



# Effect of water content in powder mixture on mechanochemical reaction of $\text{LaMnO}_3$ fine powder

Satoshi Ohara, Hiroya Abe\*, Kazuyoshi Sato, Akira Kondo, Makio Naito

*Joining and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan*

Received 26 July 2007; received in revised form 19 November 2007; accepted 25 November 2007

Available online 11 February 2008

## Abstract

Effect of water content in starting powder mixture of  $\text{La}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  on mechanochemical reaction of lanthanum manganite ( $\text{LaMnO}_3$ ) fine powder was investigated. The water content was controlled to be <0.5, 2 and 8% mass fraction in the powder mixture. An attrition-type milling apparatus was employed. This mechanochemical method has several advantages including the use of low cost raw materials, simplicity of the process and the ability to obtain fine powder. When the water content was 2% mass fraction, the single phase  $\text{LaMnO}_3$  fine powder was obtained after milling only for 30 min. On the other hand, the reaction was not completed on the drier condition (<0.5% mass fraction) and the wetter condition (8% mass fraction). For the powder mixture with the water content of 2% mass fraction, the increase of specific surface area (SSA) with structural defects (forming an activated matrix) occurred in the early stage of the milling, and then solid-state reaction proceeded in the activated matrix, which led to the synthesis of crystalline  $\text{LaMnO}_3$  phase. The SSA did not change drastically with increasing milling time for the drier powder mixture. The SSA rather decreased for the wetter powder mixture. The results indicated that the water content in starting materials influenced significantly their grinding behavior and thereby the reaction rate for  $\text{LaMnO}_3$  formation.

© 2008 Published by Elsevier Ltd.

**Keywords:** Mechanochemical reaction; Water content; Perovskites;  $\text{LaMnO}_3$ ; Powder preparation

## 1. Introduction

Perovskite type lanthanum manganite ( $\text{LaMnO}_3$ ) and the related compounds, e.g.,  $\text{La}(\text{Sr})\text{MnO}_3$ , are regarded as one of the most promising cathode materials for solid oxide fuel cells (SOFCs). The performance, such as electrochemical and physical properties of electrodes in SOFCs, strongly depends on the morphology and chemical composition of the electrodes. In other words, the performance of the SOFCs can be improved by better control of the morphology and the chemical composition of the electrodes. Therefore, we have been applying a fine  $\text{LaMnO}_3$  powder as a starting powder, because the morphology of advanced materials such as ceramics is strongly influenced by the starting powder characteristics.

Among the syntheses of  $\text{LaMnO}_3$  powders, a conventional solid-state reaction at high temperature leads to large particle size and limited degree of chemical homogeneity.<sup>1</sup>

The liquid-phase reactions have provided possibility for fine and homogeneous  $\text{LaMnO}_3$  powders.<sup>2–4</sup> However, liquid-phase reaction seems to be more troublesome than solid-state reaction because liquid-phase process requires some delicate techniques and/or the development of sintering process for the obtained  $\text{LaMnO}_3$  powder.

A satisfactory choice may be a mechanochemical method. The mechanochemical route has several advantages over both conventional solid-state reaction and wet chemical processes including a simple and green process, the use of low cost raw materials and the ability to obtain fine powder.<sup>5</sup> The mechanochemical method is characterized by the repeated welding, deformation and fracture of the constituent powder materials.<sup>6</sup> Chemical reactions occur at the interfaces of the particles that are continuously re-generated during milling.<sup>7</sup> As a consequence, the solid-state reactions can promote in milling apparatus without any need for external heating. Zhang and Saito have synthesized a fine  $\text{LaMnO}_3$  powder by planetary ball milling of constituent oxides for 180 min.<sup>8</sup>

In the mechanochemical synthesis, grinding of solid mixtures of inorganic compounds is a basic technique, and it is influenced

\* Corresponding author. Tel.: +81 6 6879 4360; fax: +81 6 6879 4360.  
E-mail address: [h-abe@jwri.osaka-u.ac.jp](mailto:h-abe@jwri.osaka-u.ac.jp) (H. Abe).

by the presence of water in starting materials.<sup>9</sup> The products of mechanochemical activation of mixtures in MgO–SiO<sub>2</sub> system were found to depend on the water content of the siliceous starting materials.<sup>9</sup> For a fine LaMnO<sub>3</sub> powder synthesis, Sato et al. have found that the mechanochemical reaction was accelerated by milling under humid air.<sup>10</sup> However, the role of water content in the mechanochemical reaction of LaMnO<sub>3</sub> synthesis has not been fully understood. The aim of this investigation was to examine the effect of water content in starting powder mixture of La<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub> on mechanochemical reaction of LaMnO<sub>3</sub> formation. The relation between the water content and the mechanochemical reaction rate of LaMnO<sub>3</sub> is shown, and the role of water content in LaMnO<sub>3</sub> synthesis is discussed.

## 2. Experiment

Commercial La<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub> powders (KCM Corporation, Japan) were used. The La<sub>2</sub>O<sub>3</sub> powder was calcined at 700 °C for 2 h to eliminate hydroxide which was formed during storage in air, and the Mn<sub>3</sub>O<sub>4</sub> powder was dried at 150 °C for 24 h to remove physically adsorbed water. The mean particle sizes calculated from the specific surface area (SSA) were 800 and 70 nm for the La<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub>, respectively. After the heat treatments, the two powders were mixed with the equimolar ratio of La and Mn (molar ratio of La<sub>2</sub>O<sub>3</sub>:Mn<sub>3</sub>O<sub>4</sub> = 3:2). Then, the water content in the powder mixture was controlled to be <0.5, 2 and 8% mass fraction by exposing to a humidified condition (25 °C and RH 80%) for 0, 3 and 24 h. Fig. 1 shows the X-ray diffraction (XRD) patterns for the three powder mixtures. When the water content was <0.5% mass fraction, the XRD peaks were identified as only those of La<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub>. La(OH)<sub>3</sub> phase was detected in the powder mixture with the water content of 2% mass fraction. When the water content was 8% mass fraction, the XRD peaks were identified as only those of La(OH)<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub>. It is noted that La<sub>2</sub>O<sub>3</sub> is hygroscopic oxide.<sup>11</sup>

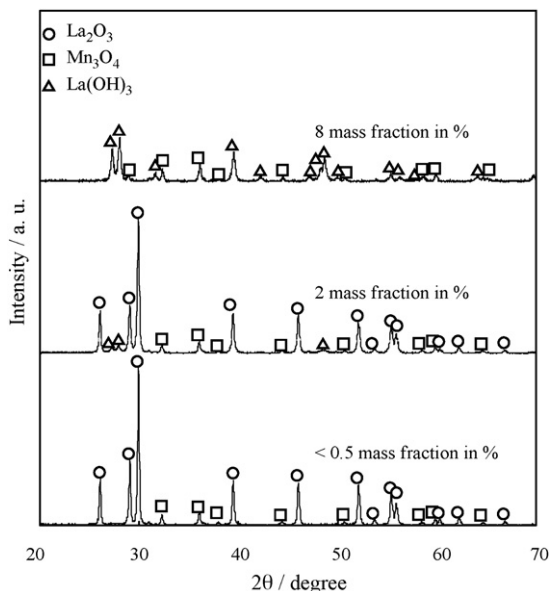


Fig. 1. XRD patterns of starting powder mixtures with different water contents.

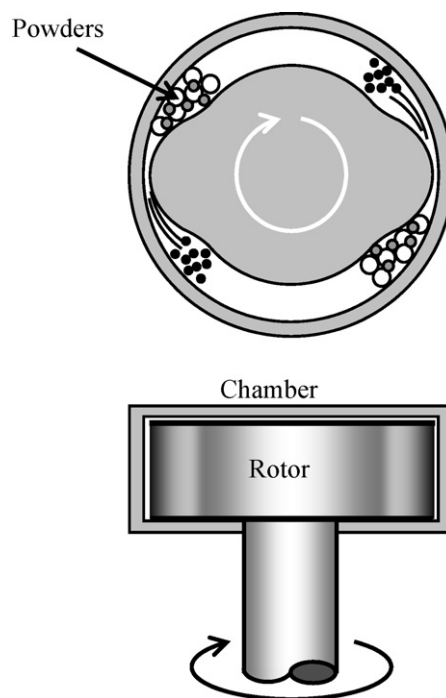


Fig. 2. Schematic illustration of apparatus used in this study.

An attrition-type milling apparatus was employed for the mechanochemical synthesis of LaMnO<sub>3</sub>.<sup>10</sup> Fig. 2 shows a schematic illustration of the apparatus and the powder mixture of 70 g was put into a chamber (400 cm<sup>3</sup>). Its main components are a fixed chamber and a rotor set with a certain clearance against the inside wall of the chamber. Both the chamber and the rotor were made from stainless steel. When the rotor rotates, the powder mixture is compressed into the clearance (1 mm in gap) and received various kinds of mechanical forces such as compression and shearing. The rotating speed of the rotor was 3000 min<sup>-1</sup> and the total milling time was 30 min. Temperature and humidity during the milling experiments were about 25 °C and 50%, respectively.

Phase evolution of the powder mixtures with the milling time was examined by XRD. Ni filtered Cu K $\alpha$  radiation was used as X-ray source. Specific surface area of the powder was measured with nitrogen gas adsorption instruments based on BET method. Morphology of the synthesized LaMnO<sub>3</sub> powder was observed by transmission electron microscopy (TEM).

## 3. Results

Fig. 3 shows the XRD patterns of the powder mixture with the water content of <0.5% mass fraction that has been milled for various time periods: 0, 10, 20 and 30 min. The peaks intensity of La<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub> decreased with increasing milling time. The peaks of LaMnO<sub>3</sub> were observed after 20 min. After milling for 30 min, the peaks mainly consisted of those of La<sub>2</sub>O<sub>3</sub> and LaMnO<sub>3</sub>.

Fig. 4 shows the XRD patterns of the powder mixture with the water content of 2% mass fraction that have been milled for various time periods: 0, 10, 20 and 30 min. Compared to those with

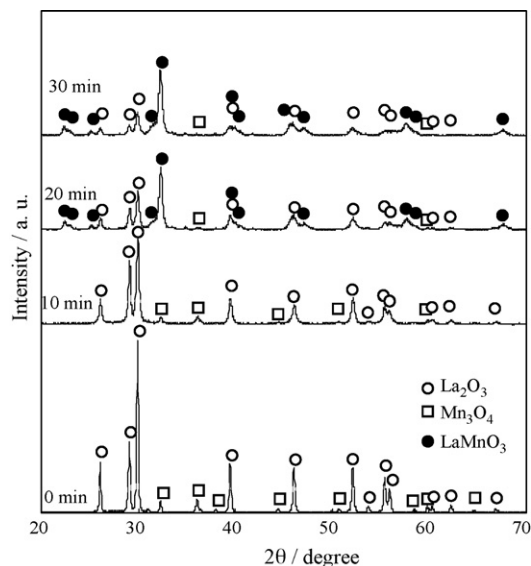


Fig. 3. Phase evolution of the powder mixture with water content of  $<0.5\%$  mass fraction.

the water content of  $<0.5\%$  mass fraction, the peaks intensity of  $\text{La}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  decreased faster with increasing milling time. The formation of  $\text{LaMnO}_3$  was promoted by extending milling time. Finally, single phase of  $\text{LaMnO}_3$  with orthorhombic symmetry (JCPDS 35-1353) was obtained after the milling only for 30 min. Fig. 5 shows the typical TEM image of fine  $\text{LaMnO}_3$  particles synthesized from the powder mixture with the water content of 2% mass fraction. As can be seen, they had highly crystalline structure. The mean particle size calculated from the SSA was about 100 nm.

Fig. 6 shows the XRD patterns of the powder mixture with the water content of 8% mass fraction that have been milled for various time periods: 0, 10, 20 and 30 min. The peaks intensity of  $\text{La}(\text{OH})_3$  and  $\text{Mn}_3\text{O}_4$  decreased with increasing milling time.

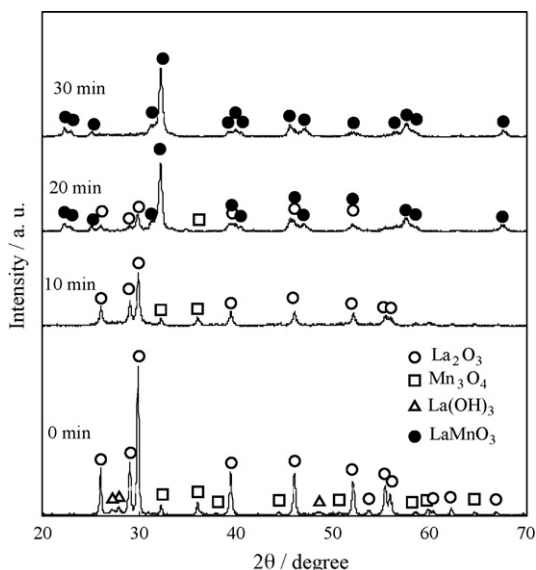


Fig. 4. Phase evolution of the powder mixture with water content of 2% mass fraction.

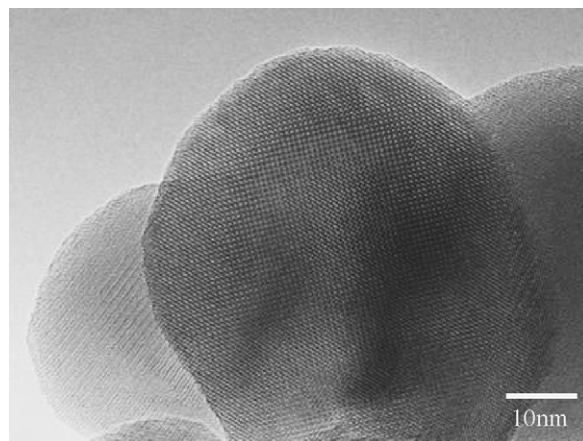


Fig. 5. HRTEM image of  $\text{LaMnO}_3$  powder synthesized from the powder mixture with the water content of 2% mass fraction.

Although the peak of  $\text{LaMnO}_3$  was detected after the milling for 30 min, the peaks of  $\text{La}(\text{OH})_3$  and  $\text{Mn}_3\text{O}_4$  considerably remained.

Fig. 7 shows the influence of the water content in starting powder mixture on change of the SSA with increasing milling time. The SSAs for starting powder mixtures with the water content of  $<0.5$ , 2 and 8% mass fraction were 6.4, 7.7 and 10.6  $\text{m}^2/\text{g}$ , respectively. Before applying mechanical activation, the SSA increase associated with the water content was observed, which was due to the increase in volume by the formation of  $\text{La}(\text{OH})_3$  from  $\text{La}_2\text{O}_3$ . When the water content was  $<0.5\%$  mass fraction, the SSA did not change significantly with increasing milling time. When the water content was 2% mass fraction, the SSA increased drastically during first 10 min, and then it kept almost constant during the further milling up to 30 min. When the water content was 8% mass fraction, the SSA decreased remarkably with increasing milling time, and it was 3.9  $\text{m}^2/\text{g}$  after 30 min.

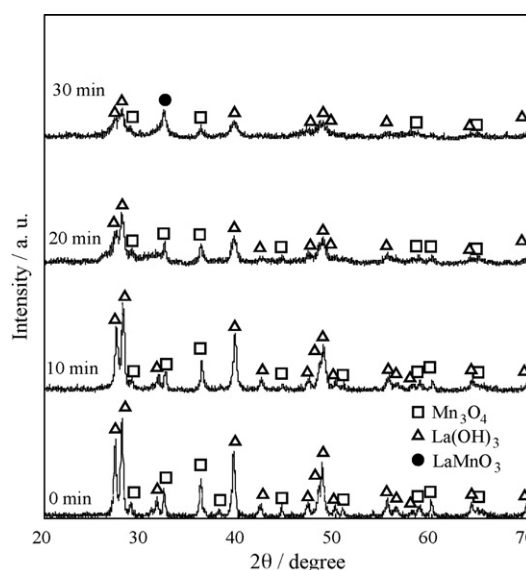


Fig. 6. Phase evolution of the powder mixture with water content of 8% mass fraction.

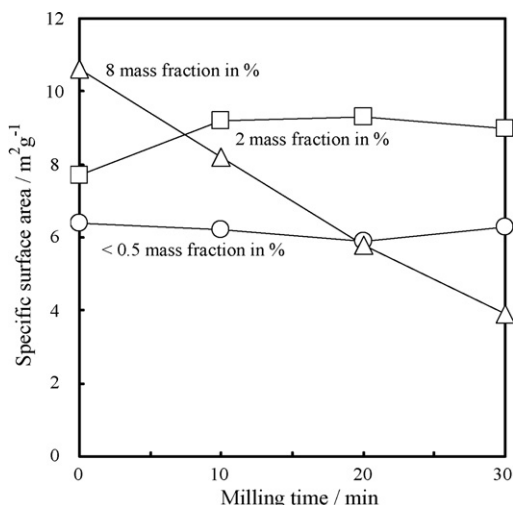


Fig. 7. Influence of water content in starting powder mixture on change of the specific surface area with increasing milling time.

#### 4. Discussion

In this study, it was demonstrated that the water content in starting materials influenced significantly their grinding behavior and the reaction rate for  $\text{LaMnO}_3$ . When the powder mixture had the water content of 2% mass fraction, the single phase  $\text{LaMnO}_3$  was obtained after milling for only 30 min. On the other hand, the reaction was not completed on the drier condition (<0.5% mass fraction) and the wetter condition (8% mass fraction). The optimized water content is currently investigated.

When the powder mixture had the water content of 2% mass fraction, it can be concluded from Figs. 4 and 7 that the following steps proceeded: (1) the finer grinding with structural defects,<sup>12</sup> forming an activated matrix, in the early stage of the milling (<10 min), and (2) solid-state reaction in the activated matrix, which led to the formation of crystalline  $\text{LaMnO}_3$  phase. Localized heating and pressure at regions of contact between the reactant grains may be a contributing factor for the phase formation in the activated matrix. The possibility for hydrothermal process under mechanical milling with water has been also discussed.<sup>9,13</sup> The present phase evolution is still complicated process, and the detail for the two step reaction will be explained in a near future.

For the dried powder mixture (<0.5% mass fraction), almost no SSA increase was seen, and  $\text{LaMnO}_3$  synthesis was not completed after milling for 30 min. The slower reaction compared to that with the water content of 2% mass fraction can be ascribed to less grinding behavior in the early stage of milling. It is known that, in ceramics, a stress enhances chemical reaction between the stretched bonds and the adsorbed polar molecules such as water, and the reaction lowers the surface energy for breaking of the bonds and therefore ceramics will break at a lower applied load.<sup>14–16</sup> The water of 2% mass fraction may have played as a grinding agent for the constituent oxides.

On the other hand, the SSA decreased with increasing milling time, when the water content was 8% mass fraction. After milling for 30 min,  $\text{La}(\text{OH})_3$  and  $\text{Mn}_3\text{O}_4$  phase considerably

remained even after milling for 30 min as shown in Fig. 6. These indicate that the mechanical milling under the excess water rather enhanced aggregation of particles. Watanabe et al. have studied the mechanism of the incipient chemical reaction for milling of  $\text{Ca}(\text{OH})_2$  and  $\text{SiO}_2$  powder mixture.<sup>17–19</sup> The bonding between  $\text{Ca}(\text{OH})_2$  and  $\text{SiO}_2$  based on the formation of  $\text{Ca-O-Si}$  was attributed to mechanochemical dehydration resulting from the acid/base reaction between silanol groups as acid site and surface hydroxyl groups on  $\text{Ca}(\text{OH})_2$  as basic sites. Taking into account the findings of Watanabe et al., it is considered that the present particle aggregation during milling is caused by the formation of oxygen bridging bonds through mechanochemical dehydration. The further studies of the particle aggregation during milling are now in progress.

#### 5. Conclusion

The water content in starting materials influenced significantly their grinding behavior and mechanochemical reaction rate for  $\text{LaMnO}_3$ . The dependence of milling time of the SSA was changed by the water content: (1) at <0.5% mass fraction, the SSA did not change significantly with increasing milling time, (2) at 2% mass fraction, the SSA increased drastically during first 10 min, and then it kept almost constant during the further milling up to 30 min, and (3) at 8% mass fraction, the SSA decreased remarkably with increasing milling time. When the powder mixture had the water content of 2% mass fraction, the single phase  $\text{LaMnO}_3$  was obtained after milling for only 30 min. On the other hand, the reaction was not completed on the drier condition (<0.5% mass fraction) and the wetter condition (8% mass fraction).

#### Acknowledgements

This study was partially supported by Industrial Technology Research Grant Program from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

#### References

- Arakawa, T., Yoshida, Y. and Shiokawa, J., The catalytic activity of rare earth manganites. *Mater. Res. Bull.*, 1980, **15**, 269–273.
- Bell, R. J., Millar, G. J. and Drennan, J., Influence of synthesis route on the catalytic properties of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ . *Solid State Ionics*, 2000, **131**, 211–220.
- Licci, F., Turilli, G., Ferro, P. and Ciccarone, A., Low-temperature synthesis and properties of  $\text{LaMnO}_{3\pm d}$  and  $\text{La}_{0.67}\text{R}_{0.33}\text{MnO}_{3\pm d}$  (R = Ca, Sr, Ba) from citrate precursors. *J. Am. Ceram. Soc.*, 2003, **86**, 413–419.
- Ghosh, A., Sahu, A. K., Gulnar, A. K. and Suri, A. K., Synthesis and characterization of lanthanum strontium manganite. *Scripta Mater.*, 2005, **52**, 1305–1309.
- Stojanovic, B. D., Mechanochemical synthesis of ceramic powders with perovskite structure. *J. Mater. Process. Technol.*, 2003, **143/144**, 78–81.
- Tsuzuki, T. and McCormick, P. G., Mechanochemical synthesis of nanoparticles. *J. Mater. Sci.*, 2004, **39**, 5143–5146.
- Koch, C. C., In *Processing of Metals and Alloys, Vol. 15 of Materials Science and Engineering—A Comprehensive Treatment*, ed. R. W. Cahn. VCH Verlagsgesellschaft, Weinheim, F.R. Germany, 1991, pp. 193–245.
- Zhang, Q. and Saito, F., Mechanochemical synthesis of  $\text{LaMnO}_3$  from  $\text{La}_2\text{O}_3$  and  $\text{Mn}_2\text{O}_3$  powders. *J. Alloys Compd.*, 2000, **297**, 99–103.

9. Avvakumov, E. G., Devyatkina, E. T. and Kosova, N. V., Mechanochemical reactions of hydrated oxides. *J. Solid State Chem.*, 1994, **113**, 379–383.
10. Sato, K., Chaichanawong, J., Abe, H. and Naito, M., Mechanochemical synthesis of  $\text{LaMnO}_{3+\delta}$  fine powder assisted with water vapor. *Mater. Lett.*, 2006, **60**, 1399–1402.
11. Leskela, M. and Ritala, M., Rare-earth oxide thin films as gate oxides in MOSFET transistors. *J. Solid State Chem.*, 2003, **171**, 170–174.
12. Thadhani, N. N., Shock-induced and shock-assisted solid-state chemical reactions in powder mixtures. *J. Appl. Phys.*, 1994, **76**, 2129–2138.
13. Boldyrev, V. V., Hydrothermal reactions under mechanochemical action. *Powder Technol.*, 2002, **122**, 247–254.
14. Gong, J. and Du, C., Environmental effects on the room-temperature static fatigue behavior of polycrystalline mullite. *Mater. Sci. Eng. A*, 2000, **283**, 76–81.
15. van der Laag, N. J., van Dijk, A. J. M., Lousberg, N. and de With, G., The influence of water on the fracture of magnesium aluminate ( $\text{MgAl}_2\text{O}_4$ ) spinel. *J. Am. Ceram. Soc.*, 2005, **88**, 660–665.
16. Richerson, D. W., *Modern Ceramic Engineering*. Marcel Dekker Inc., New York, 1992, 326 pp.
17. Watanabe, T., Liao, J. F. and Senna, M., Changes in the basicity and species on the surface of  $\text{Me}(\text{OH})_2\text{-SiO}_2$  (Me = Ca, Mg, Sr) mixtures due to mechanical activation. *J. Solid State Chem.*, 1995, **115**, 390–394.
18. Watanabe, T., Isobe, T. and Senna, M., Mechanisms of incipient chemical reaction between  $\text{Ca}(\text{OH})_2$  and  $\text{SiO}_2$  under moderate mechanical stressing. I. A solid state acid–base reaction and charge transfer due to complex formation. *Solid State Chem.*, 1996, **122**, 74–80.
19. Watanabe, T., Isobe, T. and Senna, M., Mechanisms of incipient chemical reaction between  $\text{Ca}(\text{OH})_2$  and  $\text{SiO}_2$  under moderate mechanical stressing. II. Examination of a radical mechanism by an EPR study. *J. Solid State Chem.*, 1996, **122**, 291–296.