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RBS characterization of Al_2O_3 films doped with Ce and Mn

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Abstract

Rutherford backscattering (RBS) with ^4He energies from 2 to 6 MeV has been used to study the properties of thin amorphous photoluminescent Al_2O_3:Ce,Mn films grown by spray pyrolysis on Corning 7059 glass substrates. The source solutions were $AlCl_3$, $CeCl_3$ and $MnCl_2$ dissolved in deionized water. Different molar concentrations (Ce 10%; Mn 1%, 3%, 5%, 7% and 10%) were investigated under the same deposition conditions at a substrate temperature of 300 °C. The RBS spectra show a homogeneous depth profile of both Ce and Mn within the films, and the measured quantities are consistent with the original solution concentrations. An important amount of Cl, which plays a significant role in luminescent properties, was detected, in both the doped and undoped samples.

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Keywords: RBS; Aluminum oxide; Ce; Mn; Luminescence

1. Introduction

The spray pyrolysis process involves the spraying of an aqueous solution of soluble salts of the desired compounds onto a previously heated substrate, to induce a pyrolytic reaction. The equipment is simple, inexpensive and of easy operation, and does not require expensive vacuum systems [1]. This technique is effective for the synthesis of materials in the form of powders and films [2]. Al_2O_3 is an attractive host lattice for rare earth optical activators, due to its good

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stability and optical characteristics [3]. It offers important dielectric properties, good adhesion to many surfaces, high radiation resistance, high corrosion resistance, high thermal conductivity and low permeability to alkali impurities [4,5]. It has also been employed as a matrix for impurities such as Eu, Tb, Ce, with excellent photoluminescence properties [3,6,7]. The energy transfer from donor to acceptor plays an important role in luminescence [8–10]. In particular, it is well known that Ce ions are excellent donors of excitation energy (sensitizers) and Mn ions acts as efficient activators or energy acceptors; both have been used as dopants in photoluminescent materials involving energy transfer [11,12]. The efficiency of energy transfer depends mainly on the extent of overlap between the Ce^{3+} emission and the Mn^{2+} excitation spectra. It is important to know the chemical composition and spatial distribution of the participant ions (Ce^{3+} and Mn^{2+}); this information is crucial for proper interpretation of the energy transfer phenomena within the Dexter–Forster theory.

In this work, Rutherford backscattering (RBS) studies on the chemical composition of photoluminescent Ce and Mn doped aluminum oxide coatings, deposited by the ultrasonic spray pyrolysis process are presented. The concentration of the doping ions was determined for the proper assessment of the energy transfer phenomena.

2. Experiment

The Al_2O_3 films doped with Ce^{3+} and Mn^{2+} ions were prepared using the spray pyrolysis technique [13]. The solution with the materials to be deposited is sprayed through a nozzle over a hot substrate in air at atmospheric pressure. The starting solution was 0.07 M aluminum chloride hexahydrate $AlCl_3 \cdot 6H_2O$ dissolved in deionized water (18 MΩ cm). $CeCl_3 \cdot 6H_2O$ and $MnCl_2 \cdot 4H_2O$ (Aldrich Chemical Co.) were added for doping. While maintaining the Ce chloride concentration constant (10%), the Mn chloride was incorporated at concentration values of 1%, 3%, 5%, 7%, and 10%, referred to the quantity of $AlCl_3 \cdot 6H_2O$. The spray was generated with a frequency of 0.8 MHz. Filtered air with a flow of 10 l/min was used as transport gas. The solution flow was 1 ml/min and the time of synthesis was 6 min. The substrates were Corning 7059 glass, kept at a temperature of 300 °C. The thickness of the films produced was ~5 μm, as measured with a Sloan Dektak IIA profilometer. The excitation and emission photoluminescent measurements at room temperature were obtained using a Perkin–Elmer LS50B spectrophotometer.

The RBS was performed with ^4He ions from the Instituto de Física 9SDH-2 Pelletron Accelerator at a scattering angle of 168°, after heating the specimens to reduce absorbed water.

3. Results and discussion

The XRD measurements of all the samples showed no indication of crystallinity. Fig. 1 shows a typical RBS spectrum where the Ce, Mn, Cl, Al and O steps are identified. In all the RBS spectra observed, including those from undoped films, the amount of oxygen exceeded that expected from stoichiometric Al_2O_3.

The spectra show that both Ce and Mn are distributed homogeneously within the films. Fig. 2 shows the measured concentrations of Ce and Mn versus $MnCl_2$ concentration in the solution (1%, 3%, 5%, 7%, 10%), keeping the $CeCl_3$ concentration in the solution constant at 10%. The Mn

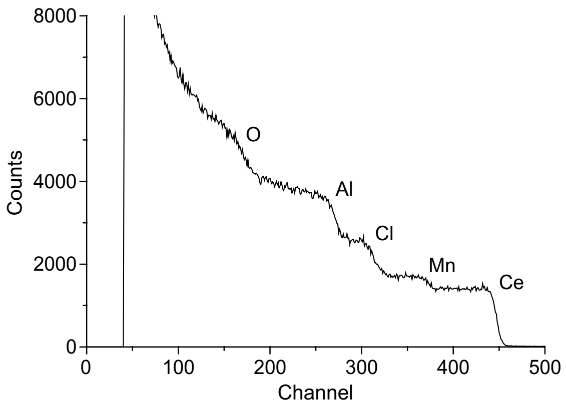

Fig. 1. Backscattered 2 MeV ^4He spectrum of a 10% $CeCl_3$, 10% $MnCl_2$ sample.

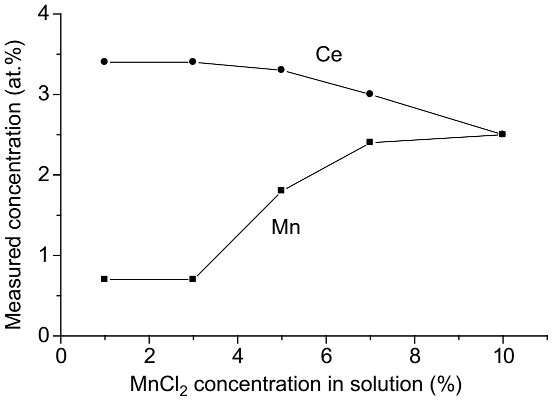

Fig. 2. Measured Ce and Mn concentration in the film versus $MnCl_2$ concentration in the solution. The point at 1% is approximately the limit of sensitivity of the technique.

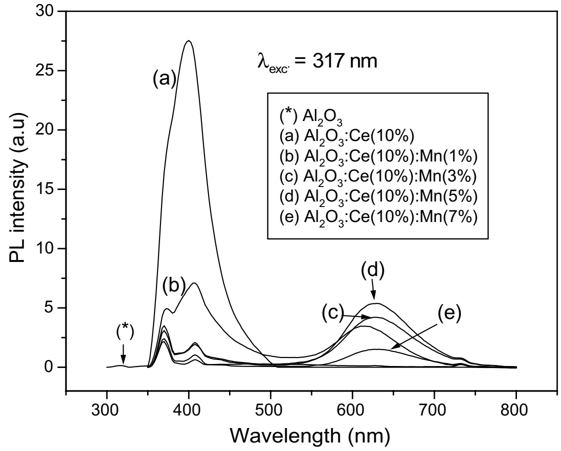

Fig. 3. The emission spectra for various cases; the excitation wavelength was 317 nm.

grows as expected, and the Ce diminishes slightly, until for equal concentrations in the solution (10%) both elements converge at 2.5 at.%. The ratio Mn/Cl is almost linear. The homogeneous distribution of both Ce and Mn and their relative concentration justifies the application of the Dexter–Forster theory, in which the overlap of the Ce emission and Mn absorption curves and the average distance between sensitizer and acceptor ions determines the efficiency of the energy transfer process.

An important amount of Cl, which could play a significant role in luminescent properties, was detected in both the doped and undoped samples. The minimum Cl was 7 at.% for the undoped sample, and the maximum was 20 at.% for the sample with 7% $MnCl_2$ in the solution.

To measure the film thickness, an RBS spectrum with 6.2 MeV ^4He was taken. The average thickness of the 10% Ce, 10% Mn sample was determined to be 10.3 μm, with a large spread of ±2.6 μm, indicating a variable thickness or porosity.

The 317 nm band of the excitation spectrum for the Al_2O_3:Ce^{3+} (10% in the solution) deposited at temperature $T_s = 300$ °C was selected for excitation of the subsequent emission spectra. Fig. 3 shows the emission spectra for various cases with an excitation wavelength of 317 nm. Curve (∗) corresponds to Al_2O_3 films without doping; no visible emission is detected. Curve (a) corresponds to Al_2O_3:Ce^{3+} (10% in the solution) films; here only a violet–blue emission, centered at 400 nm, is observed. Curve (b) is the emission from Al_2O_3:Ce (10% in the solution) + Mn (1% in the solution) films; in this case, the spectrum is constituted by two bands situated at 406 nm (violet–blue) and 614 nm (red). In addition, one may notice a decrease in the intensity of the violet–blue emission. Curves (c) and (d) correspond to Al_2O_3:Ce (10%) + Mn (3%) and Al_2O_3:Ce (10%) + Mn (5%) films, respectively. In both cases the spectra show only a red emission centered at 630 nm; the violet–blue emission disappears. As the Mn concentration increases a red shift is observed. Also, values of Mn higher than 5% in the solution lead to lower intensity of the red emission (concentration quenching). Considering the measured concentrations and distributions of the dopants, the spectra are interpreted as due to an energy transfer between the Ce and the Mn.

Fig. 4 curve (a) shows the luminescence intensity (band centered around 400 nm) as a function of the $MnCl_2$ concentration for Al_2O_3:Ce (10%), Mn (X%) films. We observe an intensity decrease with increase of $MnCl_2$. Fig. 4 curve (b) exhibits the emission intensity (band centered around 630–640 nm) with concentration of Mn; an increase of the intensity is observed. A maximum is reached for values of $MnCl_2$ around 3–5%, consis-

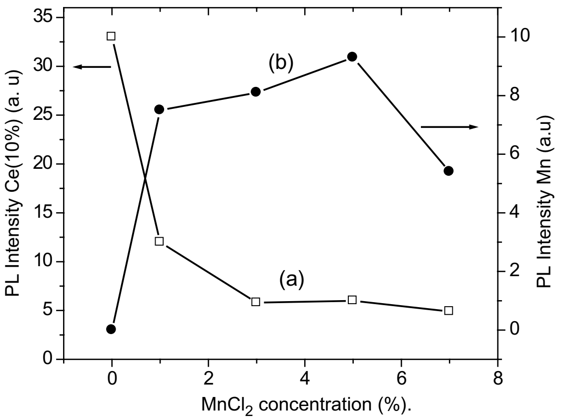

Fig. 4. PL intensities of emission spectra of Al_2O_3:-Ce(10%):Mn(X%) films as functions of manganese concentration (the excitation wavelength was 317 nm).

tent with calculations made with the Dexter–Forster theory.

4. Conclusions

RBS has been used to analyze Ce and Mn doped Al_2O_3 films grown by spray pyrolysis. The homogeneous distributions of the dopants and the linearity of their measured concentrations are important in the application of the Dexter–Forster theory of efficiency in energy transfer. A high concentration of Cl was observed, as well as a variable thickness or porosity.

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