

Effect of heat treatment time on local structure of lanthanum–aluminum–gallium–borate xerogels

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Abstract

The aim of this study was to investigate the effect of 850 °C heat treatment time on LaAlGaB₅O₂₄ amorphous xerogel. Structural changes were evidenced by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. If xerogel remains non-crystalline after 5 min treatment, nanocrystallites of LaAl_{2.03}(B₄O₁₀)O_{0.54} type are developed after 15 min treatment and this is the sole crystalline phase preserved by increasing the treatment time up to 24 h. Boron, aluminum and gallium units from amorphous xerogel are drastically changed by crystallization, but they are only slightly affected by increasing the 850 °C treatment from 15 min to 24 h.

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1. Introduction

The mixed porous oxides are intensely investigated in view of their potential applications as support materials for catalysis [1–3]. The presence of rare earths in these materials induces beside catalytical properties interesting optical and magnetic properties [4]. It was shown that rare earths, like lanthanum, contribute to a reasonable preservation of sample porosity under thermal treatments [5] and along with post-transitional elements, like aluminum and gallium, and metalloid boron induce to their systems interesting optical, magnetic and catalytic properties. These properties are in strong relation with the samples structure. The presence of aluminum and gallium in glass network makes the glasses more resistant because AlO₄ and GaO₄ structural units may cross-link the neighboring borate chains [6].

Systems with catalytical properties and structurally stable at 850 °C are expected to display high stability and durability under practical working conditions for automotive catalysts, since the temperature of the exhaust gases in auto engines does not exceed this temperature [7,8].

The present study is focused on investigation of local structure changes due to 850 °C isothermal treatment applied for different times on lanthanum–aluminum–gallium–borate LaAlGaB₅ oxide system, evidenced by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy.

2. Experimental

LaAlGaB₅O₂₄ system was prepared following sol–gel route using aqueous solutions of H₃BO₃, La(NO₃)₃·6H₂O, Al(NO₃)₃·9H₂O and Ga(NO₃)₃·xH₂O, which were mixed together at room temperature and thereafter heated at 95 °C for 90 min, resulting in a viscous gel. Further heating at higher temperatures led to xerogel samples, that remain amorphous up to 850 °C. The amorphous xerogel was isothermally treated at 850 °C for 0.5, 5, 15, 30 min, and 24 h.

X-ray diffraction (XRD) analyses were made on a Shimadzu XRD-6000 diffractometer using Ni-filtered CuK_α radiation ($\lambda=1.5418$ Å) at a scanning speed of 2°/min.

Fourier transform infrared (FTIR) spectra were recorded with a resolution of 2 cm⁻¹, 30 scans, on a Bruker spectrophotometer at room temperature using KBr disk technique.

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3. Results and discussion

The X-ray diffraction analysis points out the vitreous state of $\text{LaAlGaB}_5\text{O}_{24}$ xerogel, that is still preserved after 0.5 and 5 min treatment at 850°C (Fig. 1). After 15 min treatment, nanocrystallites of $\text{LaAl}_{2.03}(\text{B}_4\text{O}_{10})\text{O}_{0.54}$ type [9] are developed. In $\text{LaAl}_{2.03}(\text{B}_4\text{O}_{10})\text{O}_{0.54}$ crystalline phase boron and aluminum are only tetracoordinated and pentacoordinated, respectively. The treatment extension up to 24 h enhances the growth of this crystalline phase, without to promote the development of any other structurally ordered phases.

The crystallites size, estimated with Scherrer equation, slightly increases from 25 nm after 15 min, to 27 nm after 30 min, and to 31 nm after 24 h treatment at 850°C . It is worth to note the very weak size increase from the value determined after 15 min treatment to that reached after the much longer 24 h treatment, that suggests that the number of crystallites increased and not so much their size.

In multicomponent borate systems the amorphous matrix mainly consists of BO_3 and BO_4 units [10]. In the infrared

spectra of still vitreous samples after 0.5 and 5 min treatment, the absorption bands occur around 480, 694, 872, 1027, 1215 and 1400 cm^{-1} (Fig. 2). The 1215 and 1400 cm^{-1} bands are assigned to BO_3 units, that at 872 and 1027 cm^{-1} to BO_4 units, while 480 and 694 cm^{-1} bands are related to hexacoordinated and pentacoordinated aluminum, respectively [11]. A contribution from tetracoordinated aluminum to the large band around 694 cm^{-1} should be also considered [12].

In Ga_2O_3 mixed glasses was identified an absorption band around $610\text{--}620\text{ cm}^{-1}$ assigned to the vibrations of GaO_4 structural units [6,13]. Ga_2O_3 is considered to act as a network former if Ga^{3+} ions take preferentially four-fold coordination in oxide glasses. The excess negative charge on GaO_4 tetrahedra are compensated either by localization of a modifier ion nearby or by generation of three-fold oxygens. The GaO_4 tetrahedrons may enter the glass network and alternate with BO_4 tetrahedrons. In some glass networks, the gallium ions are also found to be in modifier position with GaO_6 structural units [6,14]. Gallium is heavier than aluminum and Ga^{3+} has lower field strength than Al^{3+} ; therefore is expected a shift of the infrared absorption band to lower wavenumbers than for aluminum.

After 15 min treatment, and up to 24 h treatment, the infrared spectra are highly similar (Fig. 3) but different from that recorded from amorphous samples. The former large band around 1400 cm^{-1} appears with three components at 1422, 1394 and 1315 cm^{-1} , all assigned to different stretching vibrations of B–O bonds in BO_3 units modified by local distortions [11,15,16]. These components are clearly evidenced in the smoothed absorption lines (Fig. 4). The deconvolution with three lines does not fit well the large band, but roughly comparing the relative intensity of 1422, 1394 and 1315 cm^{-1} components one can estimate their contribution as function of treatment time. One remarks the increase of 1315 cm^{-1} component on account of 1422 and 1394 cm^{-1} components (Table 1). The higher vibration frequency of the B–O bonds which give rise to 1315 cm^{-1} component indicates a shortening of the corresponding B–O bond lengths.

The absorption band occurred at 1215 cm^{-1} in the vitreous samples, also assigned to BO_3 units, is shifted to lower

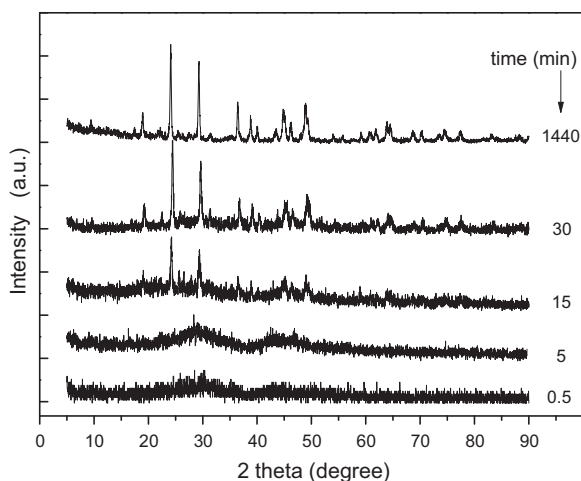


Fig. 1. XRD patterns after different treatment times at 850°C .

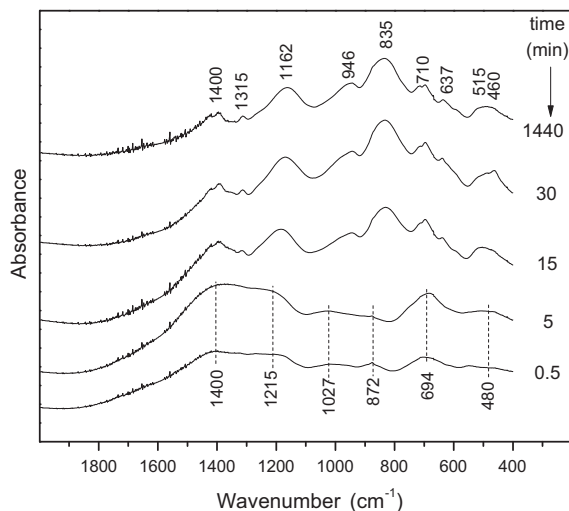


Fig. 2. FTIR spectra after different treatment times at 850°C .

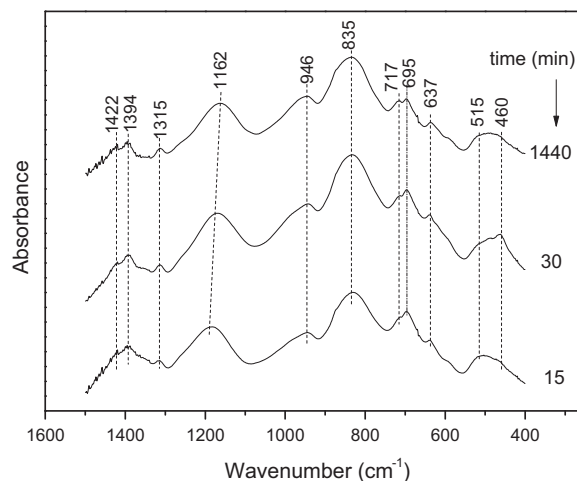


Fig. 3. FTIR spectra of samples treated from 15 min up to 24 h.

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