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Sol gel synthesis of forsterite, M-doped forsterite (M = Ni, Co) solid solutions and their use as ceramic pigments

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Abstract

This work presents the synthesis of forsterite and M-doped forsterite solid solutions ($Mg_{2-x}M_xSiO_4$; M = Ni, Co; $x = 0.2$, 0.4, 0.6, 0.8 and 1) for which the optical properties were investigated before and after enameling with an industrial transparent glaze in the aim to explore their potential as ceramic pigments. The different materials were prepared through the sol–gel process based on $(H_2Si_2O_5)_{aq}$ as silicon precursor. Pure phases were obtained by calcination at 1000 °C (forsterite) and 1200 °C (pigments). Crystal field transitions of Ni^{2+} and Co^{2+} ions in octahedral M1 and M2 sites were the only source of green and violet colors of the pigments. The color stability was satisfactory for both Ni- and Co-pigments, although the latter underwent an appreciable dissolution in glaze. Moreover, the absence of secondary phases in the tested pigments yielded very good coloring performance, which further supports their high potential use as ceramic pigments.

Keywords: Sol–gel processes; Forsterite; Ceramic pigments; Optical properties

1. Introduction

Forsterite (Mg_2SiO_4) is a member of olivine family of crystals and an important material in the magnesia–silica system.[1] The orthorhombic crystal structure of olivine (with space group *Pbnm*) consists of discrete $[SiO_4]$ tetrahedra in which all oxygen ligands are bonded to just one Si atom. These non-bridging oxygen atoms surround cations (usually divalent cations) in two distinct six-coordinated sites Ml and M2 which are both distorted from octahedral symmetry. The point symmetry of the slightly smaller and centrosymmetric M1 site is C_i, although the point symmetry of the slightly larger and acentric M2 site is C_s.[2,3]

The forsterite has a wide range of applications which include: electronics (high melting point of 1890 °C and low dielectric permittivity),[4] tunable lasers (low electrical conductivity),[5] and bio-ceramics (excellent mechanical properties and good biocompatibility).[6] Besides, forsterite has a low thermal expansion, a good chemical stability and excellent insulating properties at high temperatures.[7] However, in the field of ceramic pigments, forsterite has not been studied extensively despite the fact that pigments based on forsterite possess excellent decorative properties.[8] These decorative properties are due to the most common cause of color in minerals which is the absorption of radiation in the visible region through electronic processes producing colored transmitted and reflected light.[9,10] For olivine minerals such absorptions are generated by crystal field transitions within individual cations of the transition elements present in their crystal structures. Thus, the green or violet colors of Ni– or Co–Mg_2SiO_4 phases result from Ni^{2+} or Co^{2+} ions octahedrally coordinated to oxygen ligands in M1 and M2 sites of the crystal structure of forsterite, respectively.[11–13]

The limited references on forsterite pigments may be due to problems related to the synthesis of these materials and the difficulty in obtaining a single-phase product. Indeed, it was reported that it is very difficult to prevent the formation of enstatite ($MgSiO_3$) and/or periclase (MgO) during the synthesis of forsterite.[14] This was explained by the slow reaction of the starting oxides to form silicate which results in the formation of such phases instead of forsterite.[15] The formation of secondary phases is more notable in the case of metal-doped forsterite. Pogrebenkov and Sedel’nikova, prepared pigments of diverse colors with the forsterite structure ($(MgMe)_2SiO_4$;

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Me = Fe, Ni, Co) by the traditional ceramic route, although magnesium metasilicate, residual colorant oxides, and cristobalite have been identified as by-products in the diffraction patterns of the pigments.[16,17] Further tests also gave similar results.[18,19] Moreover, partial substitution of MgO by NiO (from 0.1 to 0.7 mol) into forsterite crystal to give the optimum green coloration, without independent coloration by NiO, appeared to be 0.3 mol in the work of Lee and Lee which synthesized green pigments based on Ni-doped forsterite for ceramic glazes by using the ceramic method (1300 °C/3 h) and H_3BO_3 (Borax) as mineralizer.[8] Secondary phases in a given pigment have a number of disadvantages; in fact the occurrence of transition metal cations in crystal structure of more than one phase produces multiples overlapping absorption bands in the optical spectra, making resolving and assigning of the bands to the transition metal in the correct site of the correct structure phase a very difficult task.[20] As a result, information on color properties of a pigment containing impurities may be deduced with low degrees of accuracy from optical spectra. Also, impurities (free oxides of colorant ions in particular) are not always resistant to the dissolving effect of glaze at high temperatures and then degrade the coloring of the initial pigment which presents their main disadvantage in applications.

Taking into account the previous observations and investigations mentioned above, the aim of this study is to synthesize for the first time pigments based on forsterite as single phase products at relatively low temperature and then, analyze their color properties, either as powders or enameled within glaze in order to explore their potential as ceramic pigments. For this purpose, solid solutions with various composition $Mg_{2-x}M_xSiO_4$ (M = Ni or Co; $x = 0.2$, 0.4, 0.6, 0.8 and 1) were synthesized by the sol–gel process based on aqueous solution of silicic acid as silicon precursor (noted by: $(H_2Si_2O_5)_{aq}$ in this paper). This method presents several advantages (low temperature synthesis, higher purity and control of particle size distribution) compared to the traditional ceramic procedure and compared to the sol–gel alkoxide route, for the preparation of silicates such as zircon, willemite and tin sphene.[21–23] In fact it was adopted as the synthesis route in the current investigation. The choice of nickel and cobalt ions as chromophores, was made for two reasons. First, their sizes and charges are comparable to those of Mg^{2+} ions, which will facilitate the Mg–(Ni, Co) atomic substitution in the crystal structure of forsterite.[20] Second, their nice green and violet colors developed when they occur in the M1 and M2 sites of olivine crystal structure. However, these chromophores are not only expensive but also toxic components. Thus, different levels of Ni and Co doping (from $x = 0.2$ to 1) were investigated aiming to reduce the Ni or Co content as much as possible to minimize their toxicity or environmental concerns, without compromising the intensity of the green or blue colors finally obtained. Similar minimization studies have been previously reported in ceramic pigments based on related willemite–olivine Zn_2SiO_4–Ni_2SiO_4 and Zn_2SiO_4–Co_2SiO_4 systems.[24,25]

Finally, the preparation of forsterite in a first stage of this work was of great interest as it allowed us to find the optimal synthesis parameters leading to the formation of a pure phase, and the formation of Ni- or Co-doped forsterite solid solutions. One of these parameters is the use of NaCl or KCl salts as mineralizers in the formation of these olivine phases. In fact, several mineralizer ratios were investigated previously in the aim to found the minimum amounts giving single phases with respect to the calcination temperature used for non- and Ni- or Co-doped frosterite samples.

In this work we first describe the preparation of forsterite powders and second we describe the synthesis of the solid solutions and their characterization as pigment powders and as colored glazes in order to evaluate their performance during applications.

2. Materials and methods

2.1. Preparation of silicon precursor

The silicon precursor $(H_2Si_2O_5)_{aq}$ was obtained from an aqueous solution of $KHSi_2O_5$ that was prepared by reacting silicon powder with potassium hydroxide in an aqueous media under heating at 80 °C for 10 min. The potassium cations were then exchanged on a cation-exchange resin (Amberlite type) to yield an aqueous solution of $H_2Si_2O_5$ with a pH of about 4. Details of the procedures are given in a previous works.[21–23].

2.2. Synthesis of forsterite powders

$(H_2Si_2O_5)_{aq}$, magnesium acetate tetrahydrate ($Mg(C_2H_3O_2)_2{\cdot}4H_2O$, Panreac, 98% purity), nickel acetate tetrahydrate ($Ni(C_2H_3O_2)_2{\cdot}4H_2O$, Fluka, 99% purity) and cobalt acetate tetrahydrate ($Co(C_2H_3O_2)_2{\cdot}4H_2O$, Panreac, 99% purity) were used as silicon, magnesium, nickel and cobalt precursors and alkaline salts of NaCl and KCl as the mineralizers. The aqueous mixture was prepared with the stoichiometric molar ratios (Mg:Si = 2:1) for forsterite samples and (Mg:Si = $2 - x$:1; M:Si = x:1) (M = Ni, Co and $x = 0.2$, 0.4, 0.6, 0.8 and 1) for pigment samples, by pouring the various metal salts into the aqueous solutions of $H_2Si_2O_5$. The mineralizers were then added to these solutions and then stirred for 30 min at room temperature to give the starting solutions of which the pH was measured to be about 6. An NaCl- or KCl-to-magnesium acetate weight ratio of 10% for forsterite and Ni-doped forsterite samples and NaCl- or KCl-to-magnesium acetate weight ratio of 2.5% for Co-doped forsterite samples were used.

The starting solution of each sample was both placed in a Teflon cup with a total volume of 60 mL and then placed into a stainless steel autoclave which was heated to 200 °C in an oven for 3 days (hydrothermal method) and was refluxed at 120 °C under stirring for 3 days (reflux method) to form gel. The gels of all samples were dried at 120 °C for 12 h to give the xerogels which are grinded and then dried to ensure complete dehydration. The resulting powders were subsequently calcined in an electrical furnace at a temperature of 1000 °C (for forsterite powders) and 1200 °C (for pigment powders) for 3 h with a heating rate of 10 °C/min. Sample codes, compositions and synthesis parameters of forsterite, Ni-pigments and Co-pigments samples are depicted in Tables 1–3, respectively.