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# Environmental-friendly yellow pigment based on Tb and M (M = Ca or Ba) co-doped $Y_2O_3$

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**Abstract**

A yellow inorganic ceramic pigment with general formula $Y_{1.86-x}M_xTb_{0.14}O_{3-x/2}$ (M = Ca and/or Zn) with $x = 0.06$, 0.32 and 0.64 were synthesized by a modified Pechini method. XRD, SEM and HRTEM/EDX analysis showed the formation of solid solution at 1300 °C when $x = 0.06$ and 0.32. The best $b^*$ yellow coordinates were obtained for Ca and Zn co-doped $Y_{1.86}Tb_{0.14}O_3$ samples. The intensity of the yellow colour in the samples is related to the presence of $Tb^{4+}$ ions. Samples with higher concentration of $Tb^{4+}$ ions lead to a better yellow colour. The chemical stability of these pigments was determinate in an industrial glaze. The glazing tests indicated that the powder samples with $x = 0.06$ and 0.32 fired at 1300 °C were stable in the glaze. These results make it a potential candidate for environmental friendly yellow ceramic pigment to be used in applications such as pigment for glazes or inkjet printers.


*Keywords:* Ceramic yellow pigment; Environmental friendly; Lanthanide; Yttrium oxide; Pechini method

## 1. Introduction

Inorganic pigments are an integral part of many decorative and protective coatings. They are used for mass colouration of materials such as plastics, glaze, ceramics and porcelain enamels. Ceramic pigments are basically white or coloured substances with high thermal stability and chemical resistance enabling their further processing at high temperatures.

There is interest to develop new yellow-coloured inorganic materials to substitute industrial pigments that are based on toxic metals hazardous to human health and the environment. Most of the ceramic pigments used in the ceramic industry are based on transition and heavy metals as chromophore ions.[1] The strong environment regulations adopted by the European Union has increased the develop of new compositions of inorganic pigments more environmental friendly, without toxic elements such as Pb, Hg, Cd, Sb, As, Co, Cr, Ni, etc.

The development of new solids with interesting colour applications is being attractive topic for researchers and industries; especially materials where the substitution of transition ions by lanthanide ions is produced. The used of lanthanides is growing due to their known low toxicity and the unique optical properties make them a promising material in a wide range of applications, that includes inorganic pigments for ceramic glazes, tunable lasers, or X-ray imaging.[2–7]

Praseodymium yellow (Pr-doped $ZrSiO_4$) has been widely used in ceramic industries due to its stability at high temperatures and low toxicity,[8–10] but this pigment requires high temperature calcinations and long times during preparation, which trends to induce particle grown of the pigment. This effect does not allow applications in which fine dispersion of the pigment is essential, for example, paints or inks. For applications such as inkjet printers, the particle size must be less than 1 μm and the re-milling process, commonly used to reduce the particle size in the ceramic industry, is not useful for this praseodymium-zircon pigment. When the milling process is used, the intensity of the yellow colour decreases. This problem is common in other pigments based on zircon solid solution such as vanadium zircon blue, and it leads to the obtain low intensity colours. Moreover, the high temperature needed also produce inhomogeneity in the final product.[11]

Based on environmental considerations, different lanthanides-based yellow inorganic pigments have been

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study for researchers as alternative to the existing toxic pigments.[12–15] Among several non-toxic yellow pigments, $CeO_2$ and related materials have attracted much attention due to their opacity, low toxicity and thermal stability.[16–18] However, the chromatic properties of these materials are not very attractive as compared with the pigments currently used in the ceramic industry.

Recently, Vishnu et al.[19] have developed a new class of yellow pigment based on solid solutions of mixed oxides with the general formula $Sm_{6-x}W_{1-y}Zr_xMo_yO_{12-\delta}$. This pigment, synthesised by solid state route, seems a good colorant for plastics and possess good chromatic properties.

Therefore, substitution of toxic elements by lanthanide ions represents an alternative and successful way to prepare more environmentally benign coloured materials. The main limitation in the use of lanthanide elements is that their *f–f* electronic transitions are forbidden by the selection rules.[20] Thus, it will give rise to compounds with low-intensity colours when these elements are present in their most usual oxidation states.

Yttria ($Y_2O_3$) has recently received special interest due to its high chemical durability, and refractory properties.[21,2,22] Usually, high pressure (>40 MPa) and/or high temperatures (>1600 °C) are needed to obtain polycrystalline $Y_2O_3$ dense ceramics.[23–30] It has been reported that the sintering temperature of $Y_2O_3$ can be reduced by doping with a divalent cations such as $Ca^{2+}$, $Mg^{2+}$, $Mn^{2+}$, $Ni^{2+}$, $Sr^{2+}$ or $Zn^{2+}$.[31–33] The most effective dopant was $Ca^{2+}$ (1 mol%) which reduced the sintering temperature for a relative density of 90% from 1700 °C to 1500 °C under conventional sintering in air.

Lanthanide ions doped yttrium oxide materials has attracted considerable interest, due to their important optical properties such as their excellent luminescent efficiency, colour purity, and chemical and thermal stability.[34,35] Among the lanthanides ions, Tb doped $Y_2O_3$ materials have been widely studied due to their important luminescence properties when they are prepared as nanoparticles.[36] In order to evaluate the effect of the particle size, different authors have prepared nanocrystalline Tb doped $Y_2O_3$ host materials and the optical properties have been measured.[37–39] Goldburt et al.[37] showed the influence of particle size in the phosphor efficiency and the luminescence behaviour. Psuja et al.[39] studied the cathodoluminescent properties of Tb doped yttria nanocrystallites, and showed that the most intensive luminescence was observed for samples sintered at 900 °C where the grain size was in the order of 40 nm. Soo et al.[40] synthesized nanocrystals of $Y_2O_3$ doped with different concentrations of $Tb^{3+}$, and showed the effect of the nanoparticles agglomeration on the optical properties.

In this work, the synthesis of $M^{2+}$ (Ca and/or Zn) and $Tb^{3+}$ codoped $Y_2O_3$ ceramics by a modification of the Pechini's method is reported to obtain new yellow pigments. Thus, in order to generate an alternative environmental friendly coloured materials without toxic chromophore elements, the optical properties of $Y_2O_3$: $M^{2+}$, $Tb^{3+}$ ceramics are reported. Structural and microstructural characterization of the materials is also studied by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectrometry (EDX) and ultraviolet–visible spectroscopy (UV–Vis). In order to obtain the best colouration of the pigment and small particle size, the synthesis temperature and the concentration of dopants is also evaluated. As far as we aware, the colour properties of Tb doped $Y_2O_3$ materials for ceramic pigment applications has not been previously reported.

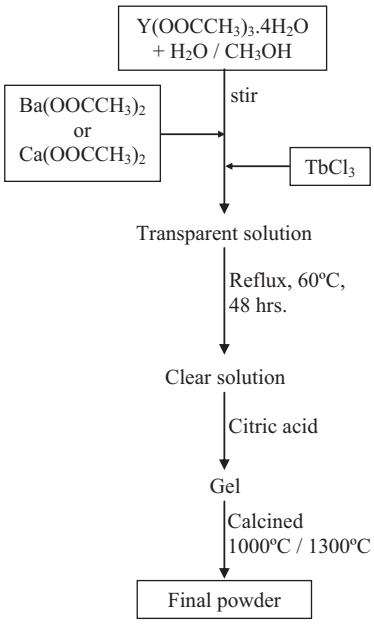


Fig. 1. Scheme of the synthesis procedure.

## 2. Experimental

Samples were prepared by a modified Pechini procedure[41] using $Y(OOCCH_3)_3{\cdot}4H_2O$ (99.9%, Strem Chemicals), $Ba(OOCCH_3)_2{\cdot}H_2O$ (98%, Sigma–Aldrich), $Ca(OOCCH_3)_2{\cdot}H_2O$ (98%, Sigma–Aldrich), $Zn(OOCCH_3)_2$ (98%, Sigma–Aldrich) $TbCl_3$ (99.9%, Strem Chemicals), as precursors. All reagents were of analytical grade and used without further purification. Distilled water and absolute methanol (Scharlab, 99.9%) were used as solvents. A scheme of the general preparation of the samples is shown in Fig. 1.

Yttrium precursor was dissolved in water and methanol with a $Y(OOCCH_3)_3$:$H_2O$:$CH_3OH$ molar ratio 1:1.4:25. Then, $Ba(OOCCH_3)_2{\cdot}H_2O$, $Ca(OOCCH_3)_2{\cdot}H_2O$ or $Zn(OOCCH_3)_2$, and finally $TbCl_3$, were added and the mixture was stirred for 20 min. This mixture was transferred into a balloon flask and, heated at 60 °C (reflux) for 48 h. The resulting solution was cooled until room temperature and then, citric acid (metal: citric acid, 1:1 molar ratio) was added. A gel was formed and it was dried in air at room temperature. Finally, the powder was annealed at temperatures of 1000 °C and 1300 °C.

### 2.1. Preliminary study

A preliminary study was conducted to determine the optimum working conditions (temperature, time and composition) in which compositions listed in Table 1 exhibited a good yellow colour after annealing. The chemical stability and the final