

New vanadium doped calcium titanate ceramic pigment

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Abstract

In this paper a new pink vanadium doped calcium titanate $\text{Ca}(\text{V}_x\text{Ti}_{1-x})\text{O}_3$ ceramic pigment in conventional ceramic glazes is obtained by ceramic route and characterized. The limit of solid solution is near by $x = 0.2$, higher amounts of vanadium crystallizes $\text{Ca}_2\text{V}_2\text{O}_7$ which dilute the real amount of saturated $\text{Ca}(\text{V}_x\text{Ti}_{1-x})\text{O}_3$ solid solution and diminish the intensity of colour. The unit cell parameter measurements of $\text{Ca}(\text{V}_x\text{Ti}_{1-x})\text{O}_3$ agrees with the substitution of Ti^{4+} by V^{5+} that is associated to a $\text{V}^{5+}-\text{O}^{2-}$ charge transfer at 420 nm on UV–vis–NIR spectra of 5% glazed samples that explain the pink colour obtained. In order to avoid the limitation due to the suppressing of oxygen vacancies by high valence cation V^{5+} substitution in a Ti^{4+} site of CaTiO_3 perovskite for to preserve the charge neutrality of the lattice; Fe^{3+} and V^{5+} codoped samples $\text{Ca}(\text{Fe}_x\text{V}_x\text{Ti}_{1-2x})\text{O}_3$, $x = 0.1, 0.2$ and 0.3 were prepared and show a brown colour fired 1000 °C, but 5% glazed do not produce colour indicating that iron codoping inhibits the pigmentation capacity of vanadium doped CaTiO_3 perovskite.

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1. Introduction

Perovskite ABO_3 is an ideally cubic phase, but really becomes a rhombic syngony (space group Pnma). A cation (Ca^{2+} , Sr^{2+} , Cd^{2+} , Ba^{2+} , Ni^{2+} , Co^{2+}) ideally occupies vertex of cube and B cation (Ti^{4+} , Zr^{4+} , Sn^{4+}) the centre, oxygen occupy face centres. Several authors have studied perovskite as ceramic pigment structure:

- (i) Eppler [1] develops black pigments from $(\text{Sr,Ca})\text{MnO}_3$ perovskites using oxides and carbonates mixed with conventional mineralizers fired at 730 °C with soaking time of 3 h.
- (ii) Pishch I and Radion [2] applies the $(\text{NiCa})\text{TiO}_3$ perovskite as yellow pigment and $(\text{CoCa})\text{TiO}_3$ as brown-turkish colorations using precipitation synthesis methods. Yellow shade increasing when Ni increase is associated to a shifting of Ni(II) bands absorption in octahedral coordination. Yellow application is limited and cobalt blue based pigment is really a solution colorant. Likewise these authors use MTiO_3 and MZrO_3 ($\text{M} = \text{Ca}, \text{Sr}, \text{Cd}, \text{Zn}$) perovskites obtained from alkaline precipitation with 1 M NaOH 1 M as white ceramic pigments [3].

- (iii) Jansen and Letschert [4] pose an alternative to cadmium sulfoselenide included into zircon pigment based on nitride solid solutions $\text{CaTaO}_{2+x}\text{N}_{1-x}$ and $\text{LaTaO}_{2+x}\text{N}_{1-x}$ that change from yellow to orange and red, in function of N amount in perovskite solid solution (as cadmium sulfoselenide in zircon in function of Cd amount). Cadmium sulfoselenide in zircon pigment does not show toxicity due to their low solubility, but it may promote biodisposal cadmium when is deposited as waste or incinerated, is for that because their use has been restricted. Although the use of cadmium sulfoselenide included into zircon pigment, may be considered sure from recently studies, there is high interest to dispose an alternative. Rare earth presence on perovskites is not a problem, but oxynitride synthesis, by ammonolysis of oxide mixture at high temperature and soaking times, is more complicated than for cadmium sulfoselenide in zircon pigment, and stability on ceramic matrices and glazes is lower than cadmium-zircon pigment also, but it is a stable alternative for polymer colouration [5].

Kim et al. [6] study crystallographic features of AMO_2N ($\text{A} = \text{Ba}, \text{Sr}, \text{Ca}$; $\text{M} = \text{Ta}, \text{Nb}$) oxynitride perovskites: BaTaO_2N structure becomes cubic (distance $\text{Ta}-\text{O}/\text{N} = 2.056 \text{ \AA}$), SrTaO_2N and CaTaO_2N show octahedral distortion showing lower distances $\text{Ta}-\text{O}/$

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$N = 2.02 \text{ \AA}$. Nb oxinitrides are isostructural with above homologous Ta perovskites with Nb–O/N distances slightly higher. The estimated band-gap from diffuse reflectance studies are: BaTaO₂N, 1.8 eV; SrTaO₂N, 2.1 eV; CaTaO₂N, 2.4 eV; BaNbO₂N, 1.8 eV; SrNbO₂N, 1.9 eV; CaNbO₂N, 2.1 eV. Impedance spectroscopy and electric transport measurements indicate that BaNbO₂N shows metallic conductivity (probably by reduction during sintering) instead tantalates are semiconductors. Likewise, Chev re et al. [7] studied optical properties of La_{1-x}A_xTiO_{2+x}N_{1-x} (A = Sr, Ba) systems obtained by ammonolysis at 950 °C from fused salts as precursors.

(iv) Stobierska et al. [8] and Matteucci et al. [9] obtain Cr and other chromophores doped YAlO₃ and characterize their performance in several ceramic matrices and glazes.

Therefore perovskite becomes a ceramic structure that must be added to DCMA list of ceramic pigments [10]. Other perovskites based on neodymium and titanium can be used as ceramic pigments [11].

In the other hand, the structural stability of a ceramic pigment into the matrix becomes associated to three main principles [12]: (a) valence changeability of the chromophore ion; versatile ion valence of chromium (III, IV, V and VI valence) or vanadium (III, IV and V valence) make them interesting chromophore and catalytic ions, (b) diffusion capacity of the chromophore ion into host crystal; in this sense there are ceramic pigments such as chrome-alumina or manganese-alumina than can be obtained by direct reaction between the chromophore and oxides, but in other cases such as chromium-sphene (Cr-CaSnSiO₅) or zircon based pigments (vanadium turquoise, pink koral and yellow of praseodymium) the crystal phase host and pigment must be prepared simultaneously, and it is well known that on the first case the pigmentation properties resides on the doped surface of the host phase particles, (c) stability of the chromophore substitution against other dopants that can be present on the ceramic matrices; it is the case of decolouring of blue or black pigments based on Co–Al, Co–Fe and Co–Ni spinels in rich zinc content glazes which interacts with spinel precipitating the high stable gahnite phase (ZnAl₂O₄).

Vanadium is the chromophore agent in several ceramic pigments listed by DCMA: vanadium-zirconia yellow (1-01-4), vanadium-antimony in rutile grey (11-21-8), vanadium cassiterite yellow (11-22-4) and vanadium zircon turquoise (14-42-2).

Lin et al. [13] study the effects of vanadium doping on resistive switching characteristics and mechanisms of magnetron RF-sputtered SrZrO₃ perovskite based thin films and propose that the Zr⁴⁺ sites might be substituted by V⁵⁺ when vanadium doped into SrZrO₃ perovskite thin films, because the ion radius of V⁵⁺ (0.54 Å of effective radius for VI coordination) is much closer to Zr⁴⁺ (0.72 Å for VI coordination) than Sr²⁺ (1.18 and 1.44 Å for VI and XII coordination index respectively) [14]. Therefore, a decrease in the lattice constants of SrZrO₃ perovskite with increasing vanadium doping concentration up to 0.2 mol% is observed,

whereas the lattice constants of 0.2, 0.3, and 0.4 mol% V: SrZrO₃ thin films are almost equal. Based on Vegard's law, the lattice constants of the films change with the concentration of vanadium up to 0.2 mol%, i.e., the concentration less than 0.2 mol% is within the solid solubility limit. The conduction mechanisms of SrZrO₃ perovskite based thin films are dominated by ohmic conduction (hopping conduction) and Frenkel–Poole emission for the low resistance state (LRS) and the high resistance state (HRS), respectively. The turn-on process might be attributed to the formation of conducting filaments consisting of oxygen vacancies with the effective barrier height in the range of 0.10–0.13 eV, whereas the turn-off process might result from thermally assisted oxidation of oxygen vacancies by the Joule heating effect. Furthermore, the introduction of the high valence cation V⁵⁺ in a Zr⁴⁺ site SrZrO₃ perovskite crystalline structure can suppress the formation of oxygen vacancies due to the charge neutrality restriction.

In the other hand Reddy et al. [15] study the effect of V₂O₅ on CaO–TiO₂ catalysts and their activity for cyclohexanol conversion. The CaO–TiO₂ binary oxide (1:1 molar ratio) was synthesized by a homogeneous co-precipitation method from ultrahigh dilute solutions of the corresponding chlorides and calcined at various temperatures from 723 to 1273 K. On the fired CaO–TiO₂ support (723 K) various amounts of V₂O₅ (2.5–10 wt.%) were deposited from ammonium metavanadate by a wet impregnation method and calcined at different temperatures. Conversion of cyclohexanol to cyclohexanone/cyclohexene was performed as a model reaction to assess the acid–base properties of the prepared catalysts. The CaO–TiO₂ mixed oxide contains mainly anatase phase and at higher calcination temperatures some portions of this mixed oxide is converted into CaTiO₃ and is thermally quite stable up to 1273 K. The CaO–TiO₂ binary oxide results a promising support for V₂O₅ dispersion. Impregnated V₂O₅ remains in a highly dispersed and amorphous state over the support and the dispersion behaviour is dependent upon the vanadia loading. In particular, the formation of CaVO₃ compound in the case of V₂O₅/CaO–TiO₂ samples as inferred by XRD and XPS observations, inhibits the formation of the most feasible V_xTi_(1-x)O₂ (rutile solid solution) at higher calcination temperatures. Finally authors concluded that the CaO–TiO₂ mixed oxide exhibits more cyclohexanone selectivity and V₂O₅/CaO–TiO₂ more cyclohexene selectivity in the conversion of cyclohexanol reflecting their basic and acidic properties, respectively.

Perovskite, CaTiO₃, shows mixed ionic and electronic conductivity at low oxygen partial pressure and maintains its structure in the presence of high concentrations of defects [16]. Substitution of calcium titanate by acceptor impurities in Ti-sites improves both ionic and electronic conductivity [17]. The most considerable increase of the electrical conductivity is achieved by iron-substitution, which makes this material particularly attractive for use as a membrane for hydrogen production. The samples of the system CaTi_{1-x}Fe_xO_{3-δ} (x = 0, 0.1...0.5) were synthesized by solid-state reaction of the corresponding oxides or carbonates by Dunyushkina [17]. These materials were weighed in the defined molar ratio and mixed in an agate mortar under ethyl alcohol for about 30–

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