

## MAS NMR AND SEM STUDY OF LOCAL STRUCTURE CHANGES INDUCED BY HEAT TREATMENT IN $\text{La}_2\text{B}_4\text{Al}_2\text{O}_{12}$

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Xerogels of composition  $\text{La}_2\text{B}_4\text{Al}_2\text{O}_{12}$ , treated between 200 and 1100°C, are investigated by magic angle spinning nuclear magnetic resonance (MAS NMR) and scanning electron microscopy (SEM). The  $^{11}\text{B}$  MAS NMR results indicate the presence of tetra coordinated boron in all investigated samples. For three coordinated boron, two sites were observed one of them being present only after heat treatment above 860 °C when the sample become crystalline. The mean values of the NMR parameters like chemical shift, asymmetry parameter and quadrupolar coupling constant are strongly influenced by the heat treatment temperature. SEM results are correlated with them obtained by NMR.

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### 1. Introduction

The porous mixed oxides based on aluminium oxide proved to be interesting candidates as supporting materials in catalytic combustion above 1000 °C [1]. The Al substitution by transition-metal or rare-earth ions induces interesting optic, magnetic and catalytic properties in these materials [2-5]. The structural stability of these compounds heat treated at temperatures of interest for their potential applications is thus a decisive point to be studied.

The stabilising effect of boron [6, 7] and lanthanum [8] on low coordinated aluminium in amorphous and crystalline aluminates has been proved to be important from a catalytic point of view.

The aim of this work is to study the effect of heat treatment on the structure of amorphous and crystalline aluminates with lanthanum and boron, prepared by sol-gel technique, over wide temperature range.

### 2. Experimental

Lanthanum alumino-borates samples with composition  $\text{La}_2\text{B}_4\text{Al}_2\text{O}_{12}$  were prepared by sol-gel route. The thermal decomposition of boric acid, lanthanum and aluminium nitrates mixture was assisted by the pyrolysis of glycerol added (10 wt %) as an organic reducing agent. The components readily dissolved in a small amount of distilled water to give a clear solution at room temperature. By heating these solutions at 95 °C for about 1.5 h viscous gels were formed and a subsequent heat treatment at the same temperature resulted in spongy, bulky, solid samples. The as formed solid samples were heat treated for 0.5 h at 200, 400, 600, 860, 1000 and 1100 °C in air flow.

Taking into account that  $^{11}\text{B}$  nucleus has the nuclear spin  $I = 3/2$  than, as a consequence of its quadrupolar moment, it is a very efficient source of information by means of Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) [9] about the local order around this nucleus. The  $^{11}\text{B}$  MAS-NMR measurements were carried out at room temperature on Chemagnetics Infinity 600 MHz spectrometer equipped with a solid-state accessory, with MAS frequency of 15 kHz. All the profiles

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were simulated with home-made software. The reference for the chemical shift was  $\text{H}_3\text{BO}_3$  in NaOH with  $\text{pH}=11.5$ .

For SEM a Philips SEM-XL30-FEG with an EDAX energy dispersive spectrometer (EDS) was used.

### 3. Results and discussion

$^{11}\text{B}$  MAS NMR spectra of investigated materials are presented in Fig. 1. The line with chemical shift around 0 ppm correspond to tetra-coordinated boron ( $\text{B}_{4c}$ ). This coordination seems to be quite stable during the heat treatment. On the other hand, we have the boron lines with chemical shift between 15 and 20 ppm assigned to three coordinated boron ( $\text{B}'_{3c}$  and  $\text{B}''_{3c}$ ). It one observes easily, from the shape of spectra, that above 860 °C the compound is crystalline, under this temperature being amorphous. There are two sites representing three-coordinated boron that indicates the presence of at least two different crystalline phases.

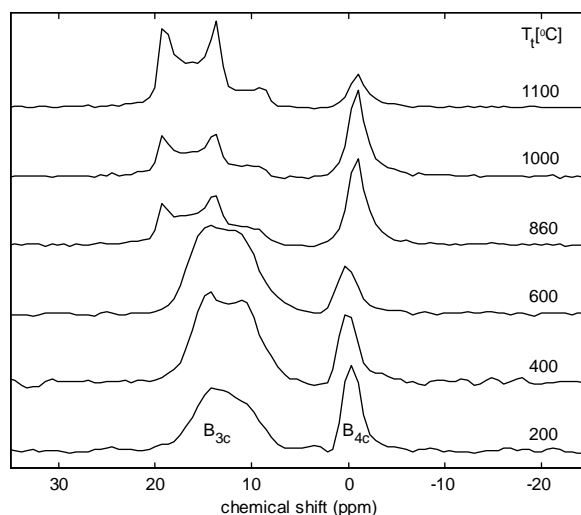


Fig. 1.  $^{11}\text{B}$  MAS NMR spectra of  $\text{La}_2\text{B}_4\text{Al}_2\text{O}_{12}$  after heat treatment.

In Fig. 2 is represented the deconvolution of the  $^{11}\text{B}$  MAS NMR spectrum of the sample obtained after heat treatment at 1100 °C.

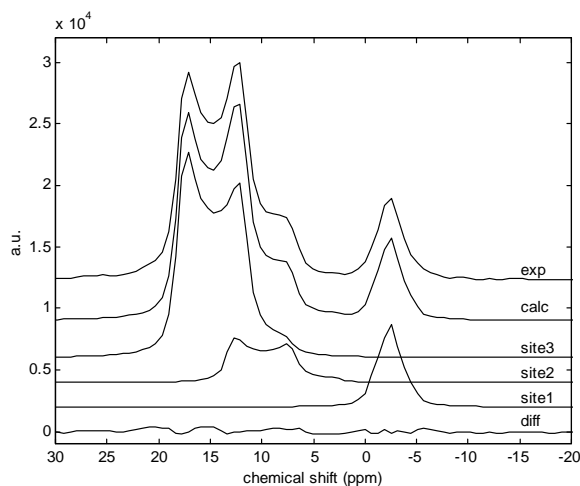


Fig. 2. Deconvolution of the  $^{11}\text{B}$  MAS NMR spectrum of  $\text{La}_2\text{B}_4\text{Al}_2\text{O}_{12}$  treated 30 min at 1100 °C.

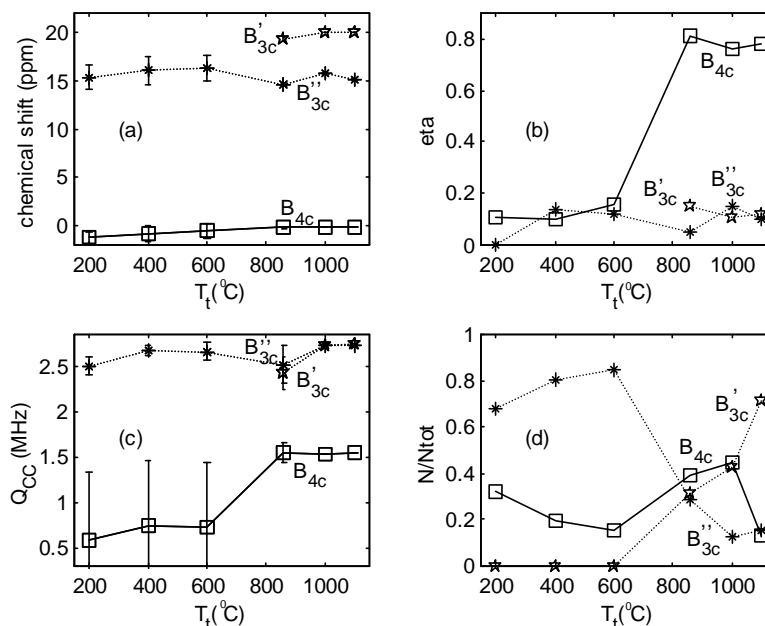


Fig. 3. The chemical shift (a), asymmetry parameter (b), quadrupolar coupling constant (c) and relative intensity of the lines (d) dependence of heat treatment temperature.

After the simulation of all spectra it was possible to draw the evolution of NMR parameters (chemical shift, asymmetry parameter, quadrupolar coupling constant) and of the relative intensity of the lines during the heat treatment, as it is shown in Fig. 3. The vertical bars represent the widths of the chemical shift and quadrupolar coupling constant distributions. The decrease of those widths with the heat treatment temperature indicates that the boron environments become more ordered. The major changes in the NMR parameters took place between 600 and 860 °C, where the crystallization occurs.

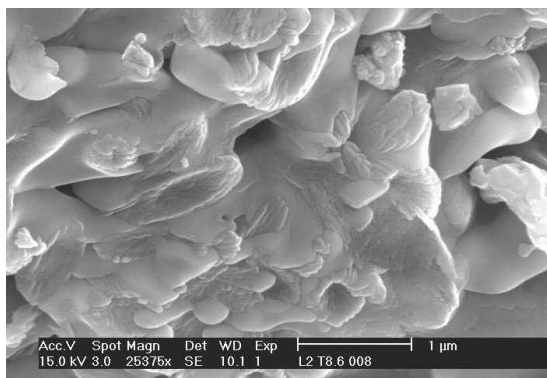


Fig. 4. SEM picture of  $\text{La}_2\text{B}_4\text{Al}_2\text{O}_{12}$  after heat treatment at 860 °C.

This fact is confirmed also by electronic microscopy. Fig. 4 shows a SEM picture of the sample after heat treatment at 860 °C. It is a very good image of the crystallisation process, which is in progress at this temperature. It is seen the amorphous zone and the nuclei of crystallisation.

Fig. 5 shows the SEM picture of the sample after heat treatment at 1100 °C. Here it can be seen all three phases present in the studied material, identified by X-ray diffraction [10]. Big crystals of light colour represent the  $\text{La}_{1-x}\text{Al}_x\text{BO}_3$  phase, the main phase in this sample. Small crystals with the shape of rice grain represent the  $9(\text{Al}_2\text{O}_3)2(\text{B}_2\text{O}_3)$  phase [11], which is in a small amount here. Big crystals of dark colour represent the  $\text{LaAl}_{2.03}\text{B}_4\text{O}_{10.54}$  phase [12].

The identified three sites for boron in the crystalline samples can be assigned to these three phases as follows:  $\text{B}_{4c}$  to  $\text{LaAl}_{2.03}\text{B}_4\text{O}_{10.54}$  phase,  $\text{B}_{3c}'$  to  $\text{La}_{1-x}\text{Al}_x\text{BO}_3$  phase and  $\text{B}_{3c}''$  to  $9(\text{Al}_2\text{O}_3)2(\text{B}_2\text{O}_3)$  phase. This doesn't apply to amorphous samples, where these phases are not yet formed.

After analysing the X-ray diffraction patterns [10], NMR and SEM results it can be concluded that  $\text{La}_{1-x}\text{Al}_x\text{BO}_3$  phase is present as main phase in sample obtained after heat treatment at temperatures between 860 and 1100 °C. This phase consist of  $\text{LaBO}_3$  with lanthanum partially substituted by aluminium. The  $\text{LaAl}_{2.03}\text{B}_4\text{O}_{10.54}$  phase is secondary and its amount decreases with temperature, in the region 860 – 1000 °C, being replaced by  $9(\text{Al}_2\text{O}_3)2(\text{B}_2\text{O}_3)$  phase.

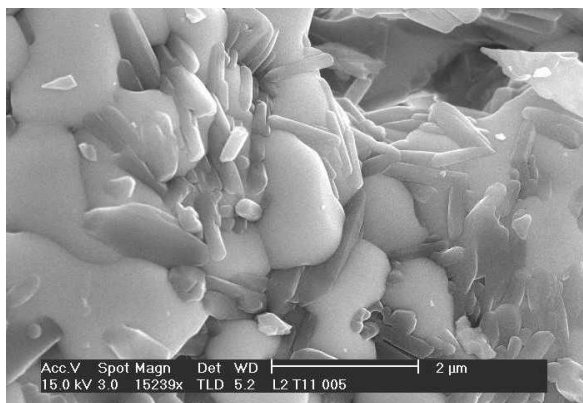


Fig. 5. SEM picture of  $\text{La}_2\text{B}_4\text{Al}_2\text{O}_{12}$  after heat treatment at 1100 °C.

#### 4. Conclusions

In the  $\text{La}_2\text{B}_4\text{Al}_2\text{O}_{12}$  xerogels treated in the temperature range 860 - 1100 °C a  $\text{LaBO}_3$  type structure is formed, that incorporates aluminium atoms in lanthanum crystallographic positions. The boron atoms are three coordinated in this phase. The (La, Al) $\text{BO}_3$  phase is accompanied by the appearance of a small quantity of  $\text{LaAl}_{2.03}\text{B}_4\text{O}_{10.54}$  transition phase with tetra-coordinated boron, which decreases as the heat treatment temperature increases up to 1100°C. In the same time the amount of  $9(\text{Al}_2\text{O}_3)2(\text{B}_2\text{O}_3)$  phase where boron atoms are three-coordinated is decreasing.

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#### References

- [1] D. L. Trimm, *Appl. Catal.* **7**, 249 (1983).
- [2] S. Ikoma, K. Kawakita, H. Yokoi, *J. Non. Cryst. Solids* **122**, 183 (1990).
- [3] J. G. Darab, R. K. MacCrone, *Phys. Chem. Glasses* **32**, 191 (1991).
- [4] S. Tanabe, K. Hiaro, N. Soga, T. Hanada, *J. Solid State Chem.* **97**, 481 (1992).
- [5] R. Bechara, A. Aboukais, J. P. Bonnelle, *J. Chem. Soc. Faraday Trans.* **89**, 1257 (1993).
- [6] S. Simon, A. van der Pol, E. J. Reijerse, A. P. M. Ketgens, G. J. van Moorsel, E. de Boer, *J. Chem. Soc. Faraday Trans.* **90** (18), 2663 (1994).
- [7] S. Simon, G. J. van Moorsel, A. P. M. Ketgens, E. de Boer, *Solid State Nucl. Magn. Reson.* **5**, 163 (1995).
- [8] D. Iuga, S. Simon, E. de Boer, A. P. M. Ketgens, *J. Phys. Chem. B* **103**, 7591 (1999).
- [9] M. Vasilescu, S. Simon, *Mod. Phys. Lett. B* **16** (12), 1 (2002).
- [10] S. Simon, M. Pop, Gh. Borodi, D. Djurado, *Mod. Phys. Lett. B*, **16**, 23&24, 915 (2002).
- [11] D. Massiot, D. Muller, Th. Hubert, M. Schneider, A. P. M. Kentgens, B. Cote, J. P. Coutures, W. Gessner, *Solid State Nucl. Magn. Reson.* **5**, 175 (1995).
- [12] P. Yang, Wentao Yu, J. Y. Wang, J. Q. Wei, Y. G. Liu, *Acta Cryst. Section C* **54**, 11 (1198).