Growth of crystalline doped β-alumina thin films by laser ablation

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Crystalline thin films of sodium β-alumina and β-aluminogallate for optical applications have been deposited onto various single-crystal substrates by the pulsed laser deposition technique. Films with a smooth surface morphology were obtained by using Cr-doped targets. Despite Na loss in the films with respect to the target composition, the β-alumina crystalline phase was grown at elevated temperature (700–800 °C), and highly textured (00*l*) films were obtained, whatever the substrates: MgO, ZrO_2, Al_2O_3 or Si. The optical properties were studied by measuring the refractive index of the films and performing the emission spectrum of the Cr^{3+} ions, providing results very similar to those of the bulk single-crystalline material.

Recently, there has been much attention paid to optical thin films for applications in waveguiding, especially as far as waveguide lasers are concerned. Among all the materials presenting the desired properties, β-alumina (of theoretical formula $NaAl_{11}O_{17}$) appears particularly interesting since it has been widely studied and is relevant for doping by luminescent ions such as Cr^{3+} or Nd^{3+}, owing to its particular crystalline structure;[1,2] the hexagonal unit cell of β-alumina resulting from stacking of spinel-type blocks and mirror planes.[3] Those planes can be doped with Nd^{3+} ions by ionic exchange with Na^+ in a molten salt: such a doping is expected to induce a laser effect in this material. This effect has been evidenced in Nd-doped β″-alumina which is very similar to β-alumina.[4] A doping of the spinel-type blocks by Cr^{3+} ions is possible by replacement of some Al^{3+} ions. This is particularly interesting, because Cr–Nd co-doped β-alumina has been shown to allow energy transfer between Cr^{3+} and Nd^{3+} ions.[1] The Al^{3+} ions can also be partly or totally replaced by Ga^{3+} ions, leading to the formation of β-aluminogallates, with a dilatation of the unit cell due to the larger size of such ions. This is of great interest as far as Cr doping is concerned, because the introduction of Ga^{3+} ions lowers the crystal field energy surrounding the Cr^{3+} ions and has a very large influence on their optical transitions.[2]

Surprisingly, crystalline β-alumina thin film growth has not been reported yet. The reason why this is so is certainly due to the material itself. The crystalline β-alumina form is not easy to synthesize because of a loss of sodium at high temperature, which makes crystal growth from molten material difficult.[1] A laser effect arising from Nd doping has never been observed because of the too small size of the single crystals provided by the usual crystal-growth methods. This could also explain the fact that the *in situ* growth of crystalline β-alumina films (*i.e.* without any post deposition annealing treatment) by classical thin-film techniques (sputtering for instance) has not been successful.[5] Pulsed laser deposition[6] could be used to solve this problem. In fact, owing its specific properties, the laser ablation process is a very popular method to grow thin oxide films of complex composition like new high-T_c superconducting cuprates, ferroelectric, magnetic or biocompatible oxides.[7]

In this paper, we report on pulsed laser deposition of β-alumina and β-aluminogallate films on single-crystal substrates such as yttrium stabilized ZrO_2, MgO, α-Al_2O_3 or Si with different orientations. A necessary condition to use such thin films as waveguides is that they must be of higher refractive index than the substrate. The aim of this study was to investigate the possibility of growing films presenting two main properties: a smooth surface morphology and a good texture. Surface defects or changes in refractive index due to differences in orientation between the different single-crystalline domains can cause light diffusion and so lower the waveguide optical performances.

Experimental

Thin films of β-alumina and β-aluminogallate were deposited onto Si, MgO, corundum or cubic stabilized zirconia single-crystal substrates (of *ca.* 1 cm^2 surface area) using the pulsed laser evaporation technique.[6] This method consists of focusing the beam of a pulsed laser on a target of the oxide. The absorption of the radiation in the near surface region of the target leads to a superficial evaporation of the material. The very short duration of this process (about 1 ns) is the reason why this evaporation is congruent. The so formed gas interacts with the laser beam (the pulse duration being *ca.* 5 ns) to become a very dense and very energetic plasma by ionization of the evaporated species. This plasma expands then in an anisotropic way, transporting the species towards the surface of the substrate, where they take part in film growth. Such a deposition may be performed under vacuum, but also under a reactive atmosphere such as oxygen, which is also of interest in growth of oxide films. In this work, the laser used was a Nd : YAG (supplied by BMI), delivering pulses of 5 ns duration at a 5 Hz repetition rate. The films were obtained at the fourth harmonic wavelength (266 nm), which was generated by frequency-doubling potassium dihydrogenphosphate crystals (KDP), the available laser intensity at the surface of the target was typically in the range 50–500 MW cm^{-2}. The *in situ* growth of β-alumina was achieved by deposition onto heated substrates (650–800 °C), under various oxygen pressures (10^{-6}–0.3 mbar), in order to grow stoichiometric oxides. After deposition, the films were cooled to room temperature at a rate of 10 °C min^{-1} under oxygen (100 mbar).

The targets used in this work were sintered pellets of 1% and 2% Cr-doped sodium β-alumina, and 0.5% and 1%

Cr-doped sodium β-aluminogallate in which half of the Al^{3+} ions have been substituted (these percentages represent the part of Al^{3+} ions and Ga^{3+} ions replaced by Cr^{3+} ions, and refer to the targets composition before heating and sintering). The theoretical formula of β-alumina is $NaAl_{11}O_{17}$. In fact, this non-stoichiometric compound usually admits and contains an excess of sodium, leading to the following composition: $Na_{1+x}Al_{11}O_{17+x/2}$ with $0<x<1$. In order to prevent sodium losses during the preparation of the targets and the deposition of the films, the initial composition of our pellets corresponded to $x=1$. These targets were prepared by mixing of the initial powders (Al_2O_3, Ga_2O_3, Cr_2O_3 and NaF) in the appropriate proportions, according to the preceding considerations. The homogeneous powder was then pressed and heated in air at 900 °C. After grinding, mixing and pressing, reaction sintering was achieved in air at 1400 °C over 10 h, to provide a 60% densification of the material. The nature of the grown material was checked by performing a powder X-ray diffraction diagram for the targets. These diagrams evidenced the presence and phase purity for each target of the desired compound, and especially revealed a c parameter of 22.5 Å for the β-alumina hexagonal cell and of 22.8 Å for the β-aluminogallate hexagonal cell, in good agreement with literature data.[2,3] UV–VIS absorption spectra for the targets in the range $\lambda=220$–800 nm were obtained using a Varian Cary 5 spectrophotometer in diffuse reflectance geometry.

By the complementary use of scanning electron microsocopy (SEM), Rutherford backscattering spectrometry (RBS) and X-ray diffraction techniques, the surface morphology of the deposited films, their atomic composition and their crystalline structure have been investigated. The RBS experiments were carried out with the 2.5 MeV Van de Graaff accelerator of the Groupe de Physique des Solides. The crystal structure was determined by using a Siemens D-5000 diffractometer, using Co-Kα radiation ($\lambda=1.7890$ Å), and performing both θ–2θ diagrams (with a 40 s counting time and a 0.03° step size) and rocking curves (with a 20 s counting time and a 0.01° step size). The optical properties of the films were also studied. Emission spectra in the 700 nm region for the Cr^{3+} ions were performed at room temperature at a wavelength excitation at 532 nm of a Nd:YAG laser at the second harmonic, using an optical grating to disperse, and a photodiode linear array (Optical Multicanal Analyser) to collect the emitted light.

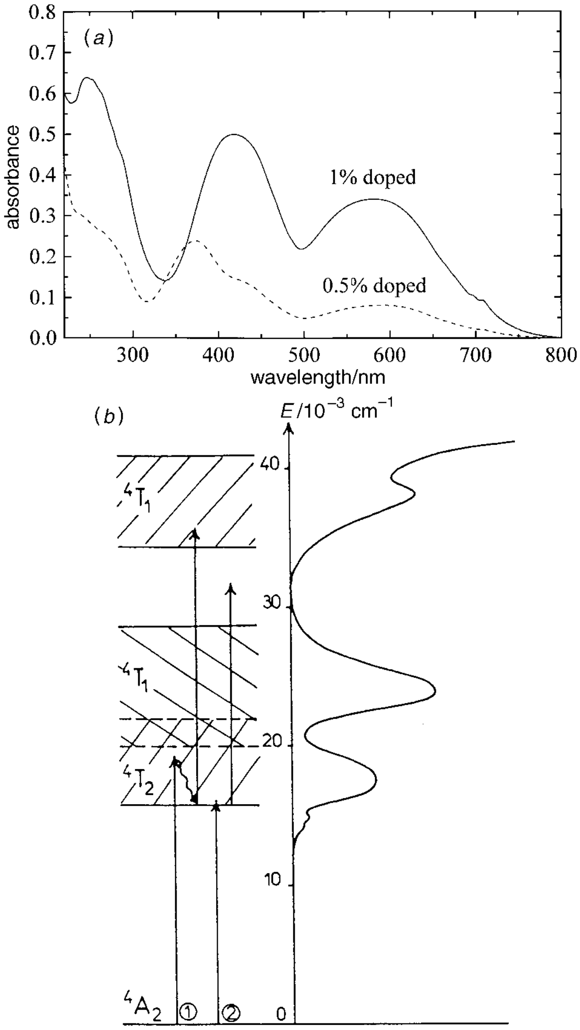

Fig. 1 (*a*) Absorbance spectra for 0.5% and 1% Cr-doped β-aluminogallate targets, and (*b*) model of the optical absorption of Cr^{3+} ions in octahedral sites according to Fig. III-15 in ref. 10.

Results

Surface morphology

The main drawback of the laser ablation technique is the presence of macroscopic particles (in the μm range) at the surface of the deposited films.[6] Such particles are believed to be ejected in the form of droplets from the molten zone of the irradiated target, due to an explosive break up of the liquid which could be locally overheated during laser irradiation.[6,8] It has been found that the surface morphology of the films depends on the targets' optical properties, the higher the optical absorption coefficient, the lower is the droplet density at the surface of the deposited films.[9] In this work, the use of Cr-doped targets essentially solved the problem of optical absorption. In fact, as can be seen in the absorbance spectra shown in Fig. 1, Cr doping leads to the presence of an absorption band due to the $^4A_2 \rightarrow {}^4T_1$ electronic transition of the Cr^{3+} ions located in octahedral sites.[10] This absorption is stronger when the Cr content increases: Fig. 1 shows that a 1% doped β-aluminogallate target is much more absorbant than a 0.5% doped target.

Laser ablated films grown from such a highly absorbing target material exhibit a rather smooth surface morphology as indicated by SEM analysis. For instance, a low density of defects (droplets with diameters <0.5 μm) can be observed on a film deposited from a 1% Cr-doped β-aluminogallate target [Fig. 2(*a*)]. By comparison, using a 0.5% doped target leads to a much more irregular surface morphology [Fig. 2(*b*)], as a consequence of the presence of large size droplets (diameter of the order of or >1 μm). Therefore, the use of a 1% or more highly doped target provides an adequate surface quality for waveguide applications.

Composition of the films

Rutherford backscattering spectrometry (RBS) measurements were performed to study the elemental composition in the films. A typical RBS spectrum for a film grown from a 2% Cr-doped β-alumina target on a corundum substrate is presented in Fig. 3. The calculated spectrum using the RUMP simulation program[11] and corresponding to the composition of the target (*i.e.* $Na_2Cr_{0.2}Al_{10.8}O_{17.5}$) is also shown. A comparison of these two spectra indicates a loss of Cr and Na in the films with respect to the target composition (more than 70% of the Na and Cr of the target was lost). These deviations in composition arise from phenomena taking place during the plasma expansion towards the substrate and/or at the film surface.[9,12] In fact, composition deviations can simply be due to differences in the sticking coefficient for the various elements: some species do not stick to the substrate and are re-evaporated. Taking into account the fact that these

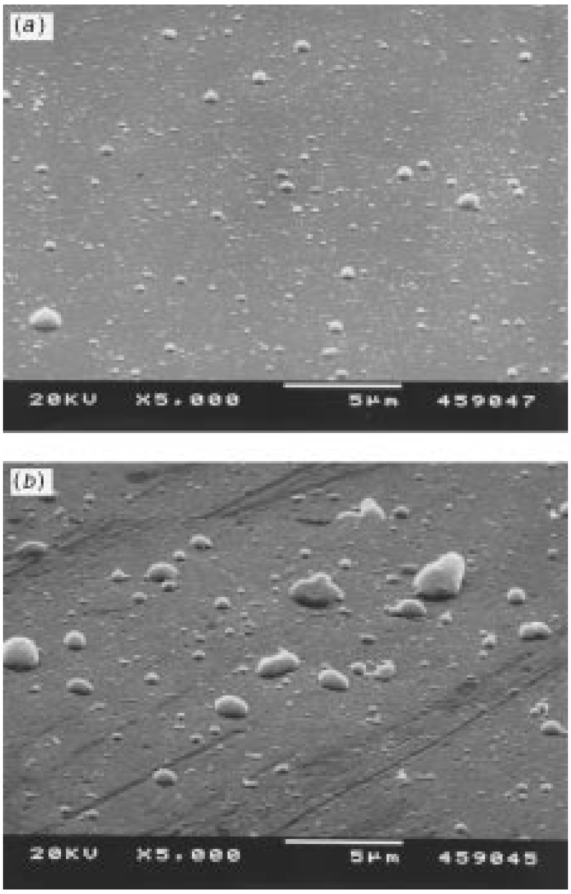

Fig. 2 SEM images for films deposited on corundum (at 750 °C under 0.1 mbar oxygen) from (*a*) a 1% Cr-doped β-aluminogallate target, and (*b*) a 0.5% Cr-doped β-aluminogallate target

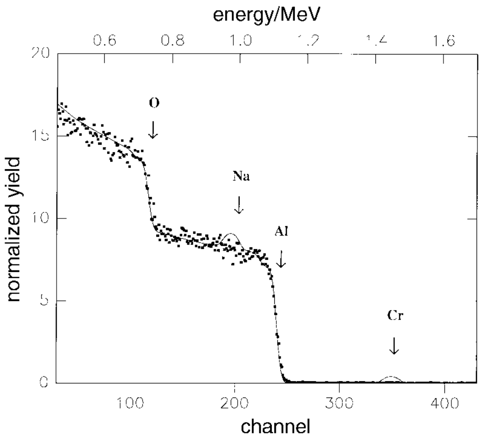

Fig. 3 Typical RBS spectrum for a β-alumina film deposited on corundum (at 800 °C, under vacuum). The solid line is the calculated RUMP spectrum for a 70 nm thick $Na_2Cr_{0.2}Al_{10.8}O_{17.5}$ film.

composition deviations were also observed during laser ablation under vacuum, it is not possible to explain them in terms of collisions between the plume and the gaseous species which broaden the angular distribution of elements and thus leads to composition deviations. However, intraplume effects, *i.e.* collisions between species emitted from the target at each laser pulse, could still occur. Such intraplume collisions could lead to a broadening of the angular distribution of the elements, and in extreme conditions to the backscattering of some species.

To check this possibility, we have analysed the composition of the target after laser irradiations. RBS analysis of the β-alumina targets in the irradiated area leads to the initial composition (*i.e.* $Na_2Cr_{0.2}Al_{10.8}O_{17.5}$), while measurements at non-irradiated regions show drastic changes in the surface composition: marked Na and Cr enrichment occurs (*i.e.* 6 Na^+ and 0.5 Cr^{3+} for 11 Al^{3+}). These results show that during laser ablation the evaporation of the target is congruent (no preferential evaporation or atomic segregation), since no composition changes are evidenced in the laser irradiated spot. Moreover, except for a possible solid-state out diffusion from the irradiated area of some elements, the Na and Cr enrichment in the non-irradiated area is solely due to the redeposition on the target of the material ejected during each laser pulse, these phenomena being related to the backscattering of Na and Cr atoms during the collisions in the high-density plasma created at the surface of the target at each laser pulse.

Texture of the films

Despite those difficulties, and whatever the substrates used (yttrium stabilized zirconia, corundum, MgO), crystalline β-alumina thin films were grown. The deposition duration was 1 h, the substrate was heated at 800 °C and the growth was performed under vacuum. Such deposition conditions allowed highly textured thin films to be obtained, as shown by the X-ray θ–2θ patterns presented in Fig. 4. Only (00*l*) peaks of β-alumina corresponding to even *l* are evident, which indicates that the *c*-axis is normal to the substrate surface and evenness is in agreement with extinction rules for this compound. The *c* parameter deduced from such diagrams does not vary from one film to another and is always 22.45 Å, the value found for the bulk target material. The diagrams obtained for films deposited on MgO substrates reveal the presence of a impurity phase probably arising from the formation of an undesirable hydroxide during or after the deposition. Nonetheless textured β-alumina films are grown on such substrates. The growth of such films is possible on silicon wafers as well: textured films have been grown from a 1% Cr-doped β-alumina target (at 650 °C, 0.5 mbar oxygen). The emerging problem in this case is diffusion into the substrate and into the film of the silver used to maintain the thermal contact between the substrate and the oven.

In order to check the texture quality of our films, rocking curve measurements were performed. A typical example from the 002 diffraction peak of a film deposited on a corundum substrate is shown in Fig. 5. It reveals that the mean *c*-axis mosaicity in these films does not exceed 0.2°. This is evidence of very good texture, which is compatible with waveguide applications.

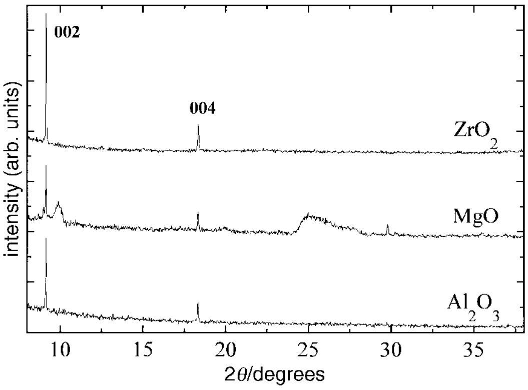

Fig. 4 X-Ray diffraction patterns for β-alumina films deposited on various substrates (at 800 °C, under vacuum)

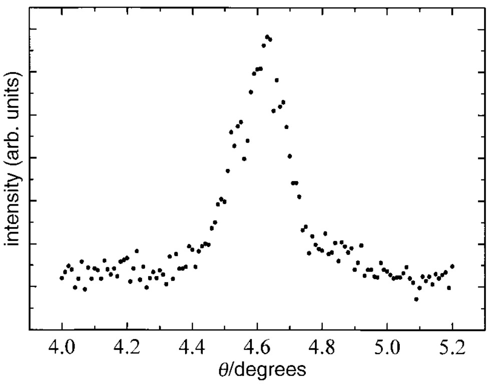

Fig. 5 Rocking curve for a 2% Cr-doped β-alumina thin film deposited on a corundum substrate (at 800 °C, under vacuum)

Influence of the growth conditions

Further investigations have been performed using 2% Cr-doped β-alumina targets, to determine the influence on the growth of the substrate temperature and the presence of an oxygen atmosphere (Fig. 6 and 7). A reason why the β-alumina is difficult to deposit is that its structure is rather complicated: during the growth, not only must the order in the crystallographic planes be maintained, but also the order in the stacking of those planes, to obtain the structure of spinel-type blocks separated by mirror planes. Therefore, the mobility of species at the surface of the growing film is of major importance to allow the formation of such an ordered structure. It is clear that the higher the substrate temperature, the higher the mobility of the adsorbed species and the better the crystallinity of the film. This is exactly what is observed in Fig. 6, and an increase in peak intensity is seen at high temperature, for a given film thickness. The effect of an oxygen atmosphere is also consistent with this argument. The presence of an atmosphere in the ablation chamber decreases the kinetic energy of the emitted species by collisions with the molecules of the ambient gas. This lowers the mobility of the species as they are adsorbed on the surface of the film: the higher the oxygen pressure, the lower this mobility and the poorer the crystallinity of the thin film as shown in Fig. 7. It appears therefore that the growth of the β-alumina phase is optimised under vacuum and at high substrate temperatures.

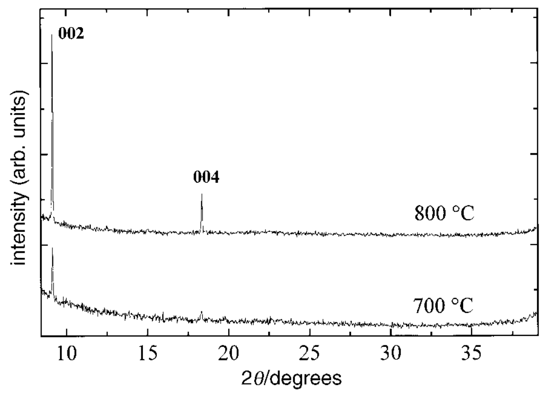

Fig. 6 Influence of the substrate temperature on the texture of the β-alumina films

Growth of β-aluminogallate films

Taking into account the above results, the optimal deposition conditions (*i.e.* substrate heated to 800 °C under vacuum) were used to grow films from 1% Cr-doped β-aluminogallate targets (the deposition duration being 2 h). The best results were obtained with 2300 Å thick films (RBS), for which diffraction diagrams (Fig. 8) show very intense diffraction peaks, as compared to those obtained with the β-alumina films (see Fig. 4). The *c* parameter deduced from this diagram is 22.85 Å, which is in accord with the value observed for the target, and for a β-aluminogallate single crystal of the same composition as the target used. The width of the diffraction peaks reveals a coherent thickness of 2500 Å for the deposited material. This shows that the films are coherent throughout.

Optical properties of the films

The optical properties of the films grown either from β-alumina or β-aluminogallate targets were studied. Emission spectra of Cr^{3+} ions in the films were measured and results obtained differed for films grown from one type of substrate to another. However, irrespective of substrate, a more or less intense emission was observed in the range 650–850 nm, indicating that Cr^{3+} ions have been incorporated into the films. For films grown on MgO, an intense and broad fluorescence was observed which does not correspond to the emission spectra of Cr-doped β-alumina compounds. This particular emission appears to be a consequence of the presence of the impurity hydroxide phase on this substrate. For films grown on corundum fluorescence was intense (with a clearly visible red color), but the emission spectra obtained was the same as that of ruby. This is certainly due to the diffusion of Cr^{3+} ions from the film into the corundum substrate during deposition at high temperature. The films grown on yttrium-stabilized zirconia showed yet different behaviour. Fluorescence was very weak and emission spectra were difficult to obtain. A typical

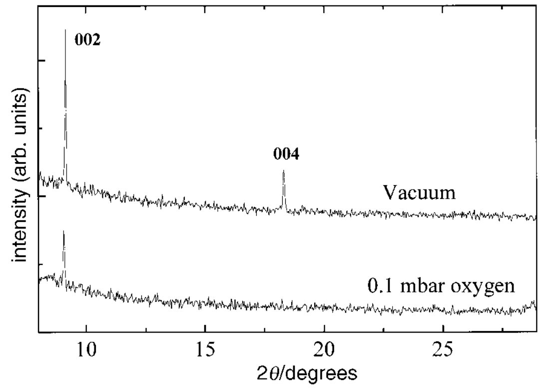

Fig. 7 Influence of the oxygen pressure on the texture of the β-alumina films

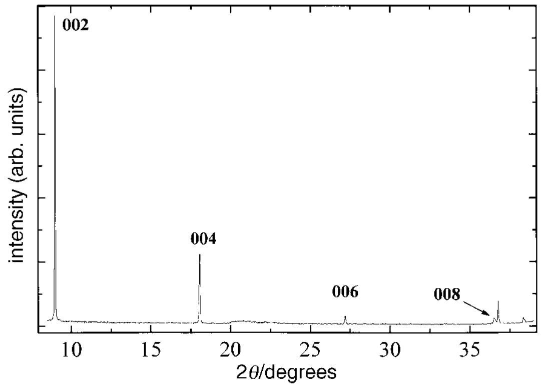

Fig. 8 X-Ray diffraction pattern for a β-aluminogallate thin film deposited on a stabilized zirconia substrate (at 800 °C, under vacuum)

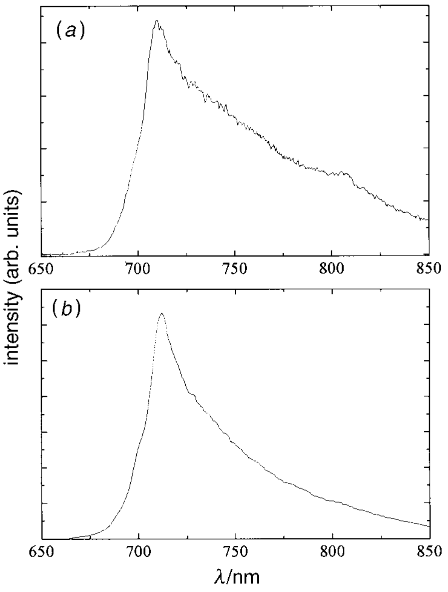

Fig. 9 Fluorescence spectra for (*a*) a β-aluminogallate thin film deposited on a stabilized zirconia substrate film, and (*b*) a bulk Cr-doped β-aluminogallate single crystal

spectrum obtained for a β-aluminogallate thin film is shown in Fig. 9(*a*). The emission is very broad with λ_{max} at *ca.* 710 nm. These results indicate emission of Cr^{3+} ions in a low-energy crystal field, which is consistent for sodium β-aluminogallate. The emission spectrum for a Cr-doped β-aluminogallate single crystal of the same composition is shown in Fig. 9(*b*). Comparison of the spectra reveals their similarity indicating that Cr^{3+} ions have not only been incorporated into the films, but that they are located in the same sites as in the bulk crystalline material.

A study by ellipsometry of a thin film of Cr-doped β-aluminogallate suggested a thickness of 2600 Å (*cf.* 2300 Å estimated by RBS) and revealed that its real refractive index (*n*) decreases from 1.75 at 350 nm to 1.625 at 800 nm. These results are in accord with values generally observed for such compounds and are data suitable for waveguide applications.

Conclusions

We have demonstrated, for the first time, the successful growth of crystalline β-alumina and sodium β-aluminogallate thin films by the laser deposition method. Using Cr-doped targets, smooth and homogeneous films are obtained, and despite a loss of Na and Cr in the films, the β-alumina crystalline phase is synthesized at temperatures near 800 °C. These films present a strong (00*l*) texture whatever the crystalline substrates used. Both smooth surface morphology and good texture make those films relevant for waveguide applications. Moreover, Cr^{3+} emission spectra performed for films grown on zirconia substrates are very similar to those obtained for the bulk crystalline material. Finally the measured refractive index is typical of values observed for such compounds.

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