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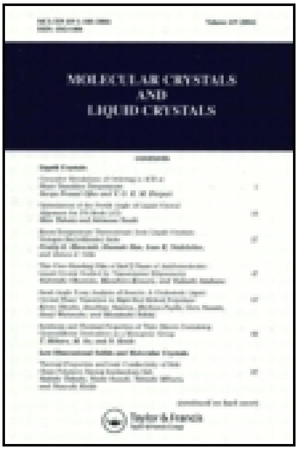

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Thin Film Materials with Samarium(III) for Room Temperature Hole Burning: Design and Photomechanism Studies

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Version of record first published: 04 Oct 2006

To cite this article: Raivo Jaaniso, Tea Avarmaa, Markko Paas, Marc Schnieper, F. Trotta & Hans Bill (1998): Thin Film Materials with Samarium(III) for Room Temperature Hole Burning: Design and Photomechanism Studies, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 314:1, 155-160

To link to this article: http://dx.doi.org/10.1080/10587259808042472

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Mol. Cryst. Liq. Cryst., 1998, Vol. 314, pp. 155–160
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Thin Film Materials with Samarium(III) for Room Temperature Hole Burning: Design and Photomechanism Studies.

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Multicomponent thin films with spectral hole burning capacity at room temperature were synthesized by using molecular beam and pulsed laser deposition techniques. All materials were activated by Sm^{2+} in low-symmetry alkaline earth sites, the synthesis involved the control of ionic diffusion rate during multilayer growth and special reduction of Samarium. Enhancement of hole burning rate by 1-2 orders is obtained in nanocrystalline films as compared to bulk and microcrystalline materials. New hypothetic mechanism involving the creation of Sm-defect (photochromic) centers is proposed for reversible photoburning.

Keywords: spectral hole burning; disordered crystals; thin films; samarium; molecular beam deposition; pulsed laser deposition

Introduction

Among the rare earth ions which can be stabilized in solids in different valence states, Samarium has proved to have the smallest modulation broadening of 4f-4f transitions in bivalent state. Therefore it keeps to be one of the best candidates as an activator for the further design of room-temperature spectral hole burning disordered crystals[1] or glasses[2,3]. Modern methods for thin film synthesis have opened new possibilities for engineering the material properties through the variations in material composition and mesoscopic structure. Thus, thin films activated with Sm^{2+} could provide additional degrees of freedom for the synthesis of new structures (incl. metastable ones) with increased spectral selectivity and efficiency of the photoburning processes.

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Design

The basic structure of the materials under the study can be generally characterized as being crystalline but disordered and always involving low-symmetry site(s) of alkaline earth ion(s). As such compounds are typically multicomponent ones, the choice of the technique for thin film growth occurs to be rather critical for the successful synthesis with predetermined stoichiometry. For example, the films grown in our molecular beam epitaxy apparatus with a single SrFCl molecular beam source were unstable because of preferential evaporation of highly hygroscopic $SrCl_2$[4]. Earlier, Sm^{2+}:$SrFCl_{0.5}Br_{0.5}$ films were grown by simple thermal evaporation[5] and also the presence of different phases was detected in XRD measurements.

Following techniques were identified to be suitable for our goals, and were then optimized for concrete materials under the study: i) multiple beam molecular beam deposition (MBD) with precise control of molecular fluxes, and, ii) pulsed laser deposition (PLD).

According to the spectral data of Ref. [1,6], the growth of multilayer films with alternating compositions within the PbFCl host structure family could result in considerably enhanced spectral multiplicities for hole burning. By using MBD, such design was realized on $Sr_xCa_{1-x}FCl$ ($0<x<0.5$), which was predicted to give the broadest spectral range for the multilayers grownable with 3 effusion cells[4]. A set of alternating layers with $x=0$ and $x=0.5$ were grown, the molecular beam sources being (CaF_2 + $CaCl_2$), and (CaF_2 + $SrCl_2$), respectively. For maintaining the right stoichiometry, the beam fluxes from different sources were carefully calibrated and stabilized prior to growth. As the ionic diffusion tends to equalize the composition of sublayers during the growth, the substrate temperature and sublayer thickness had to be adjusted for obtaining the maximum value of the inhomogeneous spectral bandwidth. The fluorescence excitation spectrum of a multilayer film with sublayer thickness of 100 nm grown at a substrate temperature of 350°C is shown on Figure 1(C).

PLD becomes more and more recognized as an universal and cost-effective technique for growing thin films of multicomponent compounds. As it is most advanced for the growth of oxide-based ceramics, we made the first test among PbFCl-type materials on Sm^{2+}:$SrFCl_{0.5}Br_{0.5}$, for which the biggest collection of single crystal reference data exist.

A simple vacuum chamber with scanning target holder and substrate heater was used together with 100 mJ XeCl (308 nm) excimer laser. Films were grown on carefully cleaned and dried quartz substrates at substrate temperatures between 20°C and 420°C. The polycrystalline films of Sm^{2+}: $SrFCl_{0.5}Br_{0.5}$ obtained were stable in air, and the shape of their fluorescence spectra was identical to a single crystal one. Thus, successful stoichiometry transfer (including the Sm valence state) occurred by using a single target material. The grain size (1 micrometer and more) was, however, bigger for these samples than for the previous films grown by MBD (~100 nm grain size).

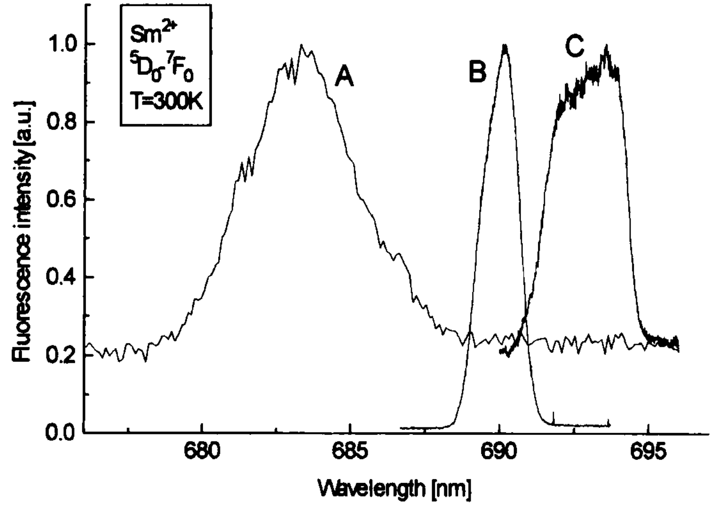

FIGURE 1. $^5D_0$-$^7F_0$ transition spectra of Sm^{2+} in CaB_4O_7 (A; grown by PLD), in $SrFCl_{0.5}$ $Br_{0.5}$ (C, grown by PLD), and in multilayer $Ca_{1-x}Sr_xFCl$ film (C; grown by MBD).

One of the potential advantages of PLD for the design of hole burning materials is the extension of thin film studies to oxide-based compounds. The interest for such studies was derived, in particular, from the correlations which exist within the PbFCl structure family between the ionicities and Debye temperatures, on the one hand, and Sm^{2+} spectral parameters, on the other hand [1,4,6]. It can be predicted by the extrapolation of these correlations that the compounds with smaller ionicity could be favorable for the further extension of the spectral range and multiplicity. One of the materials selected on this basis was CaB_4O_7. The initial powder material was transformed into the ceramic target pellet under reducing conditions (in H_2/N_2 atmosphere at 800°C). The films obtained by PLD were polycrystalline but internally strongly disordered as manifested by a large inhomogeneous width of Sm^{2+} spectrum (A in Figure 1).

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Photomechanism

Typically, for all the Sm-based compounds on which room-temperature hole burning has been observed up to now, the maximum hole depth observed is about 10-20%. Hence, the obvious starting point for the analysis is: how to explain the commonly observed saturation of the hole depth?

Following the hole burning study on Samarium(III) in BaFCl[7], the mechanism has been always assigned to photoionization of Sm^{2+} followed by electron trapping on Sm^{3+} or on some other trap. The origin of the other traps have remained unknown in all cases, with a possible exception of Sm-doped borate glasses, where a new EPR signal was observed in parallel to the acceleration of hole burning after x-ray irradiation[8]. The photoionization mechanism was briefly analytically analyzed in Ref. [1] (referred below as Model I), whereas the maximum hole depth was shown to be limited because of limited number of electron traps in the material. The second possibility we will check below is different (Model II): the phototransformation occurs in a local Sm environment and the hole depth becomes saturated because of reverse photoprocesses (which are converting the photoproduct back into Sm^{2+}). Finally, one has to consider the possibility that not all Sm^{2+} ions are photoactive but only a small fraction situated near point defects, dislocations, grain boundaries etc. (Model III). All three models can be analytically described by respective kinetic equations governing the spectral inhomogeneous distribution function[1].

The temporal dependencies of hole parameters for the $SrFCl_{0.5}Br_{0.5}$ sample are compared with the theoretical curves in Figure 2. The time-dependence of hole depth was fitted with two models. For Model II the best fit was observed at the ratio r_D/r_R=0.65 for the rates of direct and reverse photoprocesses. The fitting curve for Model III corresponds to the case of only 24% of photoactive Sm. As one can see from Figure 2, the temporal dependence of the hole width is not consistent with Model III. We note that the relative hole broadening predicted by this model exceeds the experimental one by more than one order at t=500 s. The qualitative analysis made for Model I also showed the saturation of hole depth and width at a level of 10-20%. Consequently, as Model III predicts unreasonably fast hole broadening, all Sm^{2+} seems to be photoactive.

Light-induced hole filling occurring under the resonant excitation at multiple hole burning (Figure 3, B) can be interpreted according to Model I as follows: Sm^{2+} ions, ionized at the first hole burning, will turn into Sm^{3+} electron traps for the next hole burning at different wavelength. Interestingly, as shown in the upper part of Figure 2, irradiation with the (636 nm) light nonresonant to the Sm^{2+} transition also leads to hole filling. As only partial filling occurs in this case, both reversible and irreversible photomechanisms should be present. The

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last mechanism can be ascribed to photoionization but the one which is responsible for the filling at non-resonant excitation necessitates different explanation, especially in the light of the fact that all Sm^{2+} ions are photoactive.

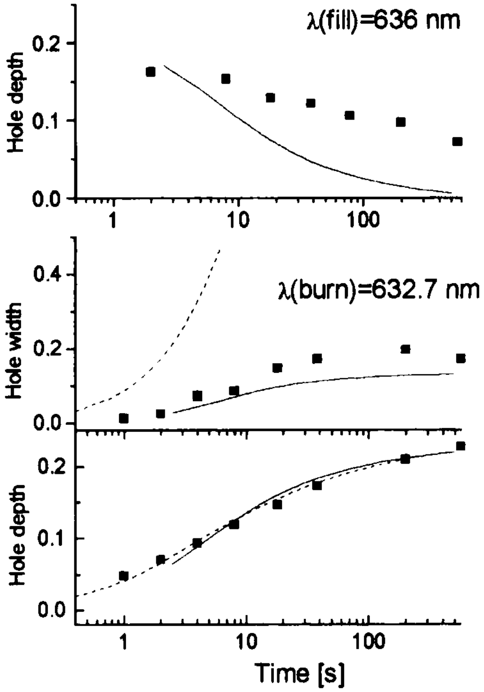

FIGURE 2. Temporal dependence of the change in relative hole depth and width at hole burning (lower subfigure) and of the hole depth at subsequent light-induced hole filling (upper subfigure) for the $^5D_1$-$^7F_0$ transition of Sm^{2+}: $SrFCl_{0.5}Br_{0.5}$. The filled square dots represent the experimental data, the full lines are theoretical curves for model II, and dashed lines for model III. The changes in hole depth and width are given with respect to (extrapolated) values at t=0.

One possible scenario, analogous to that occurring in fluorite-type crystals, is the formation of a photochromic center, where two optical electrons are shared by Sm^{3+} core and a vacancy[9]. Such center can be formed after photoelectron decay through the bound exciton state into the pair of H and F centers at Sm ion. The formation energy of H-F pair was calculated to be near 4 eV in PbFCl family crystals[10], which exactly matches the threshold energy for 2-quantum hole burning in these materials[1,7]. This type of mechanism is also consistent with the fact that the decrease in Sm^{2+} fluorescence signal is not accompanied by the increase in Sm^{3+} signal at the irradiation with Ar-laser (514+488 nm) light.

The hole burning in nanocrystalline $Sr_xCa_{1-x}FCl$ was determined to be 1-2 orders more efficient as compared to the single crystals and to the films with relatively big grain size (>1 μm). In addition, practically no hole filling occurred

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at multiple hole burning in this sample (Figure 3, C). These facts point towards the increased role of irreversible photoionization, which could result from increased possibilities of electron trapping at surfaces and grain boundaries.

Acknowledgments

This work was supported by Estonian Science Foundation (grant no. 2769), Swiss National Science Foundation and Swiss Priority Program "Optique".

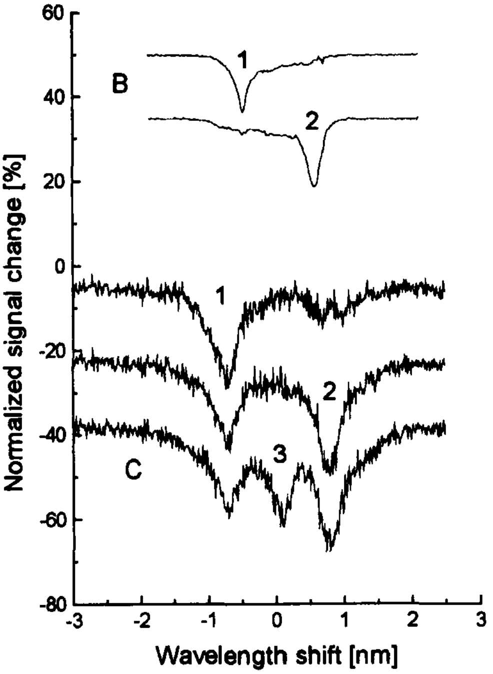

FIGURE 3. Multiple spectral hole burning in SrFCl$_{0.5}$Br$_{0.5}$ (B) and in Sr$_x$Ca$_{1-x}$FCl film (C). Hole burning was performed sequentially in the order shown at the curves.

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