EPR studies on lanthanum aluminoborates doped with paramagnetic ions

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Electron paramagnetic resonance was used to investigate the local structure around paramagnetic ions in amorphous and corresponding crystalline lanthanum aluminoborates of LaAl2B3O10.5 composition. In amorphous samples the EPR spectra are dominated by the features determined by a relative large distribution of the local structure parameters, while in crystalline counterparts this distribution is much narrow around specific values for certain sites. Three different sites for Fe\(^{3+}\) ions and only a preponderant one for Mn\(^{2+}\) and Gd\(^{3+}\) ions are identified in crystalline samples doped with paramagnetic ions. Iron and manganese ions are assumed to occupy the aluminium sites and gadolinium ions the lanthanum sites from LaAl2.03B3O10.54 phase.

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1. Introduction

Alumino-borate glass-ceramics have been proved to be proper for low temperature co-fired ceramics (LTTC) technology used in wireless communication [1, 2]. It was found that the presence of rare earths like lanthanum preserves, up to relatively high temperatures, the pentacoordinated aluminium species, this effect being important for catalytical purpose and for their electric properties [3]. The essential challenging issue in manufacturing LTTC is co-firing ceramic substrate/electrode laminate structure at desirable sintering temperature.2

Very few studies have been reported in the literature on the crystalline phase developing in amorphous lanthanum-aluminium-borates [5, 6]. Up to now only one stable crystalline phase is known in the ternary lanthanum-aluminium-boron oxide system [7]. The composition of this crystalline phase is LaAl2.03B3O10.54 (124) and in its structure the La, Al and B atoms are surrounded by O atoms in trigonal prismatic, pyramidal and tetrahedral arrangements, respectively. It is an interesting oxide compound in which all cations exhibit less usual coordinations: lanthanum is hexacoordinated, aluminium pentacoordinated and boron tetracoordinated.

Due to the lack of structural long range order in amorphous materials an unambiguous assignment of the structural groups [8] 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 LaAl2.03B3O10.54 crystalline phase can be obtained by quick undercooling of the mixture melted at 1450 °C by or sol-gel procedure [9]. The last method is much proper for following the local structural changes during the transformation from disordered system to the well-defined crystalline phase and for obtaining ceramic thin films.

Paramagnetic ions Fe\(^{3+}\) (3d\(^5\), S=3/2), Mn\(^{2+}\) (3d\(^5\), S=5/2) and Gd\(^{3+}\) (4f\(^7\), S=7/2) are all in the S state and they are frequently used in EPR investigations of glasses. By adding transition metal or rare earth elements the electric and magnetic properties can be changed adequate to electronic devices. The present study is focused on the characterisation of the local structure around paramagnetic ions in iron, manganese and gadolinium doped amorphous and crystalline LaAl2B3O10.5 using EPR spectroscopy.

2. Experimental

The investigated systems 0.5MO-99.5[LaAl2B3O10.5] (mol %), where MO = Fe\(_2\)O\(_3\), MnO or Gd\(_2\)O\(_3\), were prepared by sol-gel method from aqueous solution of La(NO\(_3\))\(_3\)-6H\(_2\)O, Al(NO\(_3\))\(_3\)-9H\(_2\)O, H\(_3\)BO\(_3\) and Fe(NO\(_3\))\(_3\)-6H\(_2\)O, Mn(NO\(_3\))\(_2\)-6H\(_2\)O or Gd(NO\(_3\))\(_3\)-6H\(_2\)O of analytical purity grade by thermal decomposition of starting nitrates and boric acid accompanied by simultaneous oxidation of glycerol. The reagents mixture solved in desalinated water appears as a transparent solution at room temperature. A viscous gel is obtained after 5 hours heating at 95°C. The 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 400 °C and 1100°C.

The EPR measurements were carried out in X band (9.4 GHz) on powder samples at room temperature using a Bruker spectrometer.

3. Results and discussion

The differential thermal analysis pointed out structural changes related to the development of crystalline phases above 750 °C. 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 LaAl2.03B3O10.5, as was confirmed by X-ray diffraction studies.
The xerogels resulted after heat treatments applied at temperatures up to 750 °C are amorphous as revealed from X-ray diffraction. The 124 phase is prevalent in the samples after heat treatment at temperature above 1000°C. No crystalline phase with significant iron, manganese or gadolinium content has been evidenced by X-ray diffraction showing that the added small amounts of these oxides are well dispersed in 124 crystalline phase.

The most common electronic processes revealed in the spectra of oxide systems are due to the unfilled electron shells of transition (d orbitals) or rare earth elements (f orbitals) [10]. For all these elements the unfilled orbitals have identical energies in an isolated ion, but the energy levels split when the atom is located in a crystal field. The splitting of the orbital energy states enables an electron to be moved from a lower level into a higher one by absorption of a photon having an energy matching the energy difference between the states. The energy levels are determined by the valence state of the atom, its coordination number, and the symmetry of the site it occupies. The levels are also influenced by the type of ligands formed, the extent of distortion of the site and the value of the metal-ligand interatomic distance.

In case of $d^1$ transition metal ions, it is known [11] that the axial distortion of octahedral symmetry gives rise to three Kramer doublets $| \pm 5/2 >$, $| \pm 3/2 >$ and $| \pm 1/2 >$. Application of Zeeman field lifts the spin degeneracy of the Kramer doublets. As the crystal field splitting is normally much greater than the Zeeman field, the resonances observed are due to transitions within the Zeeman field split Kramer doublets.

The EPR spectra (Fig. 1) of the iron doped non-crystalline sample is dominated by a very broad line arising from rich iron precipitates. It is well known that during sol-gel process the rate of iron condensation is much higher than that of aluminium [12]. Some organic radicals resulted during glycerol pyrolysis are responsible for the very narrow line [13], also centred at $g = 2.0$. The structural changes induced by the heat treatment applied at higher temperatures make possible the diffusion of iron ions in the crystalline samples where three types of sites with different local surrounding having $g$ factor values between 2.0 and 6.2 have been identified. The peaks at $g = 6.2$ and 5.8 may be assigned to Fe$^{3+}$ ions disposed in sites of rhombic symmetry with relatively strong crystalline field [14]. Due to their similar ionic radii, it is expected that the majority of the Fe$^{3+}$ ions occupy the sites of penta-coordinated Al$^{3+}$ in 124 phase and give the above mentioned EPR lines. The line with $g = 4.3$ can be assigned to Fe$^{3+}$ ions situated in the relatively distorted sites in a still non-crystalline phase [15]. A small fraction of the Fe$^{3+}$ ions is located in the sites with weak crystalline fields of octahedral symmetry and these ions give rise to the line located at $g = 2.0$.

In the Mn$^{2+}$ EPR spectrum recorded from the amorphous xerogel the signal at $g = 2.0$ shows a six line hyperfine structure (Fig. 2a) which is due to the interaction of electron spin of manganese ions with its nuclear spin $I = 5/2$. The value of the hyperfine constant, $A = 88$ G, proves the predominant ionic character of Mn-O bonds [16]. The resonances at $g = 3.0$ and 4.6 can be attributed to the rhombic surroundings of the Mn$^{2+}$ ions [17]. The hyperfine structure is not anymore resolved in the crystallized sample (Fig. 2b). The EPR spectrum mainly consists of a large resonance line at $g = 2.0$. The resonance at $g = 2.0$ is due to the Mn$^{2+}$ ions in an environment close to octahedral symmetry, in fact penta-coordinated sites, and is known to arise from the transition between the energy levels of the lower Kramer doublet, while the resonances at $g = 3.0$ and 4.6 arise from the transition between the energy levels of middle Kramer doublet [17]. The absence of the hyperfine structure suggests a relatively distorted environment, what is consistent with the larger radius of Mn$^{2+}$ ions (0.8 Å) then Al$^{3+}$ radius (0.6 Å) in penta-coordinated environment.
In the case of gadolinium doped xerogel the EPR spectrum (Fig. 3a) is similar to the well known U spectrum [18-23] specific for non-crystalline matrices containing Gd$^{3+}$ ions. After crystallisation the EPR spectra mainly consist of relative large line with $g = 2.0$ suggesting that the surrounding of Gd$^{3+}$ ions are experiencing weak crystal fields resulting from structural relaxation [24].

![EPR spectra of LaAl$_2$O$_3$ samples after heat treatment at 400°C (a) and 1100°C (b).](image)

The line is not enough narrow to conclude that the rare earth environments in 124 phase are well defined, despite the fact that according to X-ray data for 124 phase [4] the vicinity of lanthanum is built by six oxygen atoms situated at the same distances from the rare earth site.

4. Conclusions

The structural changes induced by heat treatment in amorphous lanthanum alumino-borate doped with iron, manganese or gadolinium ions are well reflected in the EPR spectra of these resonance centres. During crystallisation of the precursor xerogel the iron ions diffuse through the sample and are mainly identified in sites of rhombic symmetry, while manganese ions are disposed preponderantly in environments close to octahedral symmetry. Iron and manganese ions are assumed to enter the aluminium sites. Gadolinium ions are expected to occupy the sites of lanthanum. The Gd$^{3+}$-EPR spectrum of crystalline sample shows structural relaxed environment for gadolinium ions, but less relaxed than for lanthanum in a well defined 124 crystalline phase.

References


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