# Nanoparticle Synthesis of Willemite Doped with Cobalt Ions ($Co_{0.05}Zn_{1.95}SiO_4$) by an Epoxide-Assisted Sol−Gel Method

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Willemite nanoparticles doped with divalent cobalt ions were synthesized by a sol−gel method using propylene oxide as a gelation agent. The resulting nanoparticles show a narrow size distribution with particles in the 30−50 nm range. A highly homogeneous wet gel was achieved by the formation of M−O−Si bonds (M = Zn, Co) during the hydrolysis and condensation of the precursor salts. This high homogeneity allows a substantial reduction of the calcination temperature and time required for the formation of the mixed oxide phase as compared to the solid-state and other sol−gel routes and therefore minimizes the aggregation of the nanoparticles during calcination.

## 1. Introduction

Willemite $Zn_2SiO_4$ has proven to be an important host material for applications in the area of luminescent materials and pigments. For example, the luminescence of the host lattice $Zn_2SiO_4$ doped with $Eu^{3+}$, $Mn^{2+}$($Tb^{3+}$), or $Ce^{3+}$ covers the red, green, and blue portions of the visible spectrum, respectively.[1−4] These materials, due to their high luminescence efficiency and chemical stability, can be used in cathode ray tubes, field emission displays, and electroluminescent devices. The high-temperature stability of the host lattice $Zn_2SiO_4$ doped with $Co^{2+}$, and its intense blue coloration, allowed it to be used as a ceramic pigment.[5,6]

Currently, the new applications in the field of luminescent materials and pigments require the development of materials with smaller size, narrow size distribution, and regular morphology. Ultrafine luminescent particles are receiving considerable attention as potential materials for high-resolution imaging[7] and luminescent devices. The particle size and size distribution have also a great importance in the field of ceramic pigments, affecting the hiding power of the pigment and its stability in inks. However, the conventional solid-state method, because of the requirement of high calcination temperatures and long reaction times (the calcination temperature for the synthesis of $Zn_2SiO_4$ is around 1300 °C[6]), leads to the aggregation of the resulting particles that exhibit poor morphology and wide size distribution. The grinding process of the aggregated particles of luminescent materials by ball milling techniques results in damage to the surface of the particles and a decrease in the emission intensity. Therefore, the method cannot be applied for the preparation of ultrafine $Zn_2SiO_4$ as a host lattice for luminescent materials and pigments. Different methods have been used to obtain ultrafine $Zn_2SiO_4$ particles, such as sol−gel,[1] solution combustion,[8] spray pyrolysis,[9] polymer precursor,[10] hydrothermal,[11] and precipitation routes.[12] The conventional sol−gel preparation[1,13−15] of $Zn_2SiO_4$ usually involves the usage of tetraethyl orthosilicate (TEOS) as the silicon source and zinc salts as the zinc source, which are hydrolyzed in ethanol solutions. The lowest temperature achieved for obtaining ultrafine $Zn_2SiO_4$ particles through this sol−gel process was between 850 and 1100 °C, requiring a minimum of 30 min to obtain the $Zn_2SiO_4$ phase. Reynaud et al.[16] lowered the reaction temperature to 200 °C using an aqueous sol−gel process where $H_2Si_2O_5$ solution was used as silicon source and the reaction was carried under autogenous pressure in a Teflon-lined bomb. However, this aqueous sol−gel process cannot lead to the formation of nanoparticles.

For the preparation of mixed oxide particles, the sol−gel method offers great advantages as compared to the conventional solid-state method. A gel with a high homogeneity of the different precursor ions can be formed from a solution of the appropriate precursors, usually alkoxides. The high

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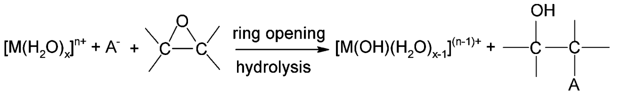
homogeneity of the gel guarantees an important reduction of the formation temperature of the mixed oxide phases, as it reduces the need of atomic diffusion during calcination and, hence, the aggregation of the particles during calcination. The major disadvantages of using the metal alkoxide-based sol−gel process are its moisture sensitivity and the unavailability of suitable commercial precursors, especially for mixed-metal oxides. The sol−gel synthesis of mixed oxides from alkoxide mixture usually suffers from the different hydrolysis susceptibilities of the individual components and the benefits of improved homogeneity can be lost during the hydrolysis of the alkoxides, which may ultimately lead to component segregation and mixed phases in the final materials. To achieve homogeneous mixed oxides with predetermined compositions, the difference in reactivity has been minimized by controlled prehydrolysis of the less reactive precursor,[17] by chemical modification of the precursors,[18] by using single-source heterobimetallic alkoxide precursors,[19] or by nonhydrolytic sol−gel processes.[20] The nonalkoxide sol−gel process, involving hydrolysis and condensation of metal salts, avoids the disadvantage of the alkoxide sol−gel process (high sensitivity to moist environment); however, it still has the disadvantage of different hydrolysis susceptibilities of the individual components.



(1)

Another recently developed nonalkoxide sol−gel route involving the usage of an epoxide as a gelation agent requires relatively few steps to obtain metal oxides and is low-temperature and low-cost. It shows a great potential for the preparation of homogeneous mixed oxide gels. The epoxide acts as an acid scavenger through protonation of the epoxide oxygen and subsequent ring opening by the nucleophilic anionic conjugate base. According to the reaction eq 1, epoxide consumes protons from the aquo complexes $[M(H_2O)_x]^{n+}$, which promotes the hydrolysis and condensation of the complexes resulting in the formation of a gel. This method has been used for the preparation of metal oxide aerogels[21−24] and nanoparticles.[25−27] The major disadvantage of this epoxide method is that metal oxide gels cannot be prepared from aqueous metal ions that have a formal charge of less than +3, due to the lower acidity of $[M(H_2O)_x]^{2+}$ complexes.[21,22] The method has proven to be successful for the formation of metal-oxide/silica compounds, with the metal ions having a formal charge of +3, resulting in homogeneous gels through the formation of Si−O−M bonds during the gelation process.[28,29] However, if the metal ions have a formal charge of less than +3, the metal ions precipitate during the gelation of the silica resulting in the segregation of the two phases. The most important feature of this method is the formation of a highly homogeneous gel precursor, which allows a substantial reduction of the temperature of calcination and reaction time, minimizing the aggregation of the particles during calcination.

The aim of this work is to prepare willemite nanoparticles doped with cobalt ions using an epoxide-assisted sol−gel method. The blue cobalt-doped willemite pigment[6] ($Co_{0.05}Zn_{1.95}SiO_4$) will be used as a target material to show the feasibility of the method to make precursor gels with high homogeneity to reduce the degree of aggregation of the resulting cobalt-doped willemite nanoparticles.

## 2. Experimental Section

**2.1. Materials.** Tetraethyl orthosilicate (TEOS), cobalt(II) chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), zinc(II) nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), and propylene oxide (PPO) were obtained from Aldrich. Ethanol was from Merck, and 35% hydrochloric acid was from Panreac. All reagents were used as received.

**2.2. Preparation of Willemite-type $Co_{0.05}Zn_{1.95}SiO_4$ Nanoparticles.** All syntheses were performed under ambient atmosphere and the same reaction parameters except for the added amount of HCl. In a typical experiment, a 15 mL clear pink ethanol mixture solution of cobalt chloride, zinc nitrate, and TEOS was obtained by dissolving $CoCl_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and TEOS in ethanol ($[Co^{2+} + Zn^{2+}] = 0.6$ mol L$^{-1}$; $[Co^{2+}]:[Zn^{2+}] = 0.05:1.95$; [TEOS] = 0.3 mol L$^{-1}$). Different amounts of 35% hydrochloric acid were added, followed by the addition of propylene oxide to the solution (PPO/Si = 20). An exothermic reaction occurred within several minutes, followed by a gradual formation of a pink rigid gel. The gel formation time, which depends on the concentration of hydrochloric acid (for a fixed concentration of metal ions and propylene oxide), varied from about 30 min to more than 24 h with the decrease of HCl concentration. The gels were aged in a closed vessel at room temperature for 24 h, dried in an open vessel at 50 °C for 24 h, and then treated at 100 °C until the xerogels were obtained. The resulting xerogels were ground to powder and calcined between 600 and 900 °C for 10 min to obtain $Co_{0.05}Zn_{1.95}SiO_4$.

**2.3. Characterization.** The thermal behavior (TG/DTA) of the samples was studied by a Seiko SSC/5200 (TG/DTA 320U) in static air atmosphere from ambient temperature to 1200 °C with a heating rate of 10 °C/min. The XRD patterns of the samples were measured in a Siemens D8 diffractometer using Cu Kα radiation. The morphology of the particles was observed using a JEOL 2000 transmission electron microscope working at 200 kV. FTIR spectra were recorded on a Nicolet 20SXC spectrometer using the KBr pellet technique.

## 3. Results and Discussion

**3.1. Gel Formation.** During the preparation of the gel, the aquo complexes $[M(H_2O)_6]^{2+}$ (M = Zn, Co) react with

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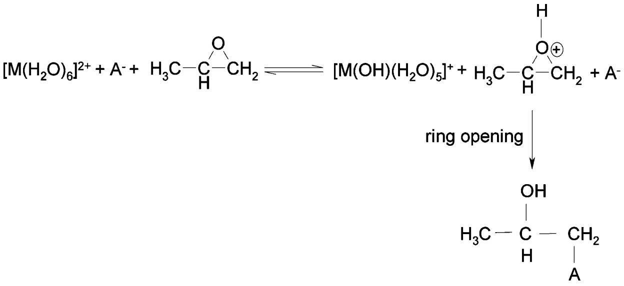
propylene oxide (PPO) to form M−OH bonds as shown in eq 2. The hydrolyzed ions will undergo condensation, releasing water and forming M−O−M bonds. The PPO acts as a proton scavenger, reacting with the protons that come from the hydrolysis of the aquo complexes. The protonated propylene oxide is then irreversibly ring-opened.



(2)

The usage of HCl has a decisive effect on the homogeneity of resulting gel. In the synthesis of gels without HCl, the weak acid environment of the solution, arising from the low acidity of the aquo complexes $[M(H_2O)_6]^{2+}$ (M = Zn, Co), slows down the hydrolysis and condensation rate of TEOS, increasing the gel formation time of the silica to more than 24 h. In addition, the low acidity of the aquo complexes slows down the protonation of propylene oxide and the subsequent rise in the pH, which allows alternative side reactions to occur to a significant degree and cause precipitation to take place within several hours. The difference of the rate of hydrolysis and condensation of TEOS and that of the metal ions results in the formation of an inhomogeneous gel. HCl reacts as a catalyst, increasing the rate of the hydrolysis and condensation of TEOS to match that of the metal ions. According to the observation in the preparation of gels, raising the concentration of HCl from 0.15 to 1.04 mol $L^{-1}$ reduces the gel formation time from approximately 210 to 150 min. However, this increase in the HCl concentration resulted in a great increase of the drying time of the gel from 1.5 days to more than 3 days. Concentrations of HCl above 1.04 mol $L^{-1}$ lead to the formation of a silica gel, leaving the metal ions not incorporated in the silica network.

These results suggest that when the HCl concentration is between 0.15 and 1.04 mol $L^{-1}$, the hydrolysis and condensation of metal ions and TEOS are in the same order of magnitude, resulting in the formation of homogeneous gels. When the HCl concentration is >1.04 mol $L^{-1}$, the slower hydrolysis and condensation rates of the metal ions reduce drastically their incorporation into the silica gel network.

**3.2. Thermogravimetric Analysis.** TG and DTA measurements (Figure 1) of the $Co_{0.05}Zn_{1.95}SiO_4$ precursor dry gel show a progressive weight loss of about 7% from room temperature to around 120 °C, accompanied by an endothermic peak at about 59 °C, that is attributed to the evaporation of adsorbed water. The two exothermic peaks observed in the DTA curve around 198 and 260 °C are due to the burning of organic matter. Above 260 °C, a flatter weight loss curve is observed due to the release of water arising from the condensation reaction. The exothermic peak around 782 °C is attributed to the formation of the willemite $Zn_2SiO_4$ phase. The total weight loss from room temperature to 900 °C is about 52.7%.

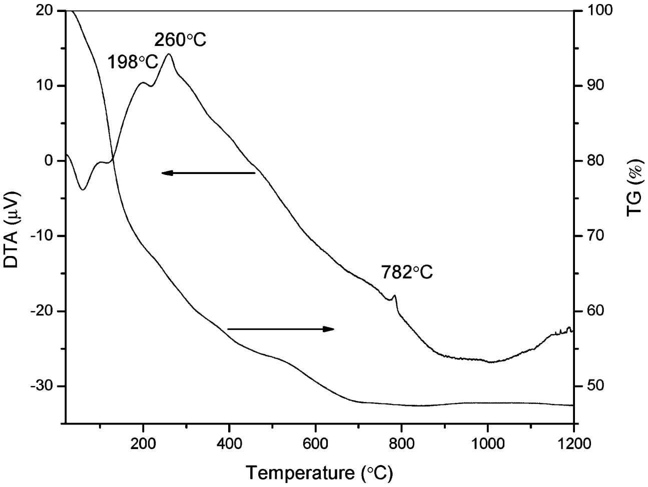


**Figure 1.** DTA/TG analysis of $Co_{0.05}Zn_{1.95}SiO_4$ precursor carried out in static air.

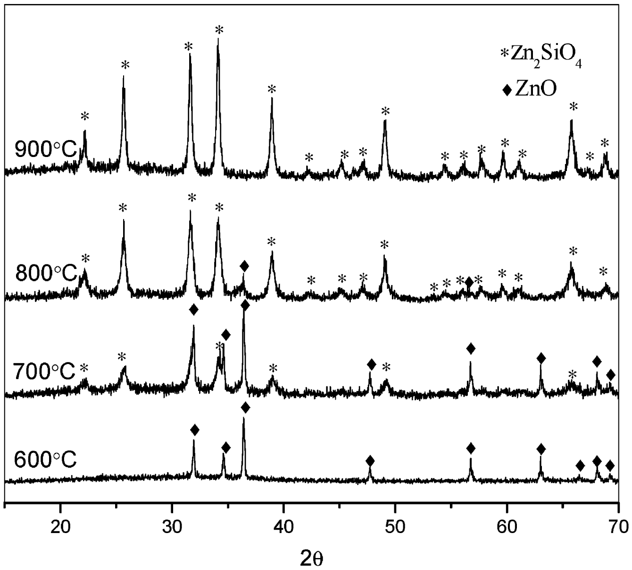


**Figure 2.** XRD patterns of $Co_{0.05}Zn_{1.95}SiO_4$ calcined at different temperatures.

**3.3. Crystallographic Analysis.** The XRD patterns of samples calcined at different temperatures are shown in Figure 2. Samples calcined at 600 °C show a pure ZnO phase (JCPDS 36-1451) in the diffraction patterns, while the $SiO_2$ remains amorphous. At 700 °C, however, a second phase, willemite $Zn_2SiO_4$ (JCPDS 37-1485), begins to form in addition to the ZnO phase. When the calcination temperature rises up to 800 °C, $Zn_2SiO_4$ becomes the main phase and only a trace of the ZnO phase is observed. After the sample was treated at 900 °C for only 10 min, a pure $Zn_2SiO_4$ phase can be seen in the XRD patterns.

**3.4. FTIR Analysis.** To clarify the role of HCl in the preparation of the $Co_{0.05}Zn_{1.95}SiO_4$ precursor gel, the FTIR spectra of five dry gels precursors prepared with different concentrations of HCl were measured. The different samples show almost the same spectra, as shown in Figure 3. In all five samples, the characteristic vibration band of Si−O(H) bond[30] is found around 928 $cm^{-1}$, and the characteristic antisymmetric ($\nu_{as}$) Si−O−Si vibration bands[31] of the $[SiO_4]$

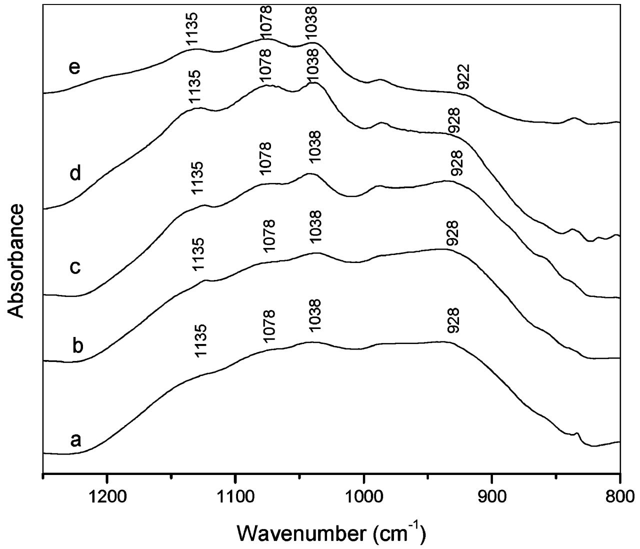


**Figure 3.** FTIR spectra of $Co_{0.05}Zn_{1.95}SiO_4$ precursors prepared with different concentrations of HCl: 0.15 mol L$^{-1}$ (a), 0.37 mol L$^{-1}$ (b), 0.74 mol L$^{-1}$ (c), 1.34 mol L$^{-1}$ (d), and 1.90 mol L$^{-1}$ (e).

unit are observed around 1135 and 1078 cm$^{-1}$. A band around 1038 cm$^{-1}$ is observed in all samples, which can be attributed to the incorporation of the metal ions into the silica structure forming Si−O−M bonds (M = Zn, Co).

The incorporation of metal ions into the silica framework leads to a lowering of the local symmetry of the nearest neighbor [$SiO_4$] unit.[32] This gives birth to a new band around 1038 cm$^{-1}$, which is lower in energy than the undisturbed [$SiO_4$] unit vibration. Similar FTIR results are also observed in the preparation of Fe−Si mixed oxide.[27,32] The coexistence of the vibration band around 1135, 1078, and 1038 cm$^{-1}$ suggests the coexistence of Si−O−Si and Si−O−M bonds. The existence of the Si−O−M bonds in the precursor mixed oxide gel shows the high degree of homogeneity obtained using this method. By comparison of the five spectra in Figure 3, it can be seen that the intensity of Si−O−M decreases and that of Si−O−Si increases with the increase of HCl concentration, which suggest a decrease in the homogeneity of the gel as the concentration of HCl is increased above 1.04 M.

FTIR measurements were also carried out on samples calcined at different temperatures; the results are shown in Figure 4. The antisymmetric vibration bands of Si−O−Si bonds around 1135 and 1078 cm$^{-1}$ shown in the spectrum of the precursor gel disappear when the samples are calcined to 600 °C, and only the bands assigned to the Si−O−M bonds around 1038 cm$^{-1}$ and Si−O(H) around 928 cm$^{-1}$ are left. The result suggests that Si atoms are replaced by metal ions to form Si−O−M bonds (M = Zn, Co). At this temperature, no bands of ZnO can be observed. However, when the sample is treated above 700 °C, the FTIR spectra show all of the typical bands[2−4] of willemite: the two bands around 617 and 577 cm$^{-1}$ attributed to the vibration of $ZnO_4$ group, the bands between 1000 and 800 cm$^{-1}$ attributed to $SiO_4$ tetrahedron vibration, and the band around 460 cm$^{-1}$ assigned to the bending vibration of O−Si−O bond. The appearance of the vibrations of $SiO_4$ and $ZnO_4$ groups suggests the formation of the $Zn_2SiO_4$ phase.

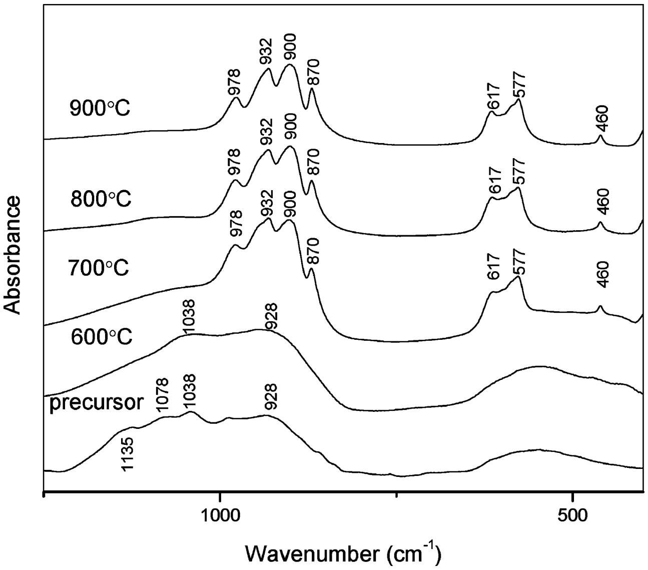


**Figure 4.** FTIR spectra of $Co_{0.05}Zn_{1.95}SiO_4$ precursor and samples calcined at different temperatures.

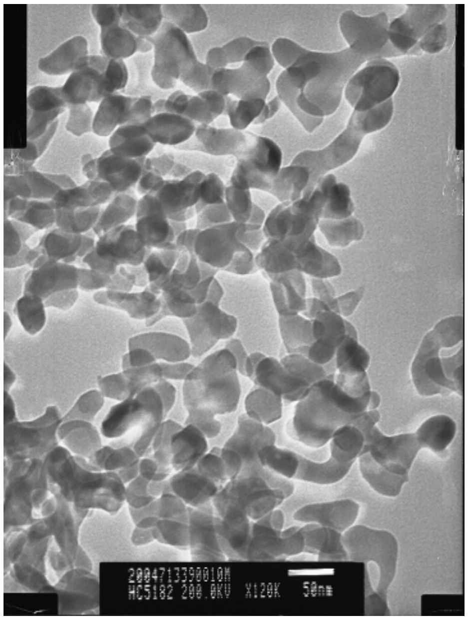


**Figure 5.** Transmission electron micrograph of $Co_{0.05}Zn_{1.95}SiO_4$ nanoparticles calcined at 900 °C.

**3.5. Transmission Electron Microscope Analysis.** TEM analysis of the $Co_{0.05}Zn_{1.95}SiO_4$ samples prepared in this work shows well-dispersed, nonagglomerated, and nearly spherical nanoparticles with crystallite size of 30−50 nm. A high magnification representative micrograph of the mixed oxide nanoparticles is given in Figure 5 to provide a fine characterization of their size and morphology.

## 4. Conclusions

A sol−gel method using propylene oxide as gelation agent has been successfully used to synthesize willemite-type $Co_{0.05}Zn_{1.95}SiO_4$ nanoparticles of 30−50 nm. The usage of

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this epoxide method results in a substantial reduction of calcination temperature and time as compared to the solid-state route and other sol−gel routes: the willemite-type phase begins to form at 700 °C and becomes the main phase at 800 °C; pure cobalt-doped willemite phase is obtained after treating the precursor gel at 900 °C for just 10 min. This reduction in the phase-formation temperature is achieved because of the high homogeneity of the gel precursor, obtained via the formation of M−O−Si bonds (M = Zn, Co) during the gelation process. It was found that the addition of HCl plays a very important role for determining the homogeneity of the gel. The addition of an appropriate amount of HCl accelerates the hydrolysis of TEOS and prevents the early precipitation of the metal ions in solution, allowing the formation of a homogeneous gel.

In this work, the cobalt-doped willemite blue pigment nanoparticles were prepared to show the capability of the method for the formation of metal ions-doped willemite precursor gel with high homogeneity and, hence, a low degree of aggregation on the resulting nanoparticles.

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