Co₂SiO₄ nanostructures: New simple synthesis, characterization and investigation of optical property

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Abstract

Herein, a new and simple method for the synthesis of Co₂SiO₄ nanostructures at low temperature is reported. The nanostructures are obtained by the solvothermal reaction of Co(CH₃COO)₂.4H₂O with tetraethyl orthosilicate (TEOS) in methanol solvent at 120–150 °C for 8–12 h, follows by calcination at 700 °C for 5 h. The effects of using polymer, mole ratio of Co:Si, reaction time and temperature have been optimized to achieve the best products on morphology and purity. It is the first time that optical property of cobalt orthosilicates and also effect of polymer on them are investigated. At the temperature of 150 °C for a 12 h period of time, when the molar ratio of Co:Si is 1:1, the product is rod-shape Co₂SiO₄ with diameters of 20–40 nm. A mixture of the rod-shape and spherical structures of Co₂SiO₄, with diameters of 20–40 nm, is obtained by making use of ratio of 2:1 of Co:Si at 150 °C for 12 h. With a decreasing reaction time to 10 h, spherical clusters of Co₂SiO₄ is prepared. The Co₂SiO₄ nanostructures are characterized by XRD, SEM and TEM to analyze their structure and morphology. The optical and magnetic properties of the nanostructures are investigated.

Keywords: Co₂SiO₄; Solvothermal; Nanostructures; Magnetic property; Tetraethyl orthosilicate.

1. Introduction

Many technological applications require materials with large surface area and small particle size [1]. Thus in recent years, extensive attention has been paid to the nanomaterials owing to their interesting properties and potential applications [2–6]. M_2SiO_4 compounds crystallizing in the olivine structure are characterized by a distorted hexagonal close-packed array of oxygen anions in which one-eighth of the tetrahedral interstices are filled by silicon and one-half of the octahedral interstices are occupied by the divalent metal cation M [7, 8]. The olivines are major components of the Earth's upper mantle and are therefore of geological and geophysical importance [9]. One of the less-studied olivine-type silicates is the synthetic Co_2SiO_4 , cobalt orthosilicate. The Co_2SiO_4 is a member of the olivine mineral family, has an orthorhombic structure and is widely used as a pigment in the ceramic industry due to its stability at high temperatures and is currently being considered to be used as a magnetic material and as catalyst [10].

The Co_2SiO_4 nanostructures have been synthesized by various methods including precipitation [11], hydrothermal [12], sol-gel [13], etc. Many methods reported for the synthesis of Co_2SiO_4 need high temperatures. Our group is interested in finding new procedures with low temperatures to obtain these systems that minimize the aggregation of the particles. In the present work Co_2SiO_4 nanostructures are synthesized by a new solvothermal method. The effects of using polymer, mole ratio of Co:Si, reaction time and temperature on the morphology, phase and purity of the products are investigated in order to optimize the reaction condition. To the best of our knowledge, it is the first time that solvothermal method is used for the synthesis of the Co_2SiO_4 nanostructures. At the first time effect of polymer on these nanostructures is investigated. Also it is the first time that optical property of cobalt orthosilicates is considered. Following this method, we herein report a convenient and controllable synthetic method by simply adjusting the different parameters at low temperatures.

2. Experimental

2.1. Materials and experiments

All the chemicals used in our experiments were of analytical grade, were purchased from Merck and were used as received without further purification. XRD patterns were collected from a diffractometer of Philips Company with X'PertPro monochromatized Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Microscopic morphology of products was visualized by a LEO 1455VP scanning electron microscope (SEM). TEM images were obtained on a Philips EM208S transmission electron microscope with an accelerating voltage of 100 Kv. Fourier transform infrared spectroscopy (FT-IR) was recorded with Shimadzu Varian 4300 spectrophotometer in KBr pellets. The electronic spectrum of the samples was taken on a Shimadzu UV2101PC UV-Vis Spectrophotometer (Shimadzu, Japan). The magnetic measurement was carried out in a VSM (BHV-55, Riken, Japan) at room temperature.

2.2. Synthesis of Co_2SiO_4 nanostructures

In the current synthetic procedure that has been shown in [Scheme 1](#), first, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ is dissolved in distilled water to form a clear solution. Then methanolic solution containing TEOS is added into the above solution. The pH is adjusted in 7–8 with ammonia. After stirring the solution for 1 h, the mixture is transferred into a Teflon-lined stainless steel container, then is sealed and maintained at 120–150 °C for 8–12 h. The resultant gray precipitates are filtered, washed, dried and then calcined at 70 °C for 5h. For investigation of effect of polymer, precursor solutions are added to PVA dispersed by ultrasound. [Table 1](#) lists the reaction conditions for the synthesis of Co_2SiO_4 nanostructures.

3. Results and discussion

When metal salt is added to water, the salt molecules dissociate into ions which disperses in the solution. In our case, the dispersed ions are Co^{2+} and CH_3COO^- . Since water has a dipolar moment, the positive charge of cations attracts the partial negative charge, that is the oxygen atom [\[14\]](#). For Co^{2+} ion, the metal complex formed is

$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. The water molecules are used to solvation of Co^{2+} and CH_3COO^- ions, the hydrolysis of the solvated metal ions and the hydrolysis process of the TEOS molecules. In the alkaline condition, TEOS molecules are not full hydrolyzed. When the hydrolysis process is incomplete, polymerized species are formed after condensation [15, 16]. During the solvothermal reaction, organic chains of the products obtained from hydrolysis and condensation of TEOS burn, which leads to silica matrices; different compounds of cobalt coexist into the SiO_2 : cobalt acetate, hexaquo cobalt complexes (ions solvated), partially hydrolysed cobalt complexes and cobalt oxides [14]. These compounds react with SiO_2 at low temperature leading to Co_2SiO_4 . The products obtained without calcination are characteristic to amorphous phases. The products calcined at 700 °C, contain Co_2SiO_4 as unique crystalline phase, according to XRD patterns. The proposed mechanism for the synthesis of Co_2SiO_4 nanostructures can be expressed in Scheme 2. Product prepared in acidic condition is cobalt oxide. In acidic condition, TEOS is hydrolyzed completely and $\text{Si}(\text{OH})_4$ obtained after complete hydrolysis of TEOS molecules. Formation of $\text{Si}(\text{OH})_4$ and also slow rate of condensation in the acidic condition will cause that product to be cobalt oxide.

Fig. 1 shows XRD patterns of products prepared with different ratios of Co:Si, without calcination. It can be observed that amorphous products are prepared. The composition of the products prepared after calcination is investigated by XRD. Fig. 2 shows XRD patterns of the products obtained at 150 °C after 12h solvothermal reaction and then calcination, with different ratios of Co:Si. Intense and sharp diffraction peaks suggest that the obtained products are well crystallized. In this figure, the peaks have been indexed with blue, green and red colors indicate the orthorhombic, cubic and cubic Co_2SiO_4 with JCPDS cards no. 83–2455, 70–2280 and 70–0323, respectively. As shown in the figure, the Co_2SiO_4 nanostructures are formed at 150 °C after 12h solvothermal reaction and then calcination with different molar ratios of Co:Si. No remarkable diffractions of other phases can be found in this figure. When ratio of Co:Si is 1:1, the products are found to be the mixture of two JCPDS cards of

Co_2SiO_4 (Fig. 2a). With change of ratio of Co:Si from 1:1 (sample no. 4) to 2:1 (sample no. 5) and 1:2 (sample no. 6), there are still the peaks of Co_2SiO_4 , but the intensities have been changed.

The effect of reaction temperature on the type and purity of the as-synthesized products with 2:1 ratio of Co:Si, is investigated. Fig. 3 shows XRD patterns of products prepared with 2:1 ratio of Co:Si, at different temperatures after 12h solvothermal reaction and then calcination. According to this figure the peaks are broad and ambiguous which failed to be identified from among the JCPDS cards.

For investigating the effect of reaction time, the solvothermal reaction carried out at 150 °C for 12, 10 and 8 h. The XRD patterns of the products obtained with 2:1 ratio of Co:Si and from different time periods are show in Fig. 4.

The diffraction peaks in this figure correspond to Co_2SiO_4 . Intense and sharp diffraction peaks show formation of the nanostructures with high crystallinity. When PVA is used (sample no.11), there are still the peaks of Co_2SiO_4 , but the intensities and crystallinity are increased (Fig. 4c). No remarkable diffractions of other phases or compounds can be found in Fig. 4c, indicating that a pure Co_2SiO_4 phase has been formed in the presence of PVA.

Fig. 5 shows the morphologies of the products obtained with different molar ratios of the Co:Si. From the images, it can be seen that agglomerated nanoparticles with different shapes have been formed after the synthesis in all samples. Diameter of these nanoparticles is about 10 nm. At the temperature of 150 °C after 12h solvothermal reaction and then calcination, when the molar ratio of Co:Si is 1:1 (sample no. 4) or 2:1 (sample no. 5), the directional linkage of the particles with uniform sizes forms rod-shape structures (Figs. 5a, b). It is observed that rod-shape structures have diameters of 20–40 nm. The as-prepared nanostructures with ratio of 2:1 of Co:Si, have two morphologies. From Fig. 5b it is found that the samples are mixture of rod-like and spherical nanostructures with diameters in the range of 20–40 nm. Increasing Si content in sample no. 6, with molar ratio of 1:2 of Co:Si, irregular prisms with uneven dimensions are formed from aggregation of nanoparticles (Fig. 5c). Fig. 5 shows that the molar ratio of Co:Si in the precursors plays an important role in the morphology and particle size of Co_2SiO_4 nanostructures.

In other side, the effect of the reaction time on the morphology of the products is investigated. Fig. 6 depicts SEM images of Co₂SiO₄ nanostructures prepared with 2:1 ratio of Co:Si at 150 °C after different times solvothermal reaction and then calcination. With decrease of reaction time from 12 h (sample no. 5) to 10 h (sample no. 9) at 150 °C, nanoparticles tend to aggregate in spherical clusters and the size of the clusters are rather constant, about 20 nm, as shown in Fig. 6a. Fig. 6b shows with decreasing reaction time to 8 h nanoparticles are collected and irregular shaped structures are formed. Fig. 6c reveals distorted spherical aggregations of nanoparticles for samples no. 11 obtained in the presence of PVA. Formation of irregular prisms with uneven dimensions, obtained from aggregation of nanoparticles, is seen in this figure. However, with increasing time of reaction, the particles have ample time to agglomerate and grow into more regular shapes. Therefore, 8 and 10 h are not long enough for the formation of rod-shape nanostructures, longer times from 8 h is need for this target. For better estimation of particle size, transmission electron microscopy was used. TEM images of Co₂SiO₄ nanostructures in Fig. 6d–f confirm synthesis of nanostructures with rather constant diameters and average particle size about 20 nm.

In continuance, Williamsone-Hall (W–H) analysis is used to study the individual contributions of crystallite sizes of the nanostructures. It relies on the principle that the approximate formulae for size broadening and strain broadening vary quite differently with respect to Bragg angle.

$$\beta \cos\theta = 2A\epsilon \sin\theta + 0.9 \lambda/D \quad (1)$$

where β is the breadth of the observed diffraction line at its half-intensity maximum, θ is Bragg angle, A is a constant number (which usually takes a value of about 1), ϵ is the lattice strain, λ is the wavelength of X-ray source used in XRD and D is the crystallite size. Comparing this equation to the standard equation for a straight line, we see that by plotting $\beta \cos\theta$ versus $\sin\theta$ we obtain the strain component from the slope ($2A\epsilon$) and the size component from the intercept ($0.9 \lambda/D$). In Fig. 7 the terms ($\beta \cos\theta$) have been plotted with respect to ($\sin\theta$) for the preferred orientation peaks of Co₂SiO₄ with the cubic and orthorhombic phases (samples no. 4, 5, 6, 10 and 11). Fit to the data, the lattice strain is extracted from the slope and the crystalline size is extracted from the y-intercept of the fit.

The crystalline sizes for samples no. 4, 5, 6, 10 and 11 are obtained 198 nm, 5 nm, 346 nm, 115 nm and 81 nm, respectively. These results confirm SEM and TEM results in Figs. 5 and 6.

FT-IR spectrum of the as-prepared product in the presence of PVA (sample no. 11) is shown in Fig. 8a. The absorption band at 1088cm^{-1} is assigned to the vibration of Si–O–Si bonds, the band around 476 cm^{-1} is attributed to the bending vibration of O–Si–O [17]. The absorption bands at 571 and 666 cm^{-1} are assigned to the Co–O (metal–oxygen) stretching mode [18]. The weak band at about 850 cm^{-1} can be assigned to the SiO_4 tetrahedron vibrations [19] and suggests the formation of Co_2SiO_4 . The broad peak at ca. 3422cm^{-1} and the band near 1622 cm^{-1} are assigned to the stretching and bending vibrations of absorption water on surface of nanostructures, respectively. There are no other significant peaks related to precursors and impurities. The study of the optical properties of the materials provides a convenient and effective method for explaining some important features concerning the band structures. The optical absorption spectrum of Co_2SiO_4 nanostructures represents in Fig. 8b. Band gap of Co_2SiO_4 nanostructures is estimated by Tauc's equation using the absorption data $\alpha = \alpha_0 (\text{h}\nu - E_g)^n / \text{h}\nu$ where α is absorption coefficient, α_0 and h are the constants, $h\nu$ is the photon energy, E_g is the optical band gap of the material, and n depends on the type of electronic transition and can have any value between 0.5 to 3 [20] The E_g has been distinguished by extrapolating the linear portion of the plot of $(\alpha h\nu)^2$ against $h\nu$ to the energy axis. The plot of $(\alpha h\nu)^2$ versus $h\nu$ inserted in Fig. 8b. Extrapolation of the linear portion of the curve to $(\alpha h\nu)^2 = 0$ gives the optical band gap, which was found to be 3.14 eV for Co_2SiO_4 nanostructures (sample no. 11).

Magnetic properties of nanostructures are very sensitive on the particle size and broad spectrum of magnetic properties has been obtained in the nanosized systems such as superparamagnetism, spin glass, high magnetization, high magnetic moment of the particles and high coercivity [21,22]. Fig. 9 shows the magnetic hysteresis plots for the samples no. 9 and 11 measured at room temperature. The plots show weak ferromagnetic behavior for both samples. The hysteresis loop of sample no. 11, obtained in the presence of PVA, has M_s and H_c values of ca. 0.0079 emu/g and 247.81 Oe, respectively. It can be seen that the M_s of sample obtained in the

presence of PVA is lower than the value of corresponding sample no. 9 obtained without polymer and it may be most likely due to the existence of polymer.

4. Conclusions

Co_2SiO_4 nanostructures are successfully synthesized by a facile solvothermal method combining with a post-calcining process. XRD patterns of the samples obtained without calcination are characteristic to amorphous phases. The samples calcined at temperature 700 °C, contain Co_2SiO_4 (olivine) as unique crystalline phase, according to XRD patterns. The using PVA, ratio of Co:Si, reaction time and temperature have significant effects on the purity and morphology of obtained products. VSM confirms that nanostructures exhibit magnetic behavior. UV–Vis absorption spectrum shows optical property of the nanostructures. This method is proved to be a new, simple, efficient and quick way for the synthesis of metal orthosilicates.

Acknowledgment

Authors are grateful to the council of University of Kashan for providing financial support to undertake this work.

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Figure captions

Fig. 1. XRD patterns of products prepared at 150 °C after 12h solvothermal reaction, without calcination, with different ratios of Co:Si: (a) 1:1 (sample no. 1) , (b) 2:1 (sample no. 2) , (c) 1:2 (sample no. 3).

Fig. 2. XRD patterns of Co₂SiO₄ nanostructures prepared at 150 °C after 12h solvothermal reaction and then calcination, with different ratios of Co:Si: (a) 1:1 (sample no. 4) , (b) 2:1 (sample no. 5) , (c) 1:2 (sample no. 6).

Fig. 3. XRD patterns of products prepared with 2:1 ratio of Co:Si, at different temperatures after 12h solvothermal reaction and then calcination: (a) 135 °C (sample no. 7) , (b) 120 °C (sample no. 8).

Fig. 4. XRD patterns of Co₂SiO₄ nanostructures prepared with 2:1 ratio of Co:Si at 150 °C after different times solvothermal reaction and then calcination: (a) 10 h (sample no. 9) , (b) 8 h (sample no. 10) , (c) 10 h in the presence of PVA (sample no. 11).

Fig. 5. SEM images of Co₂SiO₄ nanostructures prepared at 150 °C after 12h solvothermal reaction and then calcination, with different ratios of Co:Si: (a) 1:1 (sample no. 4) , (b) 2:1 (sample no. 5) , (c) 1:2 (sample no. 6).

Fig. 6. SEM images of Co₂SiO₄ nanostructures prepared with 2:1 ratio of Co:Si at 150 °C after different times solvothermal reaction and then calcination: (a) 10 h (sample no. 9) , (b) 8 h (sample no. 10) , (c) 10 h in the presence of PVA (sample no. 11) , (d, e, f) TEM images of sample no. 9.

Fig. 7. The W–H analysis of samples no.: (a) 4 , (b) 5 , (c) 6 , (d) 10 and (e) 11.

Fig. 8. (a) FT-IR spectrum of sample no. 11 , (b) UV–visible absorption spectrum (inset: the curve of $(\alpha h\nu)^2$ against $h\nu$ (sample no. 11)).

Fig. 9. M–H hysteresis at 300 K for Co₂SiO₄ nanostructures (samples no. 9 and 11).

Table 1. The reaction conditions of Co₂SiO₄ nanostructures synthesized in this work.

Scheme 1. Schematic diagram illustrating the formation of Co₂SiO₄ nanostructures at various conditions, calcination in air under the temperature of 700 °C.

Scheme 2. Schematic mechanism for the synthesis of Co_2SiO_4 nanostructures.

Table 1.

Sample no.	Co source	Silicate source	Co:Si ratio	Solvothermal (T (°C), t(h))	Calcination (T (°C), t(h))	Polymer
1	Co(CH ₃ COO) ₂ . 4H ₂ O	TEOS	1:1	150 , 12	–	–
2	Co(CH ₃ COO) ₂ . 4H ₂ O	TEOS	2:1	150 , 12	–	–
3	Co(CH ₃ COO) ₂ . 4H ₂ O	TEOS	1:2	150 , 12	–	–
4	Co(CH ₃ COO) ₂ . 4H ₂ O	TEOS	1:1	150 , 12	700 , 5	
5	Co(CH ₃ COO) ₂ . 4H ₂ O	TEOS	2:1	150 , 12	700 , 5	
6	Co(CH ₃ COO) ₂ . 4H ₂ O	TEOS	1:2	150 , 12	700 , 5	
7	Co(CH ₃ COO) ₂ . 4H ₂ O	TEOS	2:1	135 , 12	700 , 5	–
8	Co(CH ₃ COO) ₂ . 4H ₂ O	TEOS	2:1	120 , 12	700 , 5	–
9	Co(CH ₃ COO) ₂ . 4H ₂ O	TEOS	2:1	150 , 10	700 , 5	–
10	Co(CH ₃ COO) ₂ . 4H ₂ O	TEOS	2:1	150 , 8	700 , 5	–
11	Co(CH ₃ COO) ₂ . 4H ₂ O	TEOS	2:1	150 , 10	700 , 5	PVA

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Scheme 1.

Formation of products with different morphologies at various condition

Scheme 2.