Structure and optical properties of Lu 2 Si O 5 : Ce phosphor thin films

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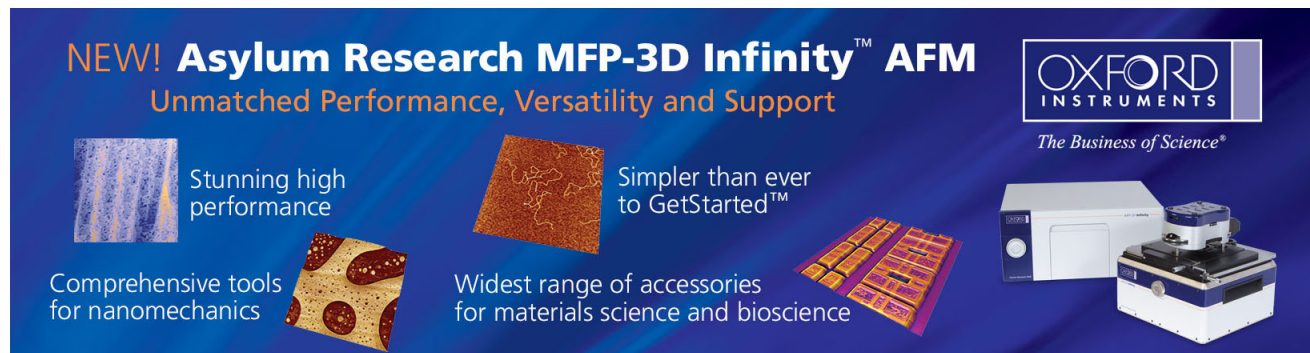### Articles you may be interested in

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Structure and optical properties of Lu$_2$SiO$_5$:Ce phosphor thin films

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Luminescent, cerium doped Lu$_2$SiO$_5$ thin films with $C2/c$ symmetry have been prepared by pulsed laser deposition (PLD) at temperatures much lower than the crystallization temperature (2150 °C) of the corresponding bulk crystals. The PLD grown films show the typical luminescence resulting from the Ce^{3+} 5d-4f transition. Maximum luminescence efficiency was observed for films prepared at an oxygen partial pressure of 200 mTorr at 600 °C. These conditions reflect a balance between Ce^{4+}/Ce^{3+} interconversion and the crystalline quality of the films. The results indicate that PLD offers a low temperature deposition technique for complex oxide phosphor materials. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2345373]

Phosphors are an integral part of modern technology because of their capability to convert radiation into light. They are used in many commercial devices including fluorescent lamps, displays, lasers, and crystal scintillation detectors for radiography. Desirable properties of a phosphor for radiation detection include high brightness in the blue or green spectral region to match existing photomultiplier tube or Si photodiode detectors, low optical absorption, nanosecond scale decay times, and high density.[1]

Among phosphor materials, rare-earth-ion doped oxyorthosilicates offer excellent scintillating properties and have been extensively studied for the potential development of new scintillating materials,[2,3] for example, Ce doped Lu$_2$SiO$_5$ (LSO:Ce) activated with around 0.05 at. % of cerium relative to the lutetium (Lu). Cerium is an excellent activator because its ground state and excited states lie within the band gap of about 6 eV for the host LSO lattice. Consequently, LSO:Ce shows good light output, 28 000 photons/MeV, fast decay time, 40 ns, a relatively high density, 7.34 g/cm^3, and minimal self-absorption.

While LSO:Ce is an exceptional phosphor, the material is difficult to prepare, especially as large single crystals. This is at least partly due to the high cost of starting materials such as high purity Lu$_2$O$_3$ powder and equipment such as iridium crucibles used for containing the Lu$_2$O$_3$ powder at the melting temperature of about 2150 °C. Moreover, stress induced cracking of the boule upon cooling from the high growth temperature severely affects the yield of large area detector elements, i.e., greater than 1 cm^2. Additionally, the low Ce segregation coefficient (0.22) in LSO makes the Ce concentration and the luminescence efficiency of LSO:Ce single crystals nonuniform along its growth direction.[4] Therefore, most of the efforts in the synthesis of LSO:Ce scintillators have been devoted to the growth of good single crystals.

There is also much interest in identifying high performance and low cost substitutes for single crystals, either as nanocrystalline powder composites or thin films.[5] Recently, a sol-gel process was successfully employed to prepare LSO:Ce films and nanosize powders.[6] However, LSO:Ce films from sol-gel process require a 1000 °C postannealing, which is still too high for depositing LSO:Ce films on many technologically important substrates such as flexible polymers and plastic scintillators. In contrast to the sol-gel process, pulsed laser deposition (PLD) has been used to facilitate low temperature deposition of many complex metal oxide films such as high temperature superconductors,[7] ferroelectrics,[8] ferromagnetics,[9] and transparent conductive oxides.[10] A general effect for extending the phase stability of metal oxides to lower temperatures is through reduction of the oxygen partial pressure.[11] A decrease in the oxygen partial pressure stabilizes the phase of various oxide materials even at lower temperature.[12] This effect is readily manifested using PLD which typically operates at oxygen partial pressures of 10^{-4}–10^{-2} atm, and has been reported previously with regard to high temperature superconducting oxides. However, thermally activated processes such as diffusion also diminish with decreasing temperature and there is a critical point balancing a thermodynamic advantage of low oxygen partial pressure and a kinetic disadvantage of low temperature.

In this letter, we demonstrate growth of polycrystalline LSO:Ce films at various PLD parameters and investigate their optical properties. It is observed that stoichiometric LSO:Ce films can be prepared even at room temperature and that the x-ray induced luminescence of LSO:Ce films is greater than that of pure LSO crystals prepared by a high temperature growth method, when normalized to the active volume.

LSO thin films were deposited using a 308 nm XeCl excimer laser on 50 nm thick Pt/Ti/(100) Si substrate by using 0.055 mol % Ce doped Lu$_2$SiO$_5$ crystal pellet as a target. In addition, a (100) MgO single crystal substrate was used to analyze the composition of as-deposited films via Rutherford backscattering spectrometry (RBS). The laser energy density on the target surface was set to be 1 J/cm^2 and

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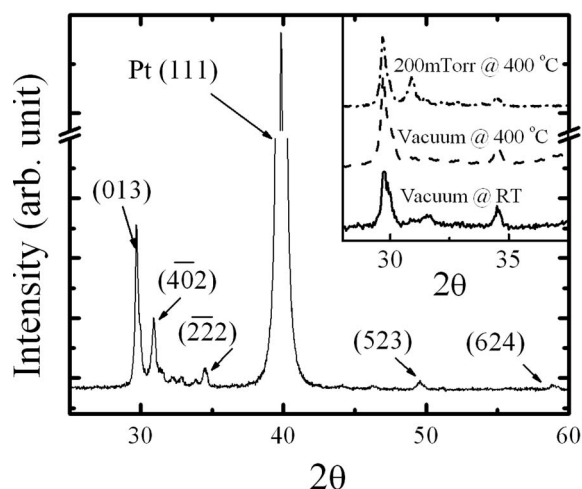
FIG. 1. X-ray diffraction patterns of Ce doped Lu_2SiO_5 (LSO:Ce) films on Pt/Ti/Si deposited at 400 °C and 200 mTorr oxygen partial pressure. Inset shows XRD spectra of three LSO films deposited on a Pt/Ti/Si substrate at different conditions.

FIG. 2. Rutherford backscattering spectrum of Ce doped Lu_2SiO_5 (LSO:Ce) films on MgO and simulation results assuming that the formula is Lu_2SiO_5. The determination of the ratio of Lu:Si near the expected 2:1 stoichiometry is observed.

the oxygen pressure was in the range of 2×10^{-3}–400 mTorr. The substrate temperature was varied from room temperature up to 800 °C. After deposition, the films were cooled to room temperature at 5 °C/min under the oxygen flow. The nominal film thickness was 400 nm.

The structure of the films was investigated by x-ray diffraction. A θ–2θ scan was performed for films in the 2θ range of 20°–60° using Cu $K\alpha$ radiation. The stoichiometry of the thin films was measured using RBS. To investigate the optical properties of the films, radioluminescence (RL) emission spectra were measured. The films were x-ray irradiated at an energy of about 25 keV and an exposure rate of 1.75 Gy s^{-1} in air. RL spectra were collected from the light emitted through an optical fiber onto the entrance slit of a 1/4 m monochromator with a charge-coupled device detector.

Figure 1 shows the results of x-ray diffraction (XRD) performed on the films as a function of temperature. The strongest diffraction peak, which appears near 40°, is from the Pt coated Si substrate. The other reflections can be assigned to LSO with $C2/c$ monoclinic symmetry, as indicated. As the deposition temperature increased, the broad peaks around 30° started to split and the XRD pattern shows the most intense peaks of polycrystalline LSO with monoclinic $C2/c$ symmetry. This indicates that the PLD method can form crystalline LSO films even at room temperature. Additionally, the XRD data of the LSO films show a small shift towards lower 2θ values with respect to the standard powder pattern. The small change in the lattice parameter indicates a residual out of plane tensile strain in the lattice of about 0.5%, presumably due to the thermal expansion mismatch between the substrate and the film.

Figure 2 shows the result of RBS analysis for a LSO film grown on the (100) MgO single crystal substrate at 200 mTorr and 400 °C. The substrate was chosen so that the Lu and Si peaks could not be buried under a substrate peak. Also shown is a simulation of the experimental data for a stoichiometric (Lu:Si=2:1) thin film. The good agreement between the simulation and the experimental data shows that a stoichiometric LSO film is readily achieved with PLD.

Figure 3 shows the RL results of LSO:Ce films as a function of the deposition temperature under nominal
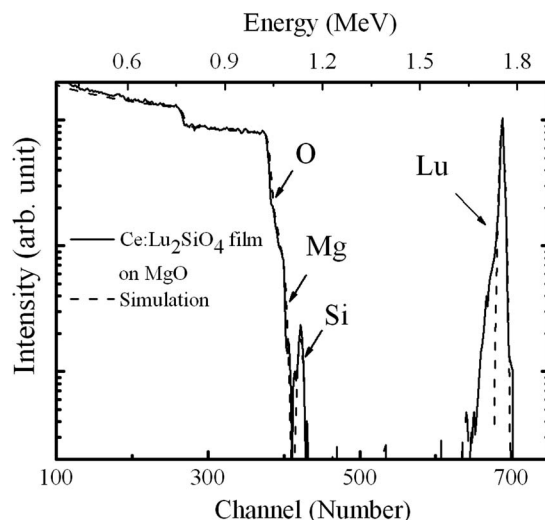
vacuum conditions (10^{-5} Torr). With increasing growth temperature, the RL intensity increased monotonically with deposition temperature and is essentially maximized at a deposition temperature of 600 °C. The Ce emission peak at 420 nm is identical to that observed in the bulk crystals, indicating that the Ce ions are located at optically active positions in the LSO host lattice.[13] Presumably, the increase in the RL intensity with deposition temperature is due to improved crystalline quality with a concomitant reduction in electronic defects that promote nonradiative relaxation. To address this point further, RL was examined between 75 and 300 K. It is well known that for single crystal LSO:Ce, the $5d$-$4f$ electronic transition is split into well defined crystal-field levels. Since the $4f$ level is split due to spin-orbit interactions, low temperature RL shows two resolved peaks in the main band emission around 420 nm below 75 K.[14] Temperature dependent RL of the PLD LSO:Ce films did not demonstrate this effect, showing only one broad emission peak down to 75 K. This indicated a significantly more disordered crystalline structure, presumably resulting from broadening
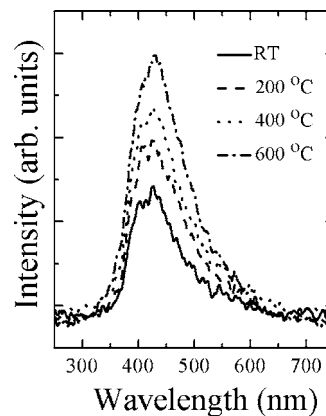

FIG. 3. RL emission spectra of four Ce doped Lu_2SiO_5 (LSO:Ce) films deposited under 2×10^{-5} Torr between room temperature and 600 °C. The RL curve at 800 °C has been omitted for clarity since it essentially overlaps the RL curve at 600 °C.
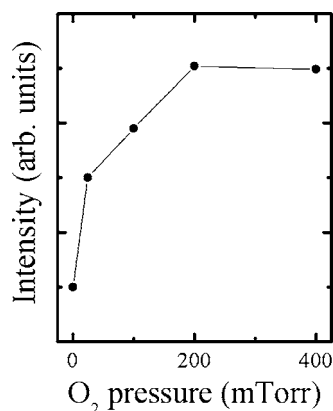
FIG. 4. Radioluminescence intensity vs the oxygen partial pressure for films deposited at 400 °C.

of the spin-orbit 4*f* levels due to the stress in films observed in XRD results of Fig. 1.

As an additional observation, the RL spectra shown in Fig. 3 were integrated and compared to bulk LSO:Ce emission. By defining a relative figure of merit of the measured intensities normalized to the active volume, it can be inferred that the thin film brightness $[(333\,000\pm33\,000)/\mathrm{cm}^3]$ at our optimal deposition conditions is nominally twice that of the single crystal LSO:Ce material $[(167\,000\pm17\,000)/\mathrm{cm}^3]$. This result suggests that the Ce emission from a polycrystalline LSO lattice is still quite efficient. This may indicate that the Ce is efficiently distributed in each of the monoclinic sites in the $C2/c$ structure, having oxygen coordinations of 6 and 7, respectively, and is essentially unaffected by disorder of the isolated silica tetrahedra. Additionally, the Debye-Scherrer broadening of the XRD peaks indicates a grain size of nominally 30–50 nm. This compares favorably with atomic force microscopy images (not shown) that indicated a 20 nm grain size and a 5 nm rms surface roughness. Luminescence studies of hydrothermally prepared Ce doped Y_2SiO_5 nanopowders in a comparable size range have also demonstrated enhanced light output consistent with these observations.[15]

Another important parameter of the metal oxide film growth is the partial pressure of oxygen during the growth. Figure 4 shows a plot of the RL intensity films as a function of the oxygen partial pressure at a fixed deposition temperature of 400 °C. An increase in RL intensity was observed with increasing oxygen partial pressure up to 200 mTorr, above which the RL intensity saturated. The saturation of light output as a function of oxygen partial pressure may be related to optical activation of Ce ions. To optimize the luminescence of LSO:Ce, Ce^{4+} in LSO should be converted to Ce^{3+}.[16] This favors a reducing environment during the film deposition. However, the growth of films in vacuum, a strong reducing environment, is expected to decrease the crystalline quality of the films with a concomitant reduction in quantum efficiency. The saturation of the RL intensity suggests that the trade-off between Ce^{3+}/Ce^{4+} interconversion and defect

formation gives rise to a maximum in the luminescence efficiency at an oxygen partial pressure of about 200 mTorr.

The present study shows that Ce doped LSO films have been grown at a temperature ranging from room temperature to 800 °C, which is much lower than preparation temperature of bulk or powder LSO:Ce. LSO:Ce thin films show efficient luminescence centered at 420 nm at room temperature, which is consistent with LSO:Ce single crystals. The luminescence of polycrystalline LSO:Ce films exhibits optimum performance when the film was grown at 600 °C under an oxygen partial pressure of 200 mTorr. The relative brightness for the optimized thin films, normalized to the irradiated volume, is higher than that for bulk single crystal LSO:Ce. These parametric studies do not allow us to unambiguously distinguish the effects that crystal cation defects and oxygen vacancies may exert on the overall light output. Further work will explore the local chemical environment of the Ce activator using electron paramagnetic resonance as well as the possibility of further increasing the thin film brightness by doping to higher Ce concentrations. The latter point is especially noteworthy since activator doping levels achievable via PLD are not restricted by the low Ce segregation coefficient in LSO, which limits the equilibrium concentration to 0.05 mol % in single crystal bulk LSO.

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