

Multiform Oxide Optical Materials via the Versatile Pechini-type Sol-Gel Process

J. Lin ^{a)}

State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry
Chinese Academy of Sciences, Changchun 13002, P. R. China

Abstract

This presentation highlights work from the authors' laboratories on the various kinds of oxide optical materials, mainly luminescence and pigment materials with different forms (powder, core-shell structures, thin film and patterning) prepared by the Pechini-type sol-gel (PSG) process. The PSG process which uses the common metal salts (nitrates, acetates, chlorides etc) as precursors and citric acid (CA) as chelating ligands of metal ions and polyhydroxy alcohol (such as ethylene glycol or poly ethylene glycol) as cross-linking agent to form a polymeric resin on molecular level, allowing the preparation of many forms of luminescent materials.

Keywords: Oxide; Optical materials; Pechini process

1. INTRODUCTION

The polymerizable-complex (PC) technique, also known as the Pechini method (later we call it Pechini-type sol-gel process, and abbreviate as PSG), is well known and used for the synthesis of homogeneous multi-component metal oxide materials. This method includes a combined process of metal complex formation and in situ polymerization of organics. Normally an α -hydroxycarboxylic acid such as citric acid (CA) is used to form stable metal complexes, and their polyesterification with a polyhydroxy alcohol such as ethylene glycol (EG) or poly ethylene glycol (PEG) forms a polymeric resin. Immobilization of metal complexes in such rigid organic polymer networks reduces segregation of particular metals, ensuring compositional homogeneity. The calcination of the polymeric resin at a moderate temperature (500-1000 °C) then generates a pure phase multi-component metal oxides. The above process is clearly shown in Scheme 1.

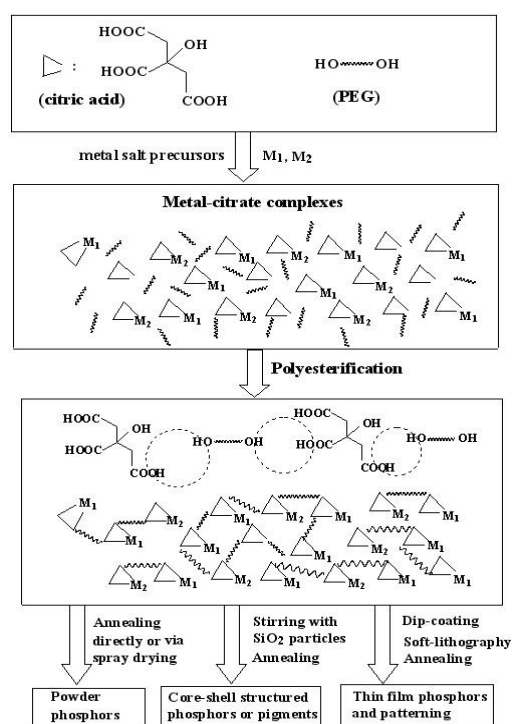
In the past five years, we have extended the application of the PSG process to the systematic synthesis of various kinds of oxide optical materials, mainly luminescence and pigment materials with different forms (powder, core-shell structures, thin film, patterning). The purpose of our research is to reveal the feasibility, versatility, advantages and disadvantages of this method for the synthesis of such optical materials, in an effort to fine control of the material morphology and find novel optical materials. ¹

2. EXPERIMENTAL AND RESULTS

The experimental processes have been described previously and can be seen in Scheme 1. ¹⁻¹⁵

A. Powder luminescent materials

One of the most common, direct and simple forms of



Scheme 1 The basic principle of Pechini-type sol-gel process and multi-form optical materials derived from it.

luminescent materials via PSG process is powder phosphor.

Here we take the preparation and physical properties of a simple phosphor β -Ga₂O₃:Dy³⁺ (2 at. % of Ga³⁺, optimized as a representative example, to illustrate the advantages of the PSG process over the conventional solid state reaction method (SSR). The Dy³⁺-doped Ga₂O₃ phosphor is of great interest and importance because of the efficient energy transfer from Ga₂O₃ host lattice to the Dy³⁺ ions. For β -Ga₂O₃:Dy³⁺ via the PSG process (GaCl₃ and DyCl₃ as starting materials, citric acid as chelating ligands

^{a)} Corresponding author. E-mail: jlin@ciac.jl.cn

to metal complexes, and poly ethylene glycol as cross-linker for polyesterification with the complexes), the sample remained amorphous after 500 °C heat treatment, began to crystallize at 600 °C, and the crystallinity increased with raising the annealing temperature and the crystallization was complete at 1000 °C (4 hours). No second phase was detected, indicating that the Dy³⁺ ions have been successfully dissolved in the β -Ga₂O₃ host lattices by substitution for the Ga³⁺. But for β -Ga₂O₃:Dy³⁺ via the SSR process (mixing Ga₂O₃ and Dy₂O₃ together followed by grinding and high temperature annealing), even after being fired at 1200 °C for 8 hours, the Dy³⁺ ions were unable to be well dissolved in the β -Ga₂O₃ host lattices, and minor amounts of Dy₃Ga₅O₁₂ were always present in spite of repeat grinding and annealing at this high temperature. β -Ga₂O₃:Dy³⁺ (PSG) phosphor is composed of spherical and slightly aggregated particles with the sizes ranging from 50 ~100 nm, while β -Ga₂O₃:Dy³⁺ (SSR) consists of irregular particles with a wide range of size distribution (0.5 – 3.5 μ m). Luminescence study demonstrates that there exists a very efficient energy transfer from β -Ga₂O₃ semiconductor host to Dy³⁺ in β -Ga₂O₃:Dy³⁺ (PSG) phosphor (no emission from β -Ga₂O₃ is observed, and the emission consists exclusively of the Dy³⁺ f-f transition lines upon excitation into the band gap of β -Ga₂O₃), while the energy transfer from β -Ga₂O₃ host to Dy³⁺ in β -Ga₂O₃:Dy³⁺ (SSR) is far from complete (a strong band emission from β -Ga₂O₃ is observed apart from the emission lines of Dy³⁺ upon excitation into the band gap of β -Ga₂O₃). As a result, the emission intensity of Dy³⁺ in the former is about twice that in the latter. Thus the advantages of PSG over the SSR in the preparation of luminescent materials are clearly indicated. Although the PSG process can prepare luminescent materials at relatively low temperature, sometimes the hydrocarbon residues can not be removed completely (< 800 °C), which are not good for the rare earth ions doped phosphors (quenching the emission of rare earth ions via their high phonon energy or as nonradiative traps for the excitation energy). So in these cases, the phosphors had better be annealed at temperature higher than 1000 °C to remove these impurities for good emission performance. On the other hand, it is also possible to utilize these carbon related impurities themselves as emission centers to get some novel luminescent materials without rare earth or transition metal ions as activators, i.e., these so-called environmentally friendly luminescent materials. Recently we found that similar kind of luminescent materials can also be prepared from other oxide systems (such as BPO₄, ZrO₂ and Y₂O₃ etc.) by the PSG process at low annealing temperature. It is shown that PGS derived BPO₄ (which is isomorphous with SiO₂) exhibits a weak purple-colored emission (λ_{\max} = 409 nm, lifetime 6.4 ns, quantum yield 17 %) under UV irradiation, and doping it with 6 mol % Ba²⁺ produces a material that emits an efficient bluish white light with a quantum yield up to 31 %. We propose that peroxy-radical hole traps, such as •OOBO₃ or •OOPO₃, and carbon-containing impurities play a key role in the

photoluminescence process. These inclusions serve as emission centers in a material that otherwise should not be especially photoactive. The same situation was observed for ZrO₂ and Y₂O₃ prepared by the PSG process followed by annealing at 500 °C. Especially, the Y₂O₃ exhibits a bright whitish emission under 365 nm UV lamp irradiation, and has a quantum efficiency as high as 65 % (using 325 nm HeCd laser as the excitation source). Note that some titanates (PbTiO₃, SrTiO₃, BaTiO₃) prepared by the PSG process followed by calcination at 300 – 400 °C also show an intense photoluminescence. Although no clear mechanism for the luminescence was given in the reports, now we believe that the carbon related impurities and oxygen defects must play a key role in such emission process as stated above.

B. Core-shell structured phosphors

Now it is well established that spherical morphology with narrow size distribution for phosphors is good for high brightness and high resolution because high packing densities and low scattering of light can also be obtained by using such phosphors. Silica can be fabricated controllably into perfectly spherical morphology from nano- to micron size, and it is frequently used in core-shell structured materials, either as a core or a shell. If the silica spheres are coated with phosphor layers, a kind of core-shell phosphor materials with spherical morphology will be obtained, and the size for the phosphor particles can be controlled by the silica cores and the number of coating cycles. Furthermore, because silica is cheaper than most of the phosphor materials (which often employ the expensive rare earth elements as the activators and/or host components), the core-shell phosphor materials will be cheaper than the pure phosphor materials. Based on above situation and consideration, we synthesized monodisperse and spherical SiO₂ particles with different sizes ranging from 250 to 1500 nm through a modified Stöber process (i.e., the hydrolysis of TEOS in an ethanol solution containing water and ammonia, and the particle size of silica depended on relative concentration of the reactants), and successfully coated them with various luminescent layers via the PSG process. This resulted in a series of SiO₂ core / phosphor shell particles, whose synthesis temperatures, core-shell sizes and emission properties are collected in Table 1. The experimental process is quite simple, i.e., just stir the as-formed SiO₂ particles in corresponding PSG precursor solutions of the phosphors (consisting of metal ions, CA and PEG), then separate the SiO₂ particles by centrifugation, followed by annealing of the SiO₂ particles at certain high temperature to form the final products. The above process can be repeated for several times to increase the thickness of the phosphor shell.

C. Thin film phosphors and patterning

In the past year, we prepared a series of oxide phosphor films by the PSG process and investigated their structure, mor

phology and optical properties. The preparation of thin film phosphors via the PSG process contains the following steps.

TABLE 1. Characteristics of some core-shell structured phosphor particles prepared by the PSG process.

Sample	Synthesis Temperature (°C)	SiO ₂ core / phosphor shell size (nm)	Emission color
SiO ₂ @Y ₂ O ₃ :Eu ³⁺	900	500 / 60	Red
SiO ₂ @YVO ₄ :Eu ³⁺ /Dy ³⁺ /Sm ³⁺	500-700	500 / 60	Red (Eu ³⁺); Yellow (Dy ³⁺); Orange (Sm ³⁺)
SiO ₂ @Gd ₂ (WO ₄) ₃ :Eu ³⁺	800	400, 500, 600, 700 / 50	Red
SiO ₂ @CaWO ₄ :Eu ³⁺ /Tb ³⁺	800	500 / 50	Red (Eu ³⁺); Green (Tb ³⁺)
SiO ₂ @LaPO ₄ :Ce ³⁺ /Tb ³⁺	1000	300, 500, 900, 1200 / 60	Purple (Ce ³⁺); Green (Ce ³⁺ , Tb ³⁺)
SiO ₂ @Y ₂ SiO ₅ :Eu ³⁺ /Ce ³⁺ , Tb ³⁺	1000	385 / 50	Red (Eu ³⁺); Green (Ce ³⁺ , Tb ³⁺)
SiO ₂ @CaTiO ₃ :Pr ³⁺	700	500 / 70	Red
SiO ₂ @Gd ₂ MoO ₆ :Eu ³⁺	800	500 / 50	Red

The first step is the preparation of the precursor solution with certain viscosity, including the dissolution of the starting materials, formation of metal chelates with citric acid (CA) and their polyesterification with poly ethylene glycol (PEG). The second step is the preparation of the amorphous precursor film by dip-coating or spin-coating process on the desired substrates (silica glasses, silicon wafers and some ceramics slides etc.). Finally, crystalline phosphor films are produced by the post annealing process at moderate temperature (500- 1000 °C) with a certain heating rate (generally slow to avoid the cracking and peeling of the films). Similar to other kinds of films prepared by the alkoxides based sol-gel process, thin film

phosphors via the PSG process the following advantages: (1) simple process and equipment, no expensive vacuum equipment is needed; (2) low processing temperature, which is particularly important because it allows the application of film to non-heat resistant substrates and the application of non-heat resistant films to substrate, making it possible to prepare films on glass, semiconductor and integrated photo-electronic devices; (3) low requirement for the shape and size of the substrate. Films can be both coated on substrates which have a large area, various shape and different material compositions; (4) easy to obtain homogenous multicomponent oxide films, and easy to control the constituents and micro-structure; (5) the thickness of the films can be controlled by the viscosity of the coating solution or the repeating number of the coating process. Additionally, the PSG process has advantages over the alkoxides sol-gel process in the low price of starting materials and easy control of the experimental process. The characteristics of YVO₄:Nd film via the alkoxides sol-gel process and YVO₄:Eu film via the PSG process can show the advantages of the latter. In both cases, the films can be crystallized after annealing at 400 °C. However, in the former the starting materials (alkoxides) and solvent [2-methoxyethanol-(ethyleneglycol monomethyl ether)] are expensive and the coating solution has to be prepared under N₂ atmosphere, while in the later the starting materials (metal nitrates) and solvent (ethanol) are common (cheap) and the coating solution can be simply prepared in ambient air condition. In general, the phosphor films via PSG process consist of nanocrystalline grains ranging from 100-500 nm, and the thin film phosphors present luminescence properties that do not differ greatly from the powder phosphors, but have lower emission intensity due to the light trapping inside the luminescent layer, and such films cannot presently compete with powder phosphors in applications that require high brightness.

On the other hand, when luminescent materials are used in display screens and devices, they need patterning. The patterning technologies of phosphor screens have a great effect on the resolution of flat panel display devices. For instance, pitches of phosphor lines for a supervideo graphics adapter with 800 x 600 lines, video graphics adapter with 640 x 480 lines and quarter video graphics adapter with 320 x 240 lines in 6 inches color displays are defined as 50.8, 63.5 and 127 μm, respectively. Therefore, a precise screening process for high resolution is desirable. The currently used patterning techniques for phosphor screen include electrophoretic deposition and screen printing etc. based on photolithography, which needs the complicated and expensive photolithographic and etching equipment. Recently however, much attention has been paid to non-photolithographic patterning techniques collectively known as soft lithography, which have the potential of becoming versatile and low cost methods for creating micrometer and sub-micrometer size structures. Many other kinds of patterned phosphor films, such as YVO₄:Eu³⁺, LaPO₄:Ce³⁺/Tb³⁺, Y₂O₃:Eu³⁺, Gd₂O₃:Eu³⁺,

can be prepared by the MIMIC technique, which are promising for future applications in the display fields. (Figure 1)

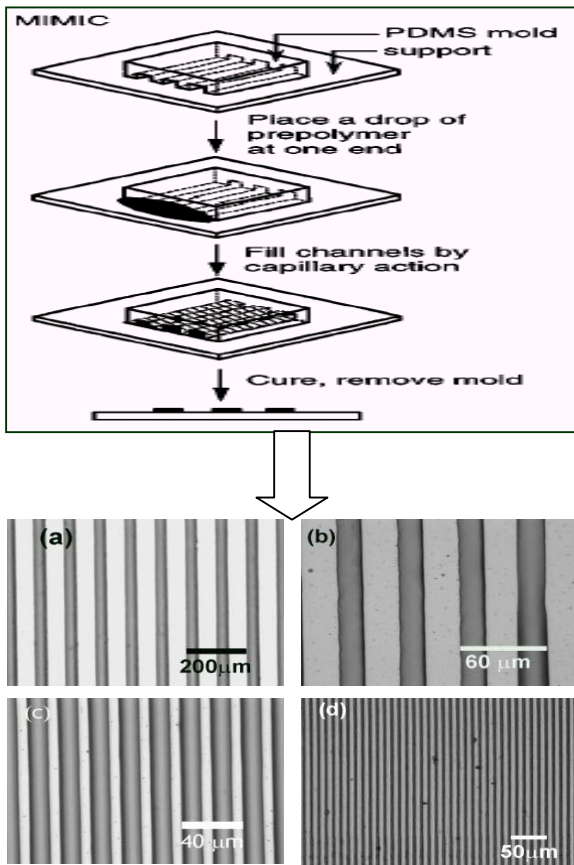


Figure 1 Schematic procedures of MIMIC for patterning of phosphor films (top) and the optical photographs for patterned $\text{LaPO}_4:\text{Ce}^{3+}$, Tb^{3+} phosphor films with different stripe width (bottom, a-50 μm , b-20 μm , c- 10 μm , d-5 μm).

3. SUMMARY

We have presented the use of Pechini-type sol-gel process for the synthesis of multiform of optical materials, including powder luminescent materials (directly or via combination with spray pyrolysis process), monodisperse and spherical core-shell structured phosphor and pigment particles (via surface modification process), and thin film phosphors (via dip-coating) and their patterning (combined with the soft-lithography process). Most of the difficulties and disadvantages that are often present in the alkoxides based sol-gel process, such as high cost, unavailability, toxicity and fast hydrolysis rate (thus difficult in controlling the homogeneity of different components during experimental processes) of the alkoxide precursors, can be avoided in the Pechini-type sol-gel process. The ideally spherical morphology for luminescence and pigment

materials, can be well controlled from the submicron to micron range by utilization of inert SiO_2 beads as templates to form core-shell structures. The final optical performances of the core-shell materials can be tuned by quite a few factors in the experimental process. The highly efficient luminescent materials without the metal activator ions via the Pechini-type sol-gel process open a door for us to explore novel environmentally friendly phosphors together with their luminescence mechanisms. Finally, thin film phosphors and their patterning via the Pechini-type sol-gel process and soft lithography techniques are possible to realize high resolution for display devices with simple and cheap equipment.

4. REFERENCES

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