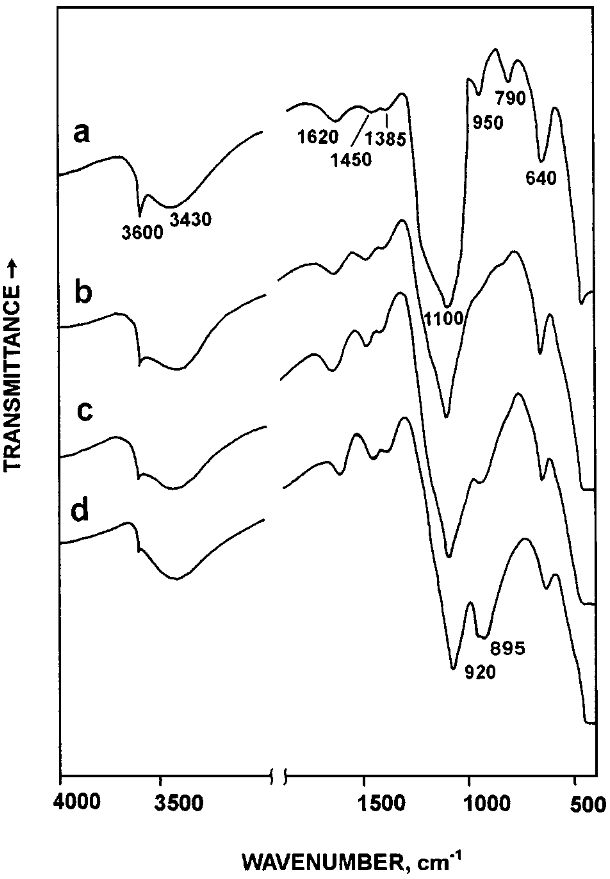

Figure 4 IR spectra of (a) LS-0, (b) LS-1, (c) LS-2 and (d) LS-3.

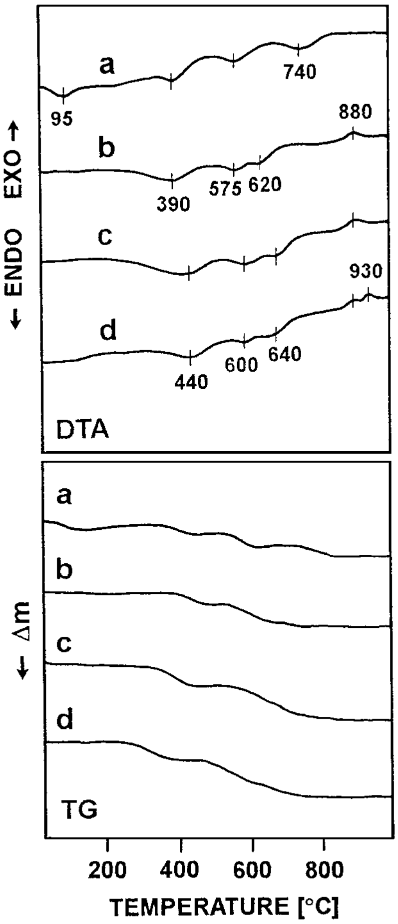

Figure 5 DTA-TG traces of (a) LS-0, (b) LS-1, (c) LS-2 and (d) LS-3.

show that the loss of adsorbed H_2O molecules takes place at around 95 °C. The other endothermic peaks are related to the loss of weight and are due to the well-known process of thermal decomposition of a product consisting of $La(OH)_3$ and hydroxycarbonate-like phase [19, 20, 23]. The latter compounds decompose simultaneously at 390–440 °C to LaOOH and $La_2O_2CO_3$, respectively. LaOOH decomposes to La_2O_3 at 575–600 °C and the last endothermic peak is due to the decomposition of $La_2O_2CO_3$ to La_2O_3 and CO_2 at 620–740 °C. The milling changes the last stage of the process significantly and, as it is shown, the decomposition of $La_2O_2CO_3$ occurs at lower temperatures in comparison with that of LS-0.

The DTA-TG traces of LS-1, LS-2 and LS-3 (Fig. 5) show that below the first stage of the already discussed decomposition process no effects, which could be assigned to the detachment of the molecular water (confirmed by the IR spectra of the same samples (see Fig. 4)) are seen. This fact is in accordance with the suggestion made by Shapkin *et al.* [26] for the mechanism of mechanochemical synthesis in multicomponent systems. The authors showed that the mechanochemically obtained amorphous state is stabilized by structure-fixing gaseous reaction products (i.e. H_2O or CO_2 molecules) and its detachment occurs just before crystallization of the final product during the subsequent heat treatment. Probably, in the present system H_2O molecules are emitted by the treated samples along with the products of the thermal decomposition of $La(OH)_3$ and hydroxycarbonate-like phase.

The milled samples show exothermic peaks at 880 °C and also at 930 °C in the case of LS-3 (Fig. 5). In order to reveal the origin of these exothermic peaks, IR spectra of LS-2 and LS-3, heated at 890 °C, 1000 °C and 1050 °C, were obtained (Fig. 6). After heating at 890 °C the IR spectra show the formation of a new compound (Fig. 6a and d). According to Ref. [24] the new absorption bands are typical of $La_{4.67}(SiO_4)_3O$. The asymmetric and symmetric stretching frequencies of the SiO_4 group appear at 890–990 cm^{-1} and 842 cm^{-1}, respectively. The corresponding deformation vibrations lie at 457–542 cm^{-1}. In these spectra, bands of non-reacted SiO_2 and lanthana are also seen. The IR spectra of the samples heated at 1000 °C (Fig. 6b and e) show the bands of the same silicate, but the band of SiO_2 at 1100 cm^{-1} in the spectrum of LS-3 is almost vanished. After heating at 1050 °C the IR spectra (Fig. 6c and f) show the bands, which coincide with the bands of La_2SiO_5 described in the literature [24, 27]. Taking into account that La_2SiO_5 (also given as $La_2(SiO_4)O$) contains isolated SiO_4 tetrahedra, the bands at 837–990 cm^{-1} are assigned to the SiO_4 asymmetric stretching vibrations, while the bands at 453–540 cm^{-1} arises from the deformation vibrations of SiO_4 group. It can be deduced from the IR observations that the exothermic peaks at 880 °C are due to the crystallization of the mechanochemically obtained silicate precursor to $La_{4.67}(SiO_4)_3O$. Obviously the second exothermic peak on the DTA trace of LS-3 is due to the additional solid-state reaction between La_2O_3 and SiO_2 that remain after

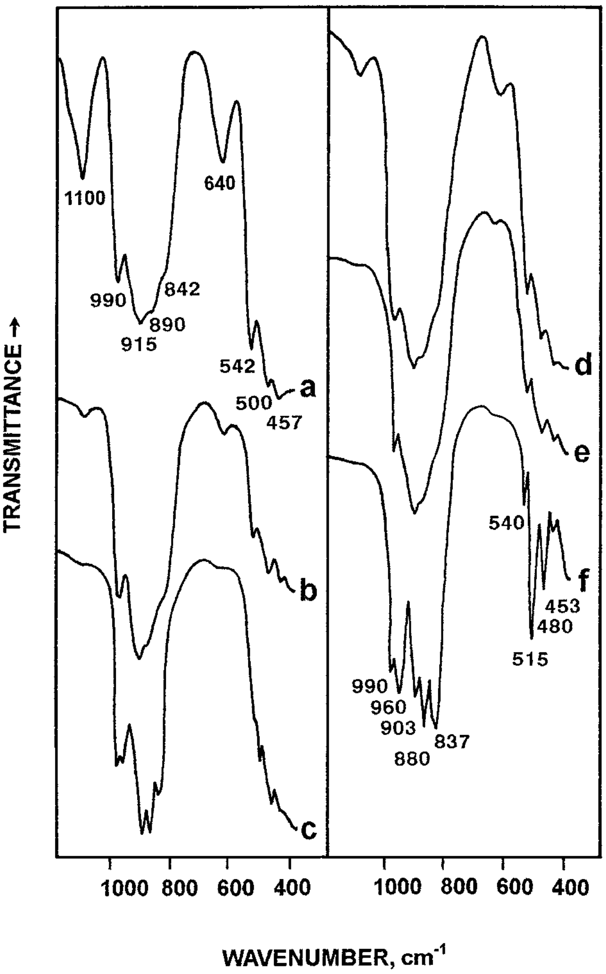

Figure 6 IR spectra of LS-2 samples heated at (a) 890 °C, (b) 1000 °C, (c) 1050 °C and of LS-3 samples heated at (d) 890 °C, (e) 1000 °C and (f) 1050 °C.

the milling. This additional interaction is a conventional thermal process, which also produces $La_{4.67}(SiO_4)_3O$. In the case of LS-1 and LS-2 this additional reaction probably occurs above 1000 °C and that is why the lack of second exothermic peak is observed. Such an additional solid-state reaction after the crystallization of the silicate precursor was observed in our previous investigations on the mechanochemical effects in the La_2O_3-SiO_2 system containing different amounts of ingredients [10, 11]. These results also confirm our suggestion [10] that $La_{4.67}(SiO_4)_3O$ is an intermediate product, which is forming in the La_2O_3-SiO_2 system regardless of the mixture composition.

The XRD patterns of LS-1, LS-2 and LS-3, all heated at 1050 °C, are presented in Fig. 7. In all three cases the diffraction peaks of La_2SiO_5, residual La_2O_3 and $La(OH)_3$ (obtained by hydration of La_2O_3 during the preparation of the samples for analysis) are observed. Some peaks of $La_{4.67}(SiO_4)_3O$ are also seen. Obviously at this temperature the formation of La_2SiO_5 is not complete. In Fig. 8 the XRD patterns of LS-1, LS-2 and LS-3, heated at 1100 °C, are presented. No peaks of impurity $La_{4.67}(SiO_4)_3O$ are observed. The LS-3 sample, heated at 1100 °C, was purified from the residual La_2O_3 by dissolving the free oxide in an NH_4NO_3 solution after the procedure described in Ref. [16]. The XRD pattern of the purified sample, washed with deionized water and dried at 100 °C (Fig. 8d) represents a pure La_2SiO_5 product.

The rate of conversion for LS-0, LS-1, LS-2 and LS-3 at 1100 °C as a function of milling time is presented in Fig. 9. The rate of conversion (α) is estimated using $\alpha = La_{\text{bound}}/La_{\text{st}}$ ratio, where La_{bound} is the amount of lanthanum bound in the product compound. La_{st} is not

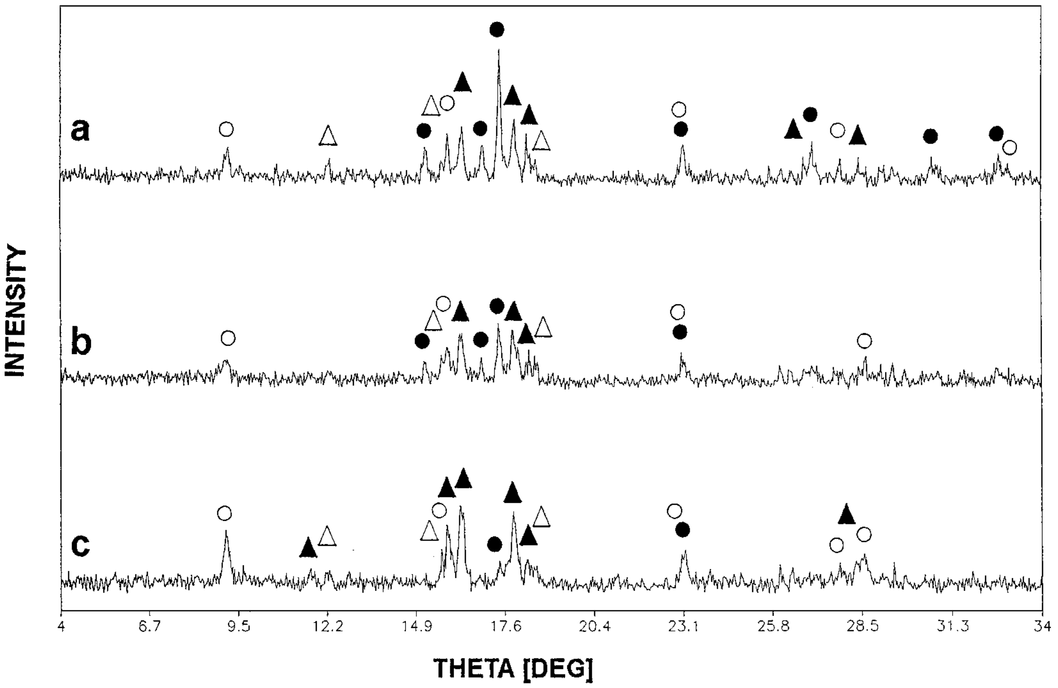

Figure 7 XRD patterns of (a) LS-1, (b) LS-2 and (c) LS-3, all heated at 1050 °C. Key: (○) $La(OH)_3$; (●) La_2O_3; (△) $La_{4.67}(SiO_4)_3O$; (▲) La_2SiO_5.

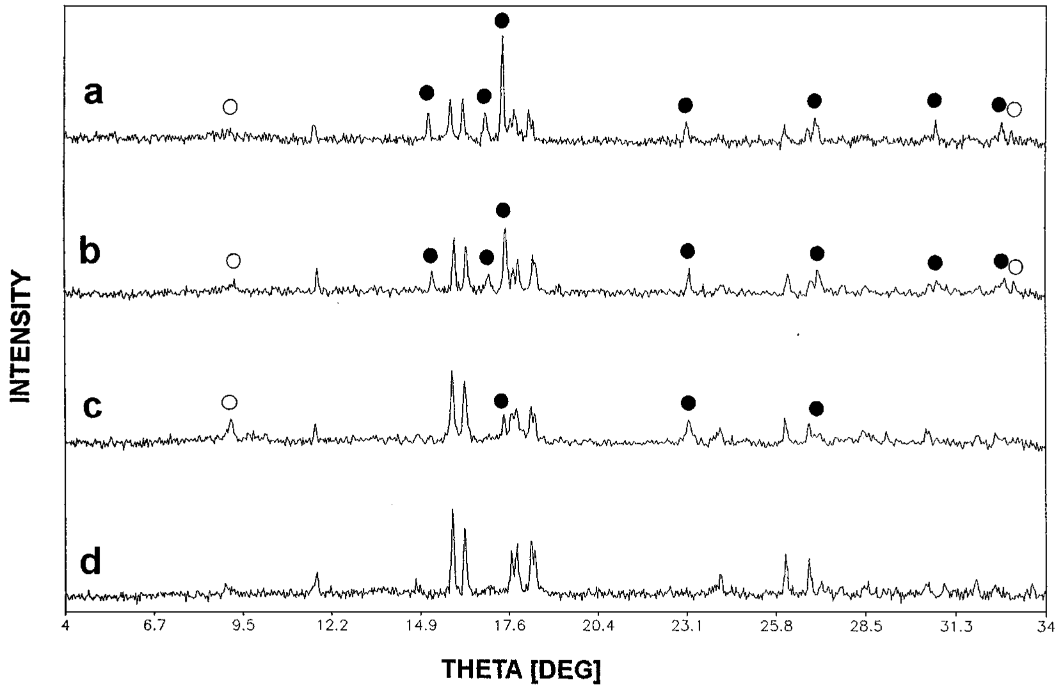

Figure 8 XRD patterns of (a) LS-1, (b) LS-2 and (c) LS-3, all heated at 1100 °C, and of (d) LS-3, heated at 1100 °C and purified from residual La_2O_3. Key: (○) $La(OH)_3$; (●) La_2O_3; the unmarked peaks are related to the La_2SiO_5.

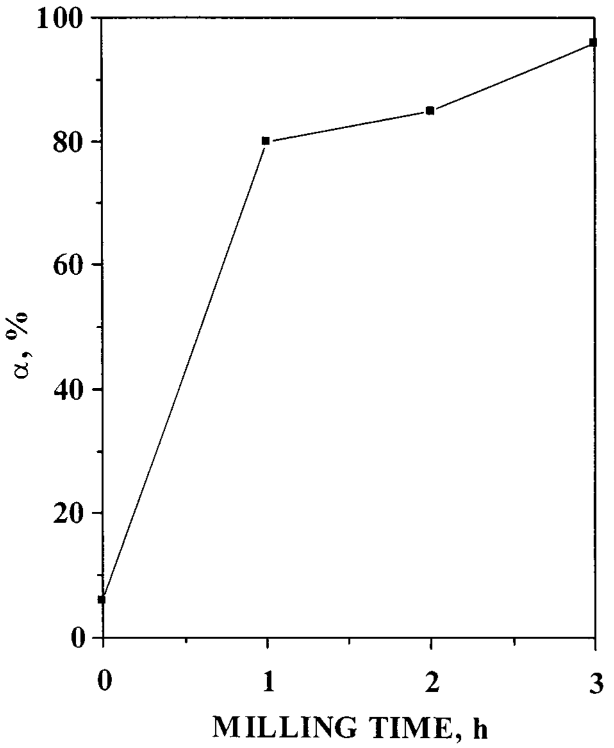

Figure 9 The rate of conversion (α) at 1100 °C as a function of milling time.

the total amount of La in the mixture, but the stoichiometric amount of La for La_2SiO_5 formation. As it is evident from Fig. 9, the rate of conversion increases with increasing the milling time, achieving 96% after preliminary mechanochemical treatment for 3 h. This result correlates well with the already presented experimental data on the mechanochemical changes in the mixture.

The amount of impurity agate in the heated at 1100 °C LS-3 sample is 1.8 wt %. This fact should be taken into account when milling equimolar mixture of La_2O_3 and SiO_2 with the same milling media, because the coexistence of $La_{4.67}(SiO_4)_3O$ after heating of the milled samples at temperatures above 1100 °C might be observed according to the phase diagram of the system [9].

4. Conclusion

A soft-mechanochemical technique appears to be able to promote the formation of La_2SiO_5. It was found that the mechanochemical treatment of a lanthana/silica gel mixture (in molar ratio $La_2O_3/SiO_2 = 4:3$) induces interaction between the ingredients, leading to an amorphous precursor of $La_{4.67}(SiO_4)_3O$. This phenomenon is beneficial for preparing La_2SiO_5 after subsequent heating of the milled mixtures at 1100 °C for 2 h. The rate of conversion increases with increasing the milling time, achieving 96% after 3 h milling.

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