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Materials Research Bulletin 43 (2008) 665–675

Materials Research Bulletin

www.elsevier.com/locate/matresbu

Chemical synthesis of environment-friendly nanosized yellow titanate pigments

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Received 26 September 2006; received in revised form 22 March 2007; accepted 2 April 2007
Available online 6 April 2007

Abstract

As yellow pigments, nanosized rutile structured $Ni_{0.1}W_{0.1}Ti_{0.8}O_2$ and priderite structured $BaNiTi_7O_{16}$ have been prepared through pyrolysis of precursor solution containing nickel nitrate, dimethyl tungstate, titanium oxalate, triethanolamine (TEA) for the former composition and barium nitrate, nickel nitrate, titanium oxalate, TEA for the later composition, respectively. In the reaction, TEA acts to minimize the agglomeration in the products through formation of a highly branched polymeric framework, which anchors the metal ions for producing nanocrystalline powders. The rutile and priderite structured titanates obtained on heat-treatment of the precursor powders at 800 °C and 850 °C, respectively, have been characterized by XRD, TGA–DTA, BET surface area measurement, UV–vis spectroscopy, CIE $L^*a^*b^*$ colour parameter measurements, TEM and HRTEM. XRD reveals the purity of the resulting rutile and priderite phases. Their crystallite sizes, average particle sizes and specific surface areas determined from XRD, TEM, and BET surface area measurement are found to be in the range between 25 nm and 30 nm, 25–45 nm and 100–120 m^2/g, respectively, for both compositions.

Keywords: A. Nanostructures; A. Oxides; B. Chemical synthesis

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1. Introduction

The most known yellow inorganic pigments are praseodymium-zircon yellow, vanadium–zirconia yellow, tin–vanadium yellow, chromates of alkaline earth metal ions (e.g. calcium, strontium, barium), lead and zinc, litharge (lead oxide), naples yellow (lead antimonate), cadmium yellow, iron oxide yellow (α and γ-FeOOH), and nickel–antimony doped rutile phase TiO_2. Among these inorganic yellow pigments, the application of iron oxide yellow gets constrained due to thermal stability only up to 220 °C [1], while the toxicity [2] of chromium(VI), cadmium and lead based yellow pigments restricts their commercial usage; and praseodymium-zircon yellow, vanadium–zirconia yellow which are even if most popular in the market of yellow inorganic pigments, they have some limitations in bulk colouration porcelainized stoneware at high temperature [3].

Nickel-doped TiO_2 with rutile as well as priderite structures are well known intense and brilliant yellow ceramic pigments [4]. They are non-toxic, chemically inert, thermally stable, photochemically inactive, and having high tinting strength for the outdoor application and hence satisfy most of the characteristics requisite for pigment application. Still

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doi:10.1016/j.materresbull.2007.04.001

they find little usage in the ceramic industry because of their partial solubility into the transparent glazes above 1000 °C [5]. However, due to their high thermal stability these pigments have gained considerable industrial interest in recent years as potential alternatives to praseodymium zircon yellow pigment, essentially for bulk colouration of porcelain stoneware tiles [6,7]. Recently Sorlý et al. reported the structure and colour of nickel doped rutile phase yellow pigment with compositions: $Ni_xA_{1-3x}B_{2x}O_2$ [A = Ti(IV), Sn(IV); B = Sb(V), Nb(V)] prepared by conventional ceramic method [3] and also studied the role of nickel precursors on the colour of pigments prepared from different nickel starting materials [8]. Matteucci et al. [5,9] studied the role of counterions (Mo, Nb, Sb, W) in doped rutile ceramic pigments with compositions $Ni_xA_{1-3x}B_{2x}O_2$ and $Ni_xA_{1-2x}B_xO_2$ [A = Ti(IV), Sn(IV); B = W(VI), Mo(VI)] and found the tungsten to be the most suitable counterion for best titanate pigments formulation in glaze applications.

For the formation of TiO_2 based yellow pigments, chromophorous ions, Ni^{2+} having ionic radii (ionic radius = 0.69 Å) slightly higher than Ti^{4+} (0.605 Å) are incorporated into the host rutile (TiO_2) lattice to generate oxide solid solutions with stable colorimetric properties. In formulations such as $Ti^{IV}(W^{VI}Ni^{II})O_2$ the colouring effect is produced when the Ti(IV), which is surrounded by six neighbouring oxygen atoms at the corners of a regular (but slightly distorted) octahedron in the rutile lattice, is substituted by transition metal ions of lower valency Ni^{2+} (ionic radius = 0.69 Å) while the higher valency ions in the lattice (e.g. A = W^{6+}; ionic radius = 0.60 Å) compensate for the charge off set such that their molar ratios ensure an overall electroneutrality in the oxide solid solution. In the present paper, nickel doped rutile phase titanate pigment with composition $Ti^{IV}(W^{VI}Ni^{II})O_2$ has been reported as a prototype. In this composition, molybdenum can play the same role of tungsten producing different yellow colour.

Solid solution of $BaNiTi_7O_{16}$ is also a recognized yellow pigment having a priderite structure. Priderite is a member of hollandite family and may have tetragonal or monoclinic structure depending upon r_B/r_A ratio. The $r_B/r_A = 0.48$ corresponds to approximate tetragonal/monoclinic boundary (at room temperature), where r_B is the average of the radius of Ni^{2+} and that of Ti^{4+} and r_A is the radius of Ba^{2+} ion [10]. For $Ba_x(Ni_xTi_{8-x})O_{16}$ (with $x = 1$) composition, the r_B/r_A value is less than 0.48 and the greenish-yellow compound can therefore be inferred to have a tetragonal structure.

For concerning the toxicity, both $Ti^{IV}(W^{VI}Ni^{II})O_2$ and $BaNiTi_7O_{16}$ are safe for environment, because they are not composed of toxic elements and they have low solubility in water and dilute mineral acids.

The ceramic pigments with grain sizes in nanoscale are commercially potent in pigment industries, because of their high surface area which assures higher surface coverage; higher number reflectance points and hence maximum scattering; and small particle size for uniform dispersion by homogenous mixing with the binders in paint formations, which enhances the mechanical strength of the paint after drying. When properly dispersed, the nanosized pigments exhibit superior effectiveness in critical abrasive and polishing applications also.

The common route to synthesize these coloured titanates is solid-state method, which requires high temperatures and repeated mixing/grinding of raw materials and produces coarse particles. In the present paper, chemical synthesis of nanosized nickel doped yellow solid solutions with compositions $Ni_{0.1}W_{0.1}Ti_{0.8}O_2$ and $BaNiTi_7O_{16}$ have been reported through an aqueous-based chemical route using dimethylammonium tungstate and titanium oxalate as innovative and stable water-soluble sources of tungsten and titanium, respectively. The method [11] involves thermolysis of precursors obtained from evaporation of aqueous based precursor solution of soluble metal salts/complexes and optimum amount of triethanolamine (TEA). Solution based on this method produces pure and single phased nanosized pigments maintaining the required stoichiometry at temperature lower compared to the conventional solid-state method [3,5]. This paper also describes the structural and colorimetric properties of these pigments.

2. Experiment

$Ni_{0.1}W_{0.1}Ti_{0.8}O_2$ and $BaNiTi_7O_{16}$ have been prepared from aqueous solutions of nickel nitrate, dimethylammonium tungstate, titanium oxalate and TEA for the former composition; and nickel nitrate, barium nitrate, titanium oxalate and TEA for the latter.

2.1. Raw materials used

Raw materials used were: (a) nickel nitrate hexahydrate (Merck India Ltd.), (b) sodium tungstate (Merck India Ltd.), (c) titanium(IV) oxide (Merck India Ltd.), (d) oxalic acid dihydrate (Merck India Ltd.), (e) TEA (Merck India