



New red-shade environmental-friendly multifunctional pigment based on Tb and Fe doped $Y_2Zr_2O_7$ for ceramic applications and cool roof coatings



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ARTICLE INFO

Article history:

Received 26 February 2016

Received in revised form

16 May 2016

Accepted 22 May 2016

Available online 24 May 2016

Keywords:

Red pigment

Sol-gel

NIR reflectance

Terbium

Defect fluorite

ABSTRACT

A new red-shade environmental friendly ceramic pigment with the general formula $Y_{2-x}Tb_xZr_{2-y}Fe_yO_{7-\delta}$ [$x = 0, 0.25$ and $y = 0.15, 0.25, 0.35$] was prepared by a polymeric sol-gel process and after calcination at $1300\text{ }^\circ\text{C}$ for 12 h. The solid solution range with defect fluorite structure was determined by XRD. The presence of terbium ions promoted the incorporation of iron ions in the structure. The evolution of the colour was studied by UV/Vis absorption measurements and CIELab chromatic coordinates were determined. The colour was related to the oxidation states of the terbium and iron ions studied by XPS and photoluminescence. Pigments presented the best chromatic coordinates when the amount of Fe(III) and Tb(IV) ions were higher. The sample with good red colouration ($x = 0.25, y = 0.35$) was tested with an industrial frit, presenting slightly better chromatic coordinates to those of the commercial ceramic pigment currently used. The pigment also showed an optimal NIR reflectance to be applied as “cool pigment” for roof isolation.

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1. Introduction

Compounds with $A_2B_2O_7$ stoichiometry have been extensively studied for their extensive field of applications and also for their ability to incorporate a wide range of chromophore ions in both position A and B [1,2]. This structure is optimal in order to develop pure colours due to the possibility of incorporating a great range of chromophores. The research of new ceramic pigments is a high priority field. One of the biggest current challenges is the preparation of a new red-shade ceramic pigment, due to the scarce variety of existing pigments available [2]. Red-shade pigments produced on an industrial scale usually employ toxic transition metal ions as chromophores like $Al_2O_3:Cr$ (corundum), $ZnAl_2O_4:Cr$, $CaSnSiO_5:Cr$ (sphene), $MnAl_2O_4:Cr$ (spinel), $Y_2Sn_2O_7:Cr$ (pyrochlore), and $CdS:CdSe$ (greenockite) [3], where chromium (III) and cadmium (II) ions are an important source of pollution due to their high toxicity. Transition metal ions are also usually incorporated as chromophores into compounds with stoichiometry $A_2B_2O_7$ in order to develop coloured compounds. As a result of the high toxicity of several of them (Cr, Ni, Co ...), other nontoxic species could play this

role. Subsequently, lanthanides have the optimum characteristics to replace the toxic chromophore ions in the $A_2B_2O_7$ structure obtaining environmental friendly pigments [4,5]. In the ceramic industry, the most used inorganic red pigment is $Fe-ZrSiO_4$ (zircon) called pink coral. It is very difficult to control the colour of the $Fe-ZrSiO_4$ pigments compared to other inorganic pigments, so there must be very precise fine grinding of the starting materials (zirconia and silica). Finer particles can give a better coral pink colour that is more reddish and yellowish in tone. Therefore, this pigment has a great problem of reproducibility and the final colour of the powder can vary widely [6].

Over the last few years, one of the interesting applications of these inorganic pigments is cool roof coatings with high near-infrared reflectance (NIR) [7–9]. These kind of coatings, for example, can improve internal thermal comfort in buildings and minimize air conditioning. Cool roofing products are made of highly reflective cool materials and can remain cooler than traditional materials when irradiated. White pigments, mainly TiO_2 [10], with high solar reflectance are often used as cool materials, but other coloured pigments have been developed because of the necessary aesthetic requirements. Cool pigments are used as coatings on building roofs in order to decrease the temperature in the interior of the house, and consequently, contribute to increased

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indoor thermal comfort levels in hot seasons, resulting in reducing the need for cooling [11]. Many of these coloured pigments with high NIR reflectivity also contain toxic metal elements like Co, Pb, Cd, Cr. These are restricted by the current environmental regulations [12–14]. In this way, some new potential cool pigments have been also reported in order to substitute these traditional toxic elements [15–18].

Among all the inorganic structures used for pigments, the pyrochlore structure, $A_2B_2O_7$, containing trivalent A and tetravalent B cations has been studied recently as a new pigment, due to its compositional versatility and high stability [2,4]. Of particular interest are oxides with Zr occupying the B-site and Y occupying the A-site, $Y_2Zr_2O_7$ (YZ). This compound has been reported to show a moderate anionic conductivity and represent a potential material for use as either electrolytes in solid oxide fuel cells (SOFC) and oxygen separation or in photocatalytic applications [19]. YZ is also a promising host due to the possibility of incorporating a great variety of dopants in the structure. The potential to incorporate different elements provides a greater variety of possibilities highlighting the solid oxide fuel cells [1,20,21] and photoluminescence material applications [22,23].

According to the radius ratios of the ions present [24], $Y_2Zr_2O_7$ acquires a defect fluorite structure under ambient conditions. The ordered pyrochlore structure (space group Fd-3m) can be transformed to the disordered defect-fluorite structure (space group Fm-3m) by a random distribution of both cations and anions onto their respective sublattices with the A- and B-site coordination number changing from the 8 and 6 respectively to an average of 7 for both [25,26]. Zhang et al. [25] have recently predicted that the coordination of cations in the $Y_2Zr_2O_7$ defect-fluorite varies depending on the species with the average coordination of Y and Zr being 7.2 and 6.8, respectively.

On the other hand, this crystalline structure is significantly flexible, i.e., the lattice can stabilize large amounts of ionic substitutions in each one of its crystalline sites, as well as vacancies and structural defects. This characteristic could be explored to obtain new ceramic pigments using chromophore elements as dopant. As far as we aware, in the field of ceramic pigments, this doped $Y_2Zr_2O_7$ structure has not been reported as yet.

The development of new solids with interesting colour applications is an attractive topic for researchers and industry; especially materials where the substitution of transition ions by lanthanide ions is explored. The use of lanthanides is increasing due to their known low toxicity and their unique optical properties make them a promising material in a wide range of applications, which includes inorganic pigments for ceramic glazes, tunable lasers, or X-ray imaging. The terbium ion is one of the lanthanides used as a dopant ion in different structures in the field of new environmental pigments. For example, De la Luz et al. [27] prepared new environmentally inorganic yellow pigments with the general formula $Y_{1.86-x}M_xTb_{0.14}O_{3-x/2}$ ($M = Ca$ and/or Ba) by the Pechini method. The intensity of the yellow colour in these samples was related to the presence of Tb(IV) ions. Athira et al. [3] also studied the role of Tb ions in the $Y_2Ce_{2-x}Tb_xO_7$ based ceramic pigments resulting in good red hues.

It should also be noted that, iron ion has been used as a chromophore ion in some pigments due to its negligible toxicity, its availability in nature as oxide, and the red shade that it provides to the matrix [6,28,29]. Moreover, iron ion is also an environmental friendly chromophore.

Taking into account all of the above-mentioned comments in this work, the synthesis of $Y_{2-x}Tb_xZr_{2-y}Fe_yO_{7-\delta}$ [$x = 0, 0.25$ and $y = 0.15, 0.25, 0.35$] by the sol-gel method is reported to obtain new red-shade pigments. Solid solution range and the role of terbium have also been studied. This new pigment has also been prepared to

be used in different applications like a ceramic pigment and with a potential pigment for roof insulation. Therefore, the pigment stability in glass has been compared with the stability of the commercial pink coral pigment, and the high NIR reflectance of the same have also been compared with a commercial pigment used in coatings to reflect solar light.

2. Experimental

Samples based on $Y_{2-x}Tb_xZr_{2-y}Fe_yO_{7-\delta}$ [$x = 0, 0.25$ and $y = 0.15, 0.25, 0.35$] were prepared by polymeric sol-gel procedure using $Y(OOCCH_3)_3 \cdot H_2O$ (99.9%, Strem Chemicals), $Zr(OCH_2CH_2CH_3)_4$ (70% Sigma-Aldrich), $TbCl_3 \cdot 6H_2O$ (99.9% Acros Organics), and $Fe(NO_3)_3 \cdot 9H_2O$ (98% Strem Chemicals) as precursors. All reagents were of an analytical grade and used without further purification. Absolute ethanol (Scharlab, 99.9%) was used as a solvent with the necessary amount of acetylacetone, acacH (99% Alfa Aesar) as a stabilizing agent for nonsilicate metal alkoxide precursors. A scheme of the general preparation of the samples is shown in Fig. 1. Zirconium precursor was dissolved in ethanol and acetylacetone (acacH:Zr molar ratio 4:1). Then $Y(OOCCH_3)_3 \cdot H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $TbCl_3 \cdot 6H_2O$ (in the samples that contains terbium) were added, and the mixture was stirred for 10 min. This mixture was transferred into a balloon flask and, heated at 70 °C for 72 h. A gel was formed and it was dried in air at room temperature. Finally, the powder was fired at 1300 °C for 12 h.

Powders of samples with optimal colour were mixed with one industrial frit (4% in weight of the pigment) using water as a dispersing medium. Then, the dispersion was applied to white twice-fired bodies, to verify composition stability as a ceramic colourant. A commercial transparent frit was chosen. The frit composition used is given in Table 1. After drying, the pieces were fired in an electric kiln. The heat treatment applied, corresponds to a standard firing cycle used in a ceramic tile industry where the highest temperature of the cycle was 1080 °C for 5 min. This cycle involves five steps: ramping to 800 °C in 18 min, heating from 800 °C to glaze firing temperature in 17 min, 5 min hold at 1080 °C, cooling to 600 °C in 20 min, and finally cooling to room temperature in 15 min.

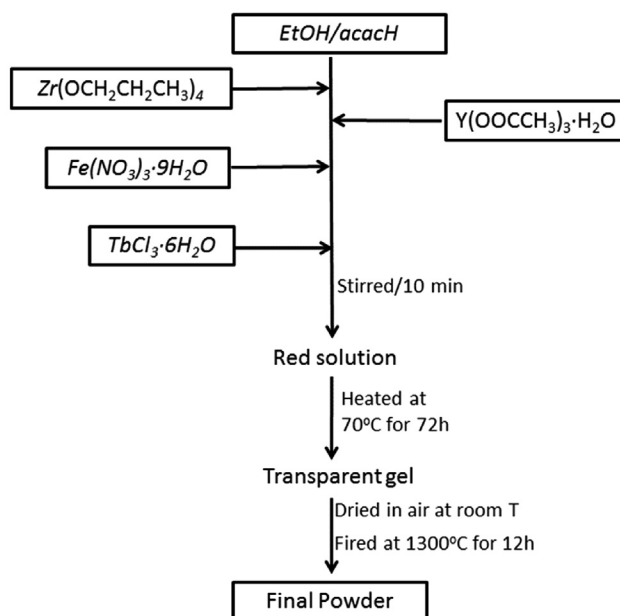


Fig. 1. Scheme for the synthesis procedure.

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