

SPECTROSCOPIC CHARACTERISATION OF CRYSTALLINE PHASES DEVELOPMENT FROM AMORPHOUS PRECURSORS

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The development of $\text{LaAl}_{2.03}\text{B}_4\text{O}_{10.5}$ (124) lanthanum aluminoborate crystalline phase from amorphous xerogels is characterised by Magic Angle Spinning Nuclear Magnetic Resonance (MASNMR), Electron Paramagnetic Resonance (EPR) and Fourier Transform Infrared (FTIR) spectroscopies. The crystallisation of amorphous xerogels takes place between 760 and 860 °C. The major changes are evidenced both in the boron and aluminium surrounding. These structural results are correlated with those obtained from ^{27}Al and ^{11}B MAS NMR spectra. The boron environment is changed from three-coordinated in amorphous samples to tetra-coordinated in the crystalline samples. Aluminium occurs in amorphous samples as hexa-, penta- and tetra-coordinated by oxygens while in the crystalline ones it appears preponderantly penta-coordinated. From FTIR measurements it results, also, that the local structure dramatically changes when in amorphous matrices are developed crystalline phases. Three different sites for Fe^{3+} ions in crystalline samples were identified by EPR measurements.

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1. Introduction

Amorphous and crystalline aluminates are intensively studied for their interesting properties that are making them suitable for different applications like supporting materials in catalytic reactions [1, 2]. It was found that the presence of rare earths like lanthanum preserves their porosity, and boron stabilises the penta-coordinated aluminium species, both effects being important for catalytical purposes [3].

Up to now only one stable crystalline phase is known in the ternary lanthanum-aluminium-boron oxide system [4]. The composition of this crystalline phase is $\text{LaAl}_{2.03}\text{B}_4\text{O}_{10.54}$ (124) and in its structure the La, Al and B atoms are surrounded by oxygen atoms in trigonal prismatic, pyramidal and tetrahedral arrangements, respectively. It is an interesting oxide compound in which all cations exhibit unusually coordinations: lanthanum is hexa-coordinated, aluminium penta-coordinated and boron tetra-coordinated.

The local arrangements of the structural disordered oxides have been investigated by different techniques like: nuclear magnetic [5-9] and electron paramagnetic resonances [10-12], Raman [13, 14] and infrared spectroscopies [15-17]. Due to the lack of structural long range order in amorphous oxides an unambiguous assignment of the structural groups is not possible without comparing their spectra with those of corresponding crystalline counterparts.

The structural disordered form of the oxide compound with a composition corresponding to $\text{LaAl}_{2.03}\text{B}_4\text{O}_{10.54}$ crystalline phase can be obtained by rapid undercooling of the mixture melted at temperatures above 1400 °C or by sol-gel procedure [18, 19]. The last method is much proper for the investigation of the local structural changes during the transformation from disordered system to the well-defined crystalline phase and for preparing the porous aluminates for catalytical applications.

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The aim of this study is to characterise the evolution of the local structure in initially non-crystalline lanthanum aluminoborate of composition $\text{LaAl}_2\text{B}_4\text{O}_{10.5}$ as a function of the heat treatment applied up to 1100 °C, using MASNMR, EPR and FTIR spectroscopies.

2. Experimental

The system $\text{La}_2\text{O}_3 \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{B}_2\text{O}_3$ was prepared by sol-gel method [18] from aqueous solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and H_3BO_3 of analytical purity grade by thermal decomposition of starting nitrates and boric acid accompanied by simultaneous oxidation of glycerol. The reagents mixture solved in desalted water appears as a transparent solution at room temperature. A viscous gel is obtained after 5 hours heating at 95 °C. Further heating at this temperature leads to a spongy solid sample initially amorphous and later crystalline. The investigated samples were obtained after heat treatment for 30 minutes at different temperatures, T_t , between 150 and 1100 °C. Noncrystalline samples of the same composition have been obtained by rapid cooling at room temperature of the corresponding oxide mixtures melted at 1450 °C for 30 minutes.

The ^{27}Al and ^{11}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 using as references aqueous solutions of boric acid and aluminium nitrate, respectively. The IR spectra were recorded on a FT/IR-610 JASCO spectrometer at room temperature in the wavenumbers range 400 - 4000 cm^{-1} using the KBr disk technique. Due to the high hygroscopicity of KBr it was difficult to avoid the water adsorption during the prolonged grinding of powdered sample in KBr. The EPR measurements were carried out on powder samples at room temperature using a Bruker 300E spectrometer at 9.45 GHz.

3. Results and discussion

The differential thermal curve points out that structural changes related to the development of crystalline phases appear above 750 °C. For samples prepared by sol-gel method this process starts at 760 °C and different changes appear up to 950 °C as a result of successive phase transformations to the preponderant final crystalline phase of composition $\text{LaAl}_{2.03}\text{B}_4\text{O}_{10.5}$. These transformations were confirmed by X-ray diffraction studies. The xerogels resulted after heat treatments at temperatures up to 750 °C are amorphous as shown by X-ray diffraction patterns. The 124 phase is prevalent in the samples after heat treatment at temperatures above 1000 °C. Some other phases like $\text{Al}_{18}\text{B}_4\text{O}_{33}$ and $\text{La}(\text{Al})\text{BO}_3$ are also developed in small amount (less than 10 %).

The ^{27}Al and ^{11}B MAS-NMR spectra of the samples prepared by sol-gel method are presented in Fig. 1. In amorphous samples three types of aluminium (tetra-, penta- and hexa-coordinated) are evidenced and two types of boron (three- and tetra-coordinated) like in other amorphous oxides [1-3, 5-9]. In the crystalline samples there are almost only penta-coordinated aluminium and tetra-coordinated boron species.

The FTIR spectra of the investigated samples are given in Fig. 2. One remarks an apparent resemblance between the spectra recorded on samples heat treated between 150 and 750 °C and for the spectra recorded on samples heat treated between 860 and 1100 °C. For the first group of spectra the profile consists in large bands typical for disordered systems, while for the second one the narrow bands are characteristic for crystalline samples. Crystalline and non-crystalline borates are known to consist of different structural arrangements, which are composed of BO_3^{3-} triangles and BO_4^- tetrahedra with or without non-bridging oxygen ions [15].

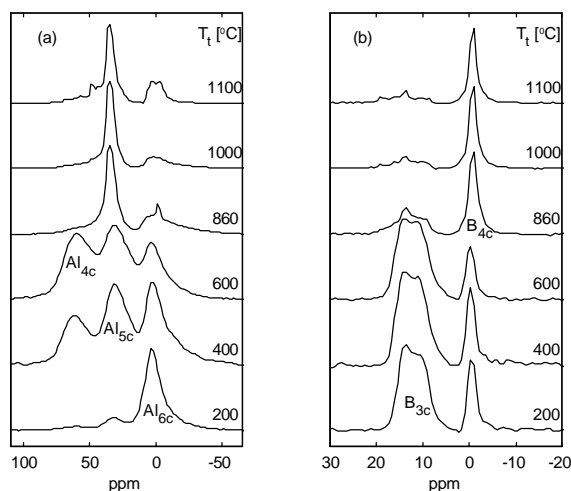


Fig. 1. MAS NMR spectra of samples prepared by sol-gel method, ^{27}Al MAS NMR (a) and ^{11}B MAS NMR (b).

The absorption bands in the infrared spectra of borate glasses are generally assigned to vibrational modes of BO_3^{3-} and BO_4^- units present in the structural grouping like boroxol, pentaborate, triborate, diborate, ring-type metaborate, chain-type metaborate, pyroborate and orthoborate [14].

In the spectrum of the sample heated at 150°C , the intense broad band at $\sim 3430\text{ cm}^{-1}$ is assigned to stretching vibrations of the OH groups from crystallisation water remained in samples from the starting reagents and from the physically adsorbed water either on the pore walls of the samples or on KBr. The intensity of this band gradually decreases and for samples heated above 410°C it is mainly due to water adsorbed during the preparation of KBr disks. The band corresponding to bending vibration from water is observed at $\sim 1630\text{ cm}^{-1}$ in all spectra. The two weak bands at 2923 and 2853 cm^{-1} that correspond to the asymmetric and symmetric stretching vibrations of the CH_2 groups, are observed in the spectra of all samples and arise from the organic impurities occurring in KBr.

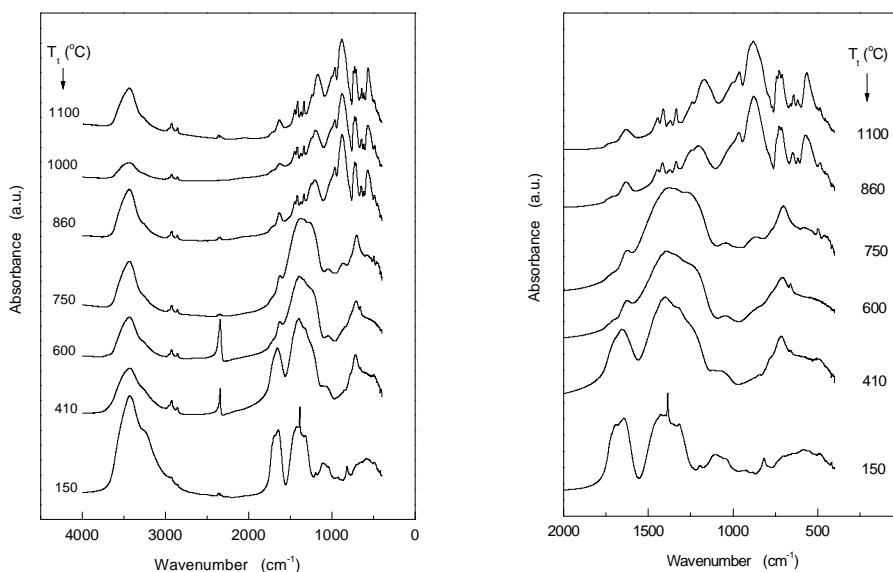


Fig. 2. FTIR absorption spectra for samples heat treated at different temperatures, recorded in the wavenumber range from 4000 to 450 cm^{-1} (a) and from 2000 to 450 cm^{-1} (b).

For a better assignment of the lines occurring in the IR spectra, the region between 2000 and 450 cm^{-1} is expanded in Fig. 2b. The band located at $\sim 1400 \text{ cm}^{-1}$ in the spectrum of the sample annealed at $T_t = 150 \text{ }^\circ\text{C}$ is assigned to BO_3^{3-} units or to other groups containing three-coordinated boron resulting from the reaction between boric acid and glycerol. When the annealing temperature increases new bands at lower wave numbers appear: $\sim 1330 \text{ cm}^{-1}$ for the sample treated to $410 \text{ }^\circ\text{C}$, ~ 1330 and $\sim 1260 \text{ cm}^{-1}$ for the sample heated to 600° or $750 \text{ }^\circ\text{C}$. This shift is partially due to the local distortions that take place when the dry xerogels are developed and surface hydroxyls are removed.

The well defined band recorded for the crystalline samples around 960 cm^{-1} corresponds to the relatively weak and large bands centred, for the amorphous samples, at about 1050 cm^{-1} and attributed to the BO_4^- tetrahedra. In the spectra of amorphous samples there was identified a small contribution from the BO_4^- units around 870 cm^{-1} . In this region develops an intense peak in the spectra of crystalline samples on the expense of the band situated in the range $1100 - 1500 \text{ cm}^{-1}$ from the spectra of amorphous samples, band assigned to BO_3^{3-} units. This intense peak is assigned to BO_4^- units from the main 124 phase where only tetra-coordinated boron exists.

The correlation between IR absorption bands and different types of aluminate polyhedra is based on IR results obtained for aluminate crystals. The Al-O stretching vibrations of tetrahedral AlO_4 groups are related to the bands in the region $900 - 750 \text{ cm}^{-1}$ and the bands in $650 - 400 \text{ cm}^{-1}$ region are associated with stretching modes of AlO_6 octahedra. Between these two relatively large regions some bands appear for the compounds with penta-coordinated aluminium [20].

Inspecting the IR spectral region below 900 cm^{-1} , a region with contributions from the aluminium polyhedra, one remarks first a relatively narrow peak at 820 cm^{-1} for the sample heat treated at $150 \text{ }^\circ\text{C}$, peak assigned to Al-OH bonds from aluminium hydrate that also gives the band at around 1110 cm^{-1} [21]. For the same sample in the region $600 - 450 \text{ cm}^{-1}$ there is a broad band related to the AlO_6 octahedra. For the next three samples, obtained after heat treatments at 410 , 600 and $750 \text{ }^\circ\text{C}$, the main band is centred at 710 cm^{-1} and can be assigned to the penta-coordinated aluminium that are the main aluminium species in amorphous aluminium xerogels after heat treatment at such temperatures [3, 8]. A relatively weak contribution from the AlO_4 tetrahedra can be identified as a shoulder on the left side of the peak at 710 cm^{-1} [22].

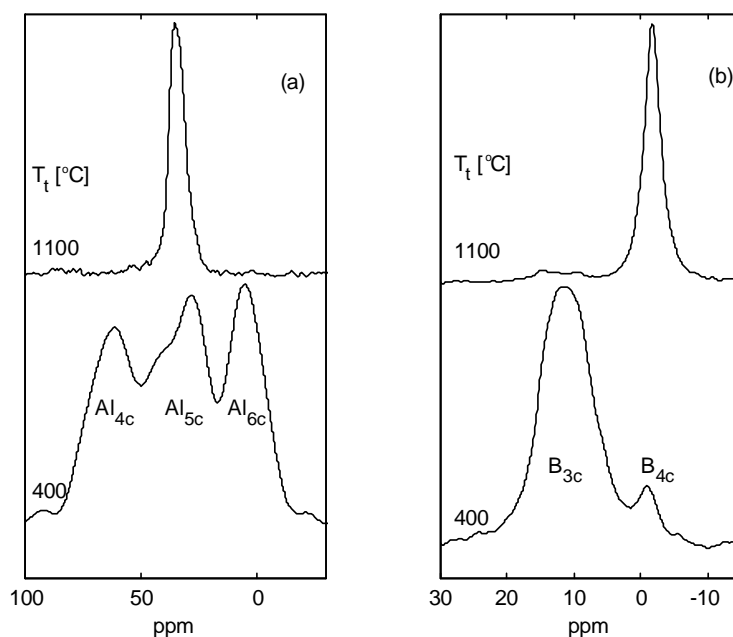


Fig. 3. ^{27}Al (a) and ^{11}B (b) MAS NMR spectra of vitreous and crystalline samples.

The contributions from different aluminium polyhedra to the IR bands are better evidenced in the spectra of crystalline samples. The peak at 565 cm^{-1} is due to the hexa-coordinated aluminium, while the contributions from different types of penta-coordinated aluminium are located at $600 - 750\text{ cm}^{-1}$. The lanthanum polyhedra are reflected by the weak peak located at 642 cm^{-1} in the IR spectra of crystalline samples.

For comparison, in Fig. 3 are presented the MAS NMR spectra of the amorphous and crystalline samples prepared by rapid undercooling of melts after heat treatment at $400\text{ }^{\circ}\text{C}$, where X-ray diffraction patterns shows an amorphous state, and after 2 hours heat treatment at $1100\text{ }^{\circ}\text{C}$, when the samples become crystalline and almost only 124 lanthanum aluminoborate phase is present.

The main difference is evidenced between MAS NMR spectra of glassy samples and amorphous xerogels showing a much distorted environment for both aluminium and boron in amorphous samples obtained by rapid cooling of the oxides mixture melt.

The same differences can be observed between the FTIR spectra of these two kind of amorphous samples (Fig. 4), particularly for the lines assigned to the boron units. The bands assigned to the boron units are wider in the case of glassy sample (Fig. 4-c) than in the case of the amorphous xerogel (Fig. 4-a).

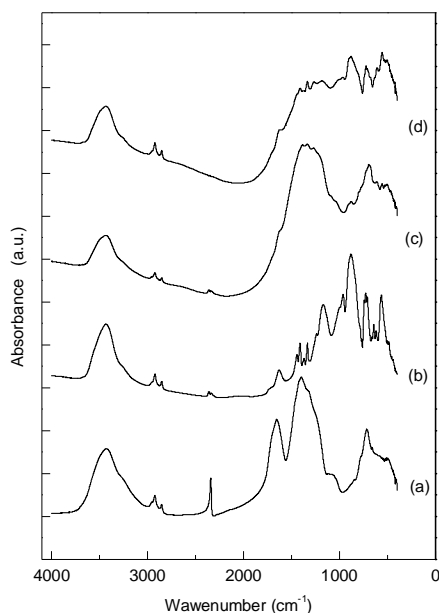


Fig. 4 FTIR spectra of (a) amorphous xerogel, (b) crystalline sample obtained from (a) after 30 minutes heat treatment at $1100\text{ }^{\circ}\text{C}$, (c) glass sample and (d) corresponding crystalline sample obtained (c) after heat treatment 30 minutes at $1100\text{ }^{\circ}\text{C}$.

There are differences, also, between the spectra corresponding to the crystalline samples showing that in the crystalline samples obtained from glass (Fig. 4-d) the environments of boron and aluminium are not so well organised as for crystalline samples obtained from amorphous xerogel (Fig. 4-b).

The ESR measurements on amorphous samples detect a signal at $g \approx 4.3$ from Fe^{3+} ions present as impurities in the investigated samples like in almost all aluminates. In the samples obtained after heat treatment at $1100\text{ }^{\circ}\text{C}$ the ESR spectra indicate that Fe^{3+} ions occupy at least three different sites corresponding probably to those of aluminium, lanthanum and boron in the crystalline 124 phase.

4. Conclusions

The spectroscopic investigations evidence in all amorphous lanthanum aluminoborates synthesised by sol-gel method or by rapid cooling of the oxide melts the occurrence of boron in BO_3 triangles and BO_4 tetrahedra and of aluminium polyhedra with aluminium tetra-, penta- and hexa-coordinated by oxygens. While borons appear mainly as three-coordinated, there is no special preference of aluminium species for a certain coordination.

Both physically adsorbed water and compounds resulted by decomposition of nitrates and by glycerol pyrolysis are identified in the infrared spectra recorded for samples obtained after heat treatments at 150 and 410 °C. That is in agreement with the sequences of sol-gel synthesis procedure.

The local order is strongly affected when one passes from amorphous xerogels to crystalline lanthanum aluminoborate phases. The most pronounced transformations are evidenced for the heat treatments applied in the range 750 - 860 °C when, by crystallisation, the boron atoms change from predominantly three-coordinated to tetra-coordinated and aluminium atoms from tetra- penta- and hexa-coordinated to predominantly penta-coordinated.

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