Sustainable inorganic cool pigments based on Tungsten doped $FeZrO_{3.5}$

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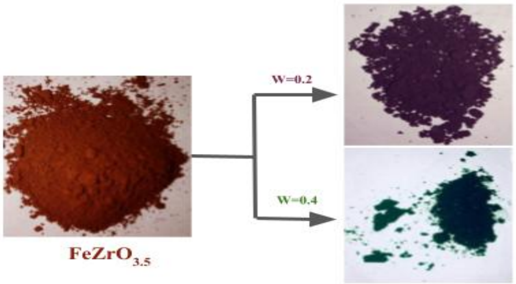
Abstract

High near-infrared reflecting inorganic nano pigments ($FeZr_{1-x}M_xO_{3.5}$; where M = tungsten (W^{6+}) and x ranges from 0 to 0.4) based on Iron zirconium doped with W^{6+} was synthesised by a novel citric acid assisted Sol-Gel route followed by calcination. The pigment and composite samples were characterised by TG-DTA, XRD and UV–Vis–NIR spectrophotometer. The results showed that the pigments crystallised completely at 600°C with particle size less than 50 nm. The substitution of W^{6+} for Zr^{4+} in $FeZrO_{3.5}$ induced the absorption in the 480-580 nm region. The red colour of the $FeZrO_{3.5}$ is found to be changed to purple upon doping 10% tungsten and blue-green upon 20% doping of tungsten. The near-infrared reflectance varied with 45-53%, varying the W^{6+} content. Thus, these pigments can be excellent candidates for use as cool pigments in walls or roofs of buildings.



Keywords: Environmentally friendly pigments, Cool pigments, Citric acid assisted Sol-Gel route, *Gelation agent,* High near-infrared reflecting, *Nanocomposites.*

1. Introduction

The use of low-toxicity raw materials in the chemical industry is becoming increasingly favoured to prevent both health hazards in the workplace and/or environmental damage. To satisfy these requirements, research on the utilization of non-toxic compounds should be encouraged. In the field of ceramic pigments, it is necessary to obtain pigments with some desired properties: (a) high thermal stability at temperatures around 1200 °C (reached during the single firing of porcelainized stoneware), (b) chemical stability towards the vitreous phases colored by the pigment, and (c) low toxicity, to satisfy health and environmental requirements. Due to their known low toxicity, in the recent past, a large number of environmentally benign inorganic pigments have been proposed as alternatives to traditional toxic inorganic pigments. Materials that are environmentally friendly and economically viable are the focus of much research to replace potentially toxic inorganic pigments.

There is great interest nowadays in developing stable and reproducible mixed oxide inorganic NIR reflective nano pigments, with more intense shades and of low toxicity which favour the use of lanthanide oxides, which can substitute pigments that contain heavy metals, such as Cd, Co, Cr, Hg and Pb, considered toxic [1-3]. If we use NIR reflective pigments in the paints, which reflect the NIR range light and pronounce the exterior finishes of the paints. Apart from that dropping the surface temperatures of roofs and walls, which, in turn, reduces the cooling-energy demand of the building to some extent [4-5]. However, many of these NIR-reflective inorganic pigments currently employed on an industrial scale generally comprise toxic metal ions like cadmium, lead, chromium and cobalt and there is a need to develop novel colored, NIR-reflecting inorganic nano-pigments that are less hazardous to the environment as nanofillers on nanocomposites. The industrially available red pigments are almost exhausted by the following systems: Al_2O_3 - Cr^{3+} (corundum), $ZnAl_2O_4$ - Cr, $CaSnSiO_5$ - Cr^{3+} (sphene), $MnAl_2O_4$ - Cr^{3+} (spinel), $ZrSiO_4$ - Fe^{3+} (zircon), and CdS-CdSe (greenockite) and $Y_2Sn_{2-x}Cr_xO_{7-\delta}$. The ceramic pigments with particle size in the nano-scale have a massive potential market, because of their high surface area, which assures higher surface coverage, higher number of reflectance points and hence improved scattering. For the preparation of mixed oxide nano-pigment particles, the sol-gel method offers great advantages as compared to the conventional solid-state method. Compared with the conventional ceramic routes, such as co-precipitation, grafting, and impregnation, the sol-gel exhibits many advantages. Among them the low process temperature, the high control of purity, composition, microstructure and textural properties of the final material [6–9] are prominent. Particularly, for mixed-oxides this synthesis procedure allows to obtain materials characterized by a high dispersion of the active phase in the matrix on both molecular and nanometer scales. The traditional sol-gel method and co-precipitation process, which are easy to cause segregation when heating, are not always effective in maintaining a homogeneous distribution of precursors. As a result, undesirable phases form during the process of calcination. Among the modified sol-gel methods, the process of chelation of citric acid is an effective method.

In this study, develop sustainable inorganic cool nano pigments of $FeZr_{1-x}W_xO_{3.5}$ displaying colors as viable alternatives to the existing toxic inorganic pigments through citric acid-assisted sol-gel route which avoids the use of ethylene glycol.

The developed pigments were well characterized and their optical properties were investigated. Superior red hue and high solar radiation reflectivity have been achieved by the nano-pigments.

2. Experimental Section

2.1. Materials

The chemical reagents Cerium nitrate hexahydrate (Sigma Aldrich, 99.9%), Zirconyal nitrate ($ZrO(NO_3)_2xH_2O$) (Sigma Aldrich, 97%), Ferric chloride ($FeCl_3$) (Merk, 99.9%), Sodium tungstate (Na_2WO_4), Citric acid (Sigma Aldrich), 2N HCl are analytical grade and used without further purification. All syntheses were performed under the same experimental conditions.

2.2. Preparation of $FeZr_{1-x}M_xO_{3.5}$ nano pigments

$FeZr_{1-x}M_xO_{3.5}$ powders were synthesized by the citric acid- sol-gel method. Stoichiometric amounts of Zirconyl nitrate ($ZrO(NO_3)_2xH_2O$), Ferric chloride ($FeCl_3$) and Sodium tungstate (Na_2WO_4), were dissolved in a minimum amount of 2N HCl with constant stirring. Subsequently, the calculated amount of citric acid is dissolved separately in 2N HCl and the solutions are stirred continuously for 15 minutes. The mixture is heated in an electric oven for 1.5 hours at 70°C. Gel formation begins to occur. The gel obtained is heated at 150°C for 3 hours so that gel formation is complete. The temperature of the oven is adjusted to 200°C and the mixture is heated for 8 additional hours. The xerogel obtained is cooled, powdered in an agate mortar and calcined for 1 hr at 600°C. The calcination of the xerogel samples was carried out in a high-temperature electrical furnace by heating the samples in silica crucibles. The heating of the furnace was programmed to increase the temperature to 5ºC/min.

2.3. Characterization Techniques

Thermo-gravimetric (TG) and differential thermal analysis (DTA) were performed in a Pyris Diamond TG/DTA Perkin Elmer make. All the experiments were run in a platinum crucible from 50 to 1000˚C with a heating rate of 20˚C/min in the nitrogen atmosphere. The phase purity of the calcined pigment samples was determined using powder X-ray diffraction in a diffractometer (Philips X'pert Pro) employing Ni-filtered Cu Kα ($\lambda = 0.154060$ nm) radiation. Data were collected by step scanning over a 2θ range from 20˚ to 70˚ with a step size of 0.08˚ and 5 s counting time at each step. The diffuse reflectance of the powdered pigment samples was measured in the wavelength range 380–700 nm using a UV–vis Spectrometer (Shimadzu UV-2450 with an integrating sphere attachment, ISR-2200) using illuminant D_{65}, 10˚ standard observer and measuring geometry d/8˚. The near-infrared reflectance spectrum of the powdered pigment samples was recorded with a UV-vis-NIR spectrophotometer (Jasco V670). Optical measurements were carried out in the 700-2500 nm range.

3. Results and Discussion

3.1. The thermogravimetric analysis

The observed exothermic peak in the DTG curve between 80 and 180ºC with respective weight loss for the xerogel indicates the removal of absorbed water molecules. The DTG scan of $FeZrO_{3.5}$ has a sharp exothermic peak at 267.05ºC showing the organic compound degradation and a second exotherm is observed at 450ºC due to the elimination of nitrous oxide. The at 600ºC is responsible for the crystalline phase formations shown in Fig. 1. Above these temperatures only a small weight loss is observed, which is attributed to the release of water arising from condensation reactions.

3.2. Powder X-ray diffraction analysis of nano pigments

The optimized calcination temperature required for the formation of the typical pigment sample $FeZrO_{3.5}$ was ascertained by calcining the dried gel at 600˚C for 1h in an air atmosphere. The sample calcined at 600˚C for 1h shows the characteristic reflections of the $FeZrO_{3.5}$ face-centered cubic structure as verified by (JCPDS 89-7932). Fig. 2 displays the PXRD profiles of $FeZr_{1-x}W_xO_{3.5}$ with different doping content of W, where $x = 0$, 0.2, and 0.4 calcined at 600˚C/1 h. The XRD patterns obtained upon doping with tungsten (W^{6+}) match with that of $NiWO_4$ (JCPDS No. 15-0755). Thus the additional peaks obtained are assumed to be due to the presence of tungsten.

3.3. Diffuse reflectance properties of nano pigments

In Fig 3, the reflectance spectrum of $FeZr_{1-x}W_xO_{3.5}$ shows a greater absorption in the visible region with an increasing number of chromophore ions because the gap between the valence and conduction bands narrows. This causes the color of the pigment to vary from red to green (Fig. 4).

The position of the absorption edge critically depends on the concentration of W present in the pigment sample. The band gap of the sample is obtained from the absorption spectra simply by a straightforward extrapolation method was found to be around 1.8 eV. This allows excitation to the conduction band and hence the sample appears red (480-500) in color. Whereas when it is doped with W the sample shows an absorption in the yellow-green region (450-580 nm), the color of the pigment sample becomes purple because it is the complementary color to yellow-green. Furthermore, the doping of W into the $FeZrO_{3.5}$ lattice will result in an additional energy level between the O-2p valence band and the W conduction band. Thus, reducing the band gap and enabling the excitation of electrons.

3.4. NIR reflectance analysis of nano-pigments

It can be seen from the NIR reflectance (700-2000 nm) of the tungsten-doped $FeZrO_{3.5}$ powdered pigment samples shown in Fig. 5 that the NIR reflectance increases (from 33 to 53%) with the increase in the concentration of W^{6+} from 10 to 20%. However, the high NIR reflectance values highlight the potential for the utility of these pigment samples as cool pigments.

4. Conclusions

In the present study, the citric acid-assisted sol-gel method offers great advantages as compared to the conventional methods. The prepared nano pigments based on $FeZrO_{3.5}$ are non-toxic and are environmentally secure for surface coating applications. This method offers a reduction of the required calcination temperatures with previously reported methods and minimization of the undesired aggregation of the particles. In comparison to the Pechini method, the citric acid-assisted sol-gel method avoids the usage of toxic ethylene glycol. The powder-XRD of the compound indicates that the compound synthesized is in the nano-scale 5-6 nm. The UV-VIS and NIR spectrum of the prepared compounds indicates that they are NIR reflective and hence can be used as cool pigments. A decrease in particle size of the pigment increases the surface area which further contributes to high surface coverage, higher number of reflectance points and hence more scattering. The absorbance or reflectance properties were studied to characterize the color of pigments. The obtained pigments show red, purple and bluish-green shades. Thus we have succeeded in synthesizing environment-friendly and economically viable NIR Reflective inorganic pigments that can now widely be excellent candidates for use as cool pigments in walls or roofs of buildings.

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Availability of data and materials

Methods, including statements of data and materials availability and any associated accession codes and references, are available in the online version of this paper.

Declaration of Competing Interest

The author certifies that she has no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

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Figure Captions

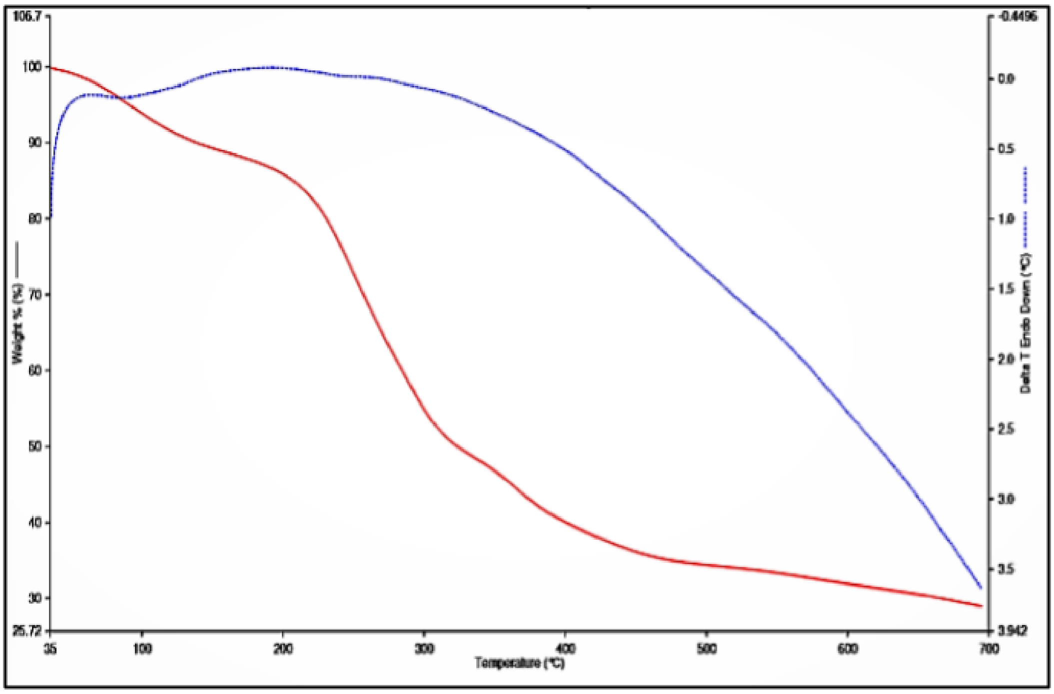
Fig. 1. TG curve of synthesized $FeZrO_{3.5}$ nanopowder.

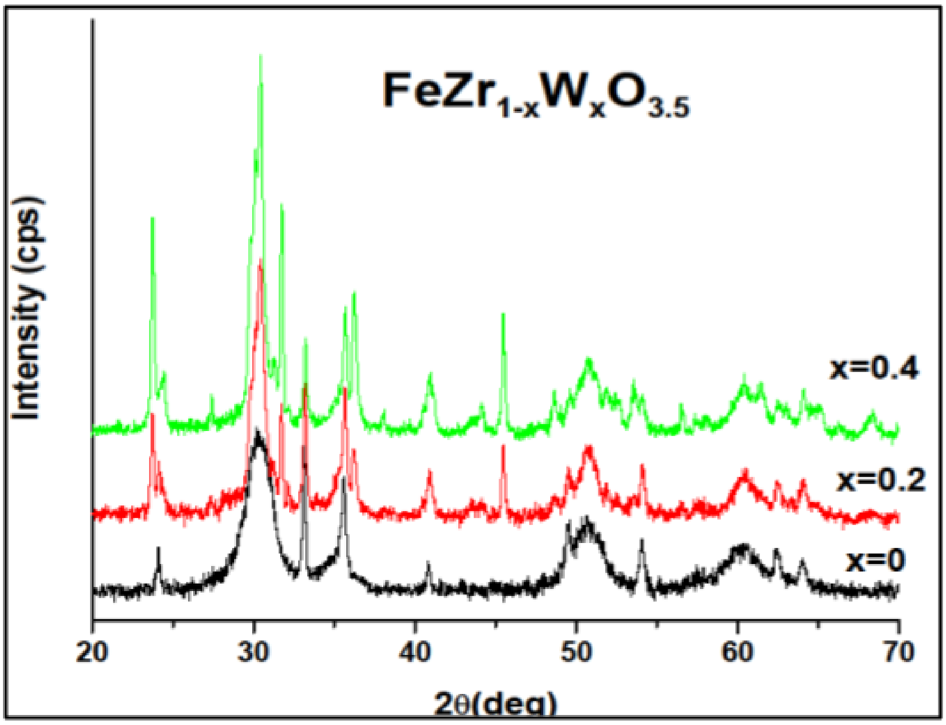
Fig. 2. The XRD pattern of $FeZr_{1-x}W_xO_{3.5}$ of nanopowders (x= 0, 0.2 and 0.4) samples (Calcination temperature: 600˚C; Time duration 1 h).

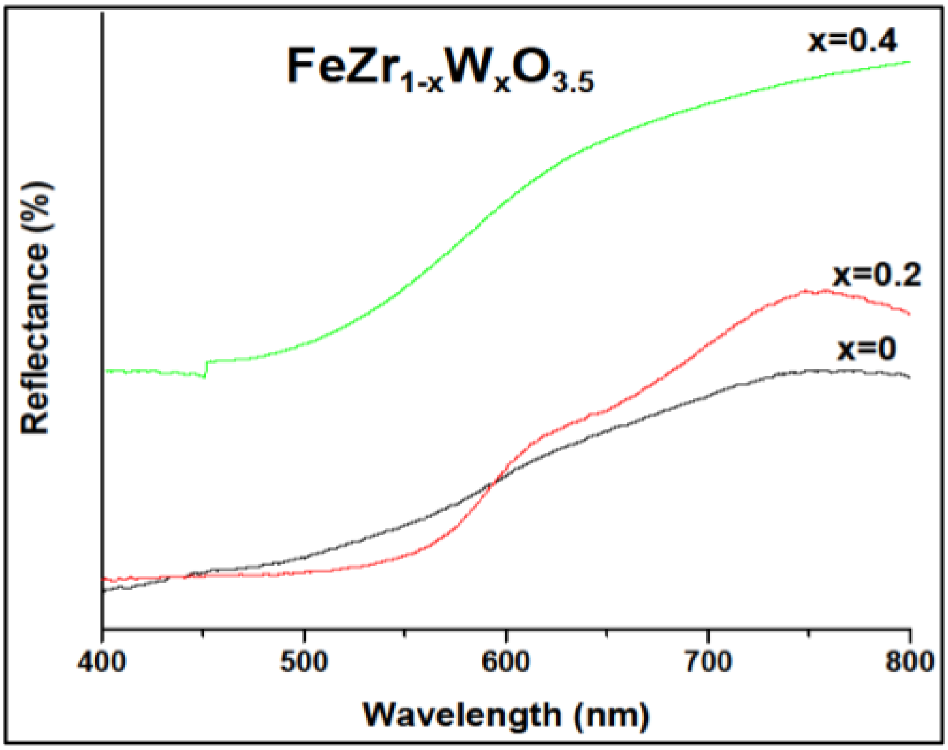
Fig. 3. UV- Vis reflectance spectrum of $FeZr_{1-x}W_xO_{3.5}$ powders

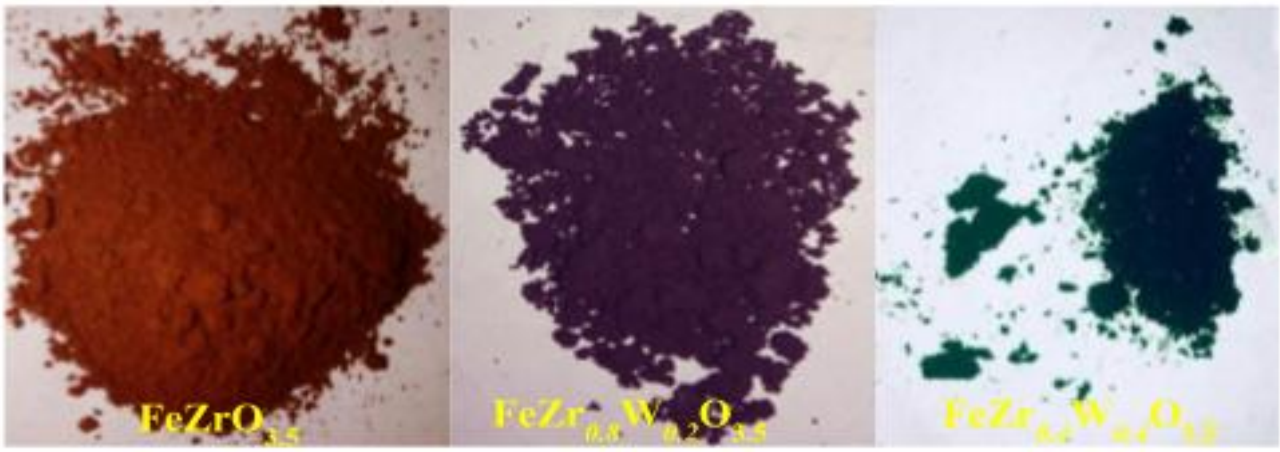
Fig. 4. Photographs of synthesized $FeZr_{1-x}W_xO_{3.5}$ (x = 0, 0.2, 0.4 respectively) pigments

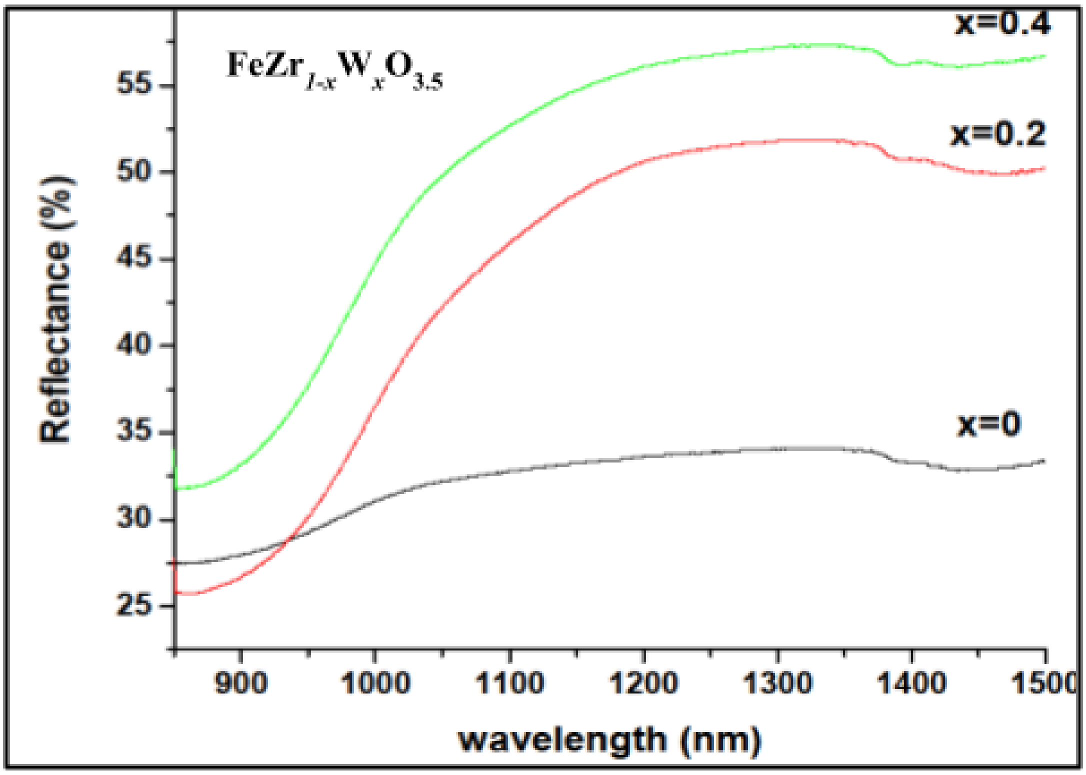
Fig. 5. NIR reflectance spectrum of $FeZr_{1-x}W_xO_{3.5}$ powders




FeZr$_{1-x}$W$_x$O$_{3.5}$
Intensity (cps)
x=0.4
x=0.2
x=0
20
30
40
50
60
70
2θ(deg)


FeZr$_{1-x}$W$_x$O$_{3.5}$
x=0.4
x=0.2
x=0
Reflectance (%)
400
500
600
700
800
Wavelength (nm)


FeZrO3.5
FeZr0.8W0.2O3.5
FeZr0.6W0.4O3.5


FeZr1-xWxO3.5
x=0.4
x=0.2
x=0
Reflectance (%)
55
50
45
40
35
30
25
900
1000
1100
1200
1300
1400
1500
wavelength (nm)