Luminescent materials: glasses as substrate, matrix and active medium

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Light generation and manipulation has gained new impetus in the last years due to the development of new concepts in lighting and display technology, notably by the advent of high brightness LED's, large area LCD displays with TV capability, the availability of planar light sources and the prospects of full organic systems (OLED's) for lighting applications. In addition to serving only as a substrate for luminescent materials, this contribution discusses some aspects of glasses for light generation.

Glass substrates and luminescent powders

For several decades now, glasses transparent in the visible part of the optical spectrum have been serving in the display and lighting industry as substrates for powder layers of luminescent materials. The main advantage of glass here is the variability in shape and colour as well as the feasibility of sealing vacuum-devices like cathode ray tubes and fluorescent light tubes for consumer applications. Thus, the function of light generation has been separated completely from the mechanical and optical functions provided by glass. The interface between glass and luminescent material in these applications is crucial: in most cases, luminescent powders need to adhere without binders on the glass surface, mediated only by the surface chemistry of glass and luminescent material [1]. Especially cathode ray tubes meanwhile are very large devices, and as vacuum devices they need to be mechanically stable under all circumstances after delivery to the customer. Glass in cathode ray tubes must also act as shield against X-rays generated by the typical 30 keV electron beam. This function is provided by lead oxide, barium oxide and strontium oxide components in these glasses. Nowadays, these components pose serious problems during recycling of end-of-life cathode ray tubes, since no other large-scale application for these components is available.

In novel lighting devices and displays based on organic conductors end emitters, glass still is the substrate, but does not need to provide the casing for a vacuum device operated with high voltage. Therefore, these glasses are sheet-like, thin and (partially) flexible; but still the optical and electrical functions are provided solely by layers deposited on the glass body.

Sol-gel derived glasses doped with lanthanide complexes

The obvious ways to combine emissive functions with the advantages of a glassy matrix is doping with luminescent ions. Due to their large *Stokes*-shift and their narrow emission, lanthanide ions play a prominent role in luminescent materials - glasses doped with lanthanide oxides thus may look as the natural choice. Unfortunately, direct excitation of f-f transitions in lanthanide ions by optical absorption is quantum mechanically not allowed; only f-d and charge transfer transitions can be exploited directly for optical excitation with high efficacy. In most cases, therefore sensitization is needed for the absorptive part. Organic complexes of the lanthanides in this respect look especially promising, since they may combine intense absorption in the organic ligands after energy transfer with the desired emission from the lanthanide ions [2, 3, 4]. These complexes (typically aromatic carboxylates and diketonates) are chemically not stable enough for direct application and thus need a protective matrix. This can be provided e.g. by zeolites [5] or by a sol-gel-derived glass, since process temperatures may be low enough to accomodate the complexes in an e.g. nanoporous silica host. It turned out, that the resulting hybrid sol-gel glasses still can show quite high quantum efficiencies of luminescence [6]. The main advantage of the sol-gel-route is the possibility to prepare thin and thick layers at low temperatures and ambient conditions, e.g. by dip- or spin-coating (see fig.1, film thickness is about 900 nm). Additionally, mild heat treatment optimizes emission [7].

Defect–sensitized luminescence in germania–doped glass

The main disadvantage of sol-gel-glass doped with lanthanide complex is the thermal and photochemical fragility of the complexes. More stable systems need to contain solely inorganic components. An interesting way to sensitize the forbidden lanthanide transitions is the exploitation of point defects, which may show very intensive optical absorption. An example is sol-gel silica, codoped with germania and terbium oxide and reduced e.g. by heat treatment in oxygen-free atmosphere. The resulting reduced Ge-

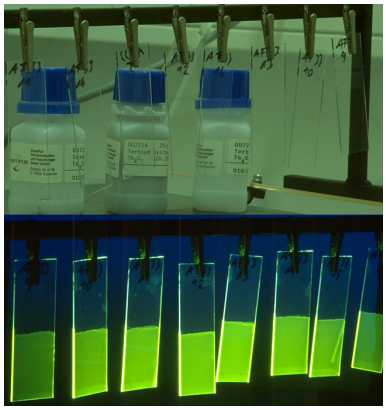

Figure 1: Photographs of dip–coated Tb–benzoate doped silica layers under daylight illumination (top) and under 254 nm illumination (bottom)

defects are capable of very strong UV absorption; nearby Tb ions accept the energy thus absorbed and emit with their typical emission lines [8]. Fig. 2 shows excitation and emission spectra of such a reduced, codoped sample. However, film formation and control of defect density at low temperature are still unresolved issues in these systems.

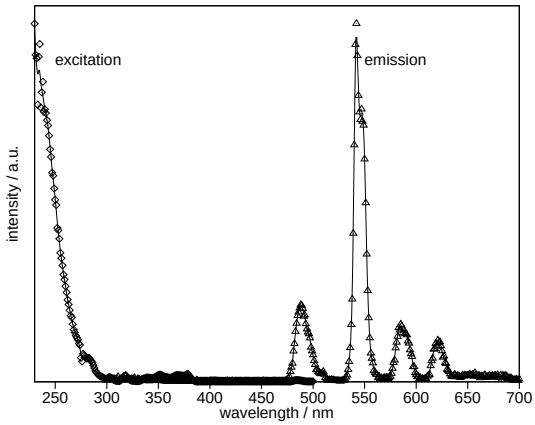

Figure 2: Room temperature excitation (541 nm monitor) and emission (254 nm excitation) spectra for a reduced Ge,Tb codoped sol-gel-derived silica sample. Lines are guidelines for the eye. Reprinted with permission from [8]

Microstructured emissive glass layers

Depositing thin and thick films by sol-gel-based techniques also offers the possibility to generate laterally microstructured emissive glassy layers, doped with different luminescent complexes or entities. These can be produced by adaptation of photolithographic techniques [9] or the use of various printing techniques. Fig. 3 shows examples of transparent layers on glass (film thickness about one micrometer), structured by standard photolithography and spin-coated side by side in two steps. The red and green

colour under UV irradiation (generated by Eu-picolinate and Tb-picolinate, respectively) prove the feasibility of micrometer-resolved structures with sol-gel-derived glassy layers. Similar results have been achieved on silicon, aluminum and various polymers.

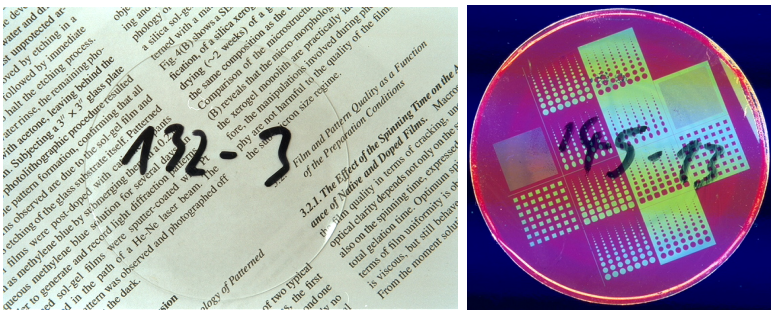

Figure 3: Spin–coated and photolithographically structured silica layers doped with Tb-picolinate and Eu-Picolinate. Left: daylight illumination. Right: UV (254nm) illumination. Reprinted with permission from [9]

An alternative to lateral structures on flat substrates is the coating of optical fibre tips [10]. Fig. 4 shows an example of a standard gradient index fibre coated at its tip with Tb-picolinate in silica matrix. The light generated can be guided by the fibre some dozen meters. Such as system (perhaps with fibres with various different coatings on the tip) may serve as sensor tip for UV light or chemicals, since the optical properties of several lanthanide complexes are sensitive to their chemical environment.

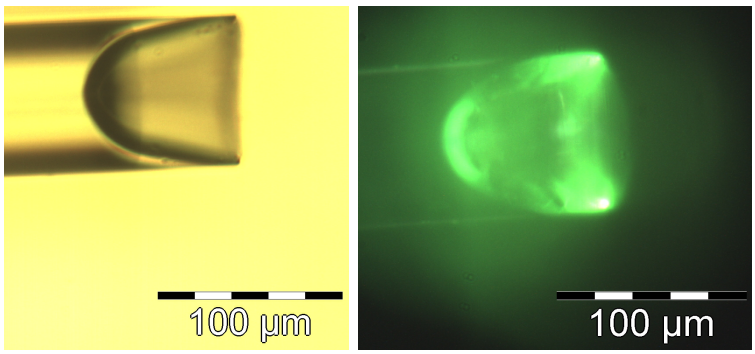

Figure 4: Dip-coated (Tb-picolinate doped silica) optical fibre tip. Left: daylight illumination. Right: UV (254nm) illumination. Reprinted with permission from [10]

Luminescent nanoparticles and glass

The main disadvantage of organic/inorganic hybrid materials is the poor photochemical and thermal stability of the organic part. Apart from the use of defects as described above, inorganic luminescent nanoparticles can be used as dopants. Several of the available particles are toxic (CdSe, CdTe) and thus are not suited for any mass applications. Luminescent nanoparticles on the basis of ZnS are non-toxic, but have a larger

band–gap (even widening under quantum confinement conditions), so that dopants are necessary for visible emission. Fig. 5 shows examples of luminescent nanoparticles in aqueous dispersion under UV illumination and a transparent silica layer doped with ZnS:Mn nanoparticles of diameter 10 nm.

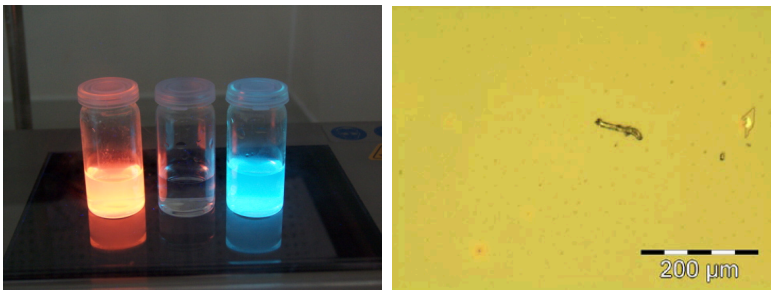

Figure 5: Luminescent ZnS nanoparticles (ZnS:Mn, undoped, ZnS:Cu) under UV-light illumination (left). Right: ZnS:Mn-doped dip–coated transparent silica layer

Outlook: organic electronics protected in glassy matrix ?

The examples for light generation within a glassy matrix described so far all take advantage of the protective function of the matrix. This should be even more important when considering the organic components of fully organic electronic devices like OLED's. Combination of glass and organic electronics thus would incorporate also the switching functions into glass. The possibility of immobilization of complex organic entities in sol–gel glasses has let already to the proposition of glass-dispersed liquid crystals (GDLC) [11, 12]. Such systems might lead to liquid crystal (LC) displays without polarizers. The extension to luminescent GDLC's seems possible by specifically designed lanthanide compounds, dissolved in a nematic solvent and dispersed in a glassy matrix. First results with these materials have been presented by Binnemans [13]). If it should turn out to be possible to combine such structures with electronically active structures in the glass, display and lighting concepts fully encapsulated in a glassy matrix might become feasible.

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