

Synthesis and characterizations of CoTiO₃-clay nanocomposites by sol-gel method

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Abstract

CoTiO₃-clay nano-composites were synthesized via a conventional sol-gel method; the gel was calcinated at 500 - 800°C for 2 hours. The presence of rhombohedra phase of CoTiO₃ in clay matrix was confirmed by XRD, FTIR, SEM. Cobalt titanate-clay nano-composites were prepared with 5-20% (w/w) by sol-gel method. The spectra results were investigated at 20% (w/w) concentration. The optimum condition for nano-composite preparation in 20 % (w/w) at 600°C is obtained.

Keywords: CoTiO₃ Clay, Nanocomposite, Sol-gel method, X-ray diffraction, SEM, FT-IR

1. Introduction

Nano-composite materials have recently been studied extensively because of their application potentials, such as in the manufacture of high density magnetic recording media, ferrofluids and catalysts [1-6]. Various techniques, such as vapor deposition [7], RF sputtering [8], reducing from metal oxide [9], hydrothermal precipitation [10], sol-gel method [11, 12], etc., have been employed to prepare ultrafine particles. The sol-gel method appears attractive because of lowering the process temperature, high homogeneity and purity of resulting materials, possibility of various forming process [13].

The metal titanates based oxide including metals, such as nickel, cobalt, ferrite, Zinc, copper and lead are universally known as inorganic functional materials with wide applications.

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These compounds with ilmenite structure in rhombohedra system are important for chemical and electrical applications due to their weak magnetism and semiconductivity [14-17]. Clay minerals have found major industrial applications in the paper, ceramic, paint, plastic, rubber and cracking catalyst industries [18]. The layers of kaolinite are built of only a sheet of silicon, tetrahedrally bonded to oxygen atoms and a sheet of aluminum octahedrally bonded to oxygen atoms and hydroxyl groups. As a consequence, the aluminum side of the layer is covered in hydroxyl groups (aluminum) and one third of the octahedrons are vacant in order to maintain a neutral sheet (di-octahedral). The silicon side is covered in oxygen atoms (siloxane surface) and the same distorted hexagonal cavity present in the 1:2 group, is observed [19].

In the present investigation, CoTiO₃ Nano-particles and a series of CoTiO₃-clay nano-composites were synthesized via sol-gel method. The results revealed that the sol-gel process is the most effective in comparison with hydrothermal method.

2. Materials and methods

2.1. Chemicals

The chemicals used in this study were titanium (IV) n-butoxide as a titanium source, cobalt acetate as a cobalt source, stearic acid as a complexation reagent from Merck Co., with high purity. Clay was obtained from Iranian mineral as natural kaolinite source. Mineral analysis and chemical composition are shown in (0.25, 0.5, 0.75 micrometer mesh, cation exchange capacity (CEC) = 7.478meq/100gr clay, pH= 8.70).

2.2. Cobalt titanate nanoparticles and CoTiO₃ clay composite preparation

Cobalt titanate nano-particles and CoTiO₃/clay nano-composites were prepared by the sol-gel method. In this procedure, cobalt acetate was added to the melted stearic acid and dissolved to form a dark blue transparent solution. Then, titanium (IV) n-butoxide was added to the solution, stirring to form a homogenous light red-brown sol (suspension A) naturally, cooling down to room temperature and drying in oven at 120 °C for 24 hours. Then, the dried gel was calcinated at 600 °C for 2 hours in atmospheric furnace with programmable temperature adjustment. For composite preparation, clay added to suspension A (was prepared again). The mixture was refluxed at 70°C and stirring for 4 hrs until sol phase would be obtained. The sol was dried in oven at 100°C overnight followed by calcinations at 500, 600, 700 and 800 °C for 2 hours with 5 °C/min rate.

2.3. Characterization

Phase identification and crystallite size of the cobalt titanate-clay nano-composites were characterized by X-ray diffraction (XRD) obtained on Philips X-pert diffract meter using a scan rate 2 °/min and Cu K α line radiation in the range from 5° to 70° (2 θ). The crystallite size of the powders was determined by Scherer equation. The morphology of the product was studied by scanning electron microscopy (SEM. Philips XL30). The Fourier transform infrared spectroscopy (FTIR) analysis was performed using a Brokers- Tensor 27.

3. Results and discussion

The diffraction patterns of the pure natural clay (a) and nano-crystalline cobalt titanate powder (b) are shown in (Figure 1). For the clay, it is well recognized that (001) basal reflections are important for structure interpretation. The clay gives a strong (002) reflection at 12.43° (2θ). In addition, there are three (001), (003) and (004) reflections at 6.22 , 18.73 and 25.09° (2θ) (Figure 1).

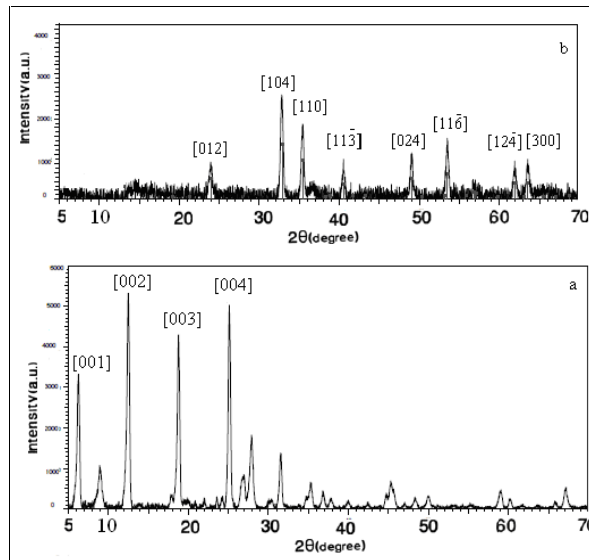


Fig.1. XRD patterns for clay (a) and nanocrystalline CoTiO_3 powder calcined at 600°C (b).

Figure 1b shows the XRD patterns of the cobalt titanate powder. The nano-powders displayed a sharp and intense peaks indicating fine crystalline rhombohedra CoTiO_3 phase. All corresponding to rhombohedra phase matched well with database in JCPDS (file number 77-1373). The calculated lattice parameters by least square fit are $a=b=5.066 \text{ \AA}$, $c=13.918 \text{ \AA}$.

The particle size from Scherer's formula ($t=K \lambda/\beta \cos \theta_\beta$) that t is the average size of the particles, assuming particles are spherical, $K=0.9$, λ is the wavelength of X-ray radiation, β is the full width at half maximum of the diffracted peak and θ_β the angle of diffraction) is calculated about 25 nm .

Figure 2 shows the XRD patterns of the CoTiO_3 -clay composite after heat-treatment from 500 to 800°C for 2 hours in programmable temperature furnace. Figure 2a, show the characteristic peaks appeared at $2\theta = 32^\circ$, $2\theta = 35.35^\circ$ and confirm the presence of CoTiO_3 phase in nanocomposites. The existence of clay in XRD patterns is clearly evidenced from the presence of all peaks, with the formation of the nanocomposite at 600°C . The (002), (003) and (004) reflections of clay is not seen in XRD patterns. Further, by increasing the calcinations temperature up to 800°C the clay phases were decreased by increasing CoTiO_3 phase.

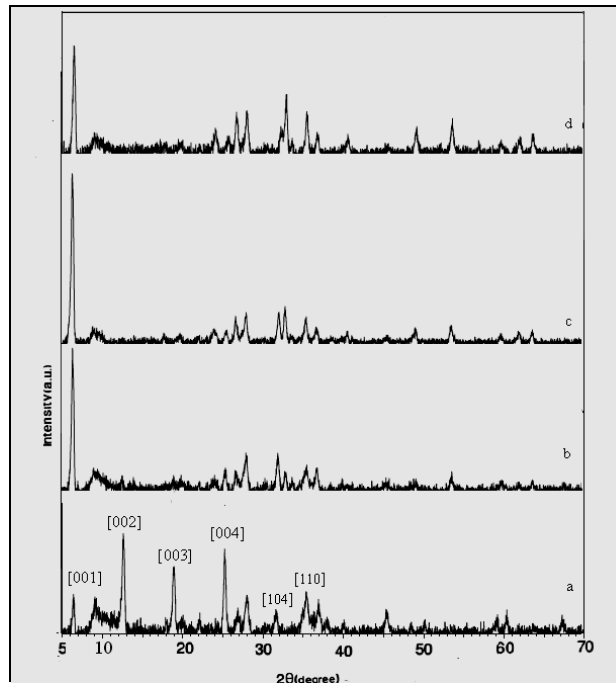


Fig.2. X-ray diffraction patterns of CoTiO₃-clay nanocomposite 20% (w/w) calcined (a) 500 °C; (b) 600 °C and (c) 700 °C 800 °C (d) for 2 h.

The FT-IR spectra of CoTiO₃ nanopowders and clay are shown in Figure 3 (a, b). In Figure 3a, the FTIR peaks of CoTiO₃ powders showed below 800 cm⁻¹ which are assigned to the Ti-O stretching vibration, and corresponding to the formation of cobalt titanate. In Figure 3b, the 3405.57 cm⁻¹ and 3548.27 cm⁻¹ absorption bands represent the vibration of OH structure and the bands at 760.91 cm⁻¹ comes from stretching vibration of Si-O-Al structure [20].

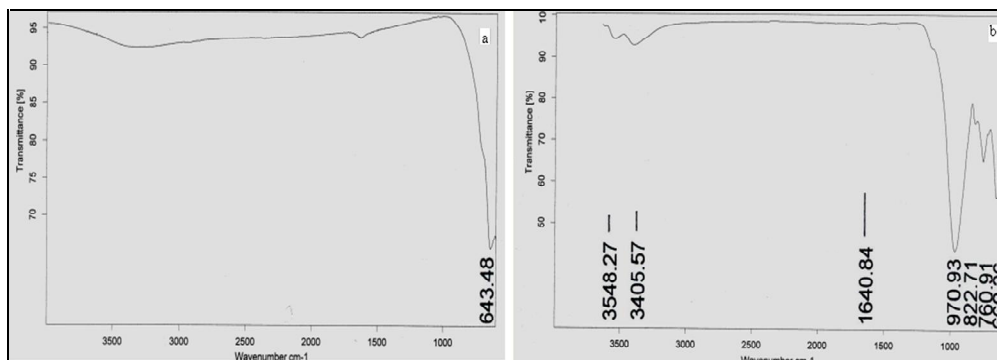


Fig.3. FTIR spectra of nano-crystalline CoTiO₃ powder (a) and clay (b)

Figure 4 shows the FTIR spectra for the CoTiO₃/clay nano-composites at different temperature. In comparison with clay spectra, one band is seen around the 947-981 cm⁻¹ that can be described to the stretching vibration of Ti-O-Si bridges [21]. The assignment of bands observed in the FTIR spectrum of clay, nano-particle and nanocomposites is presented in Table 2.

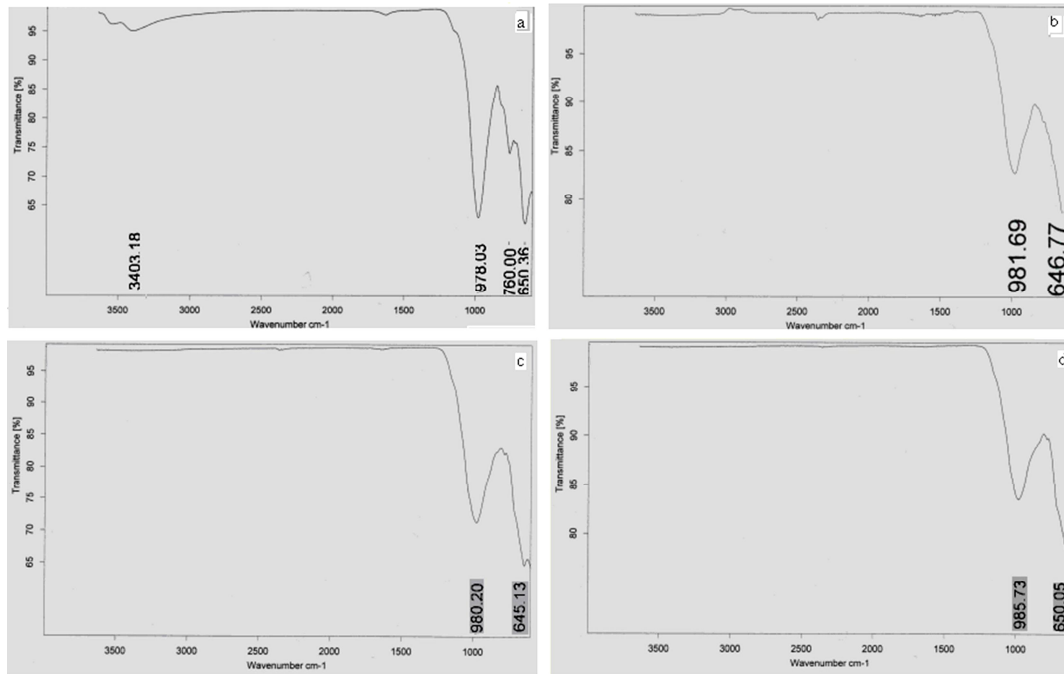


Fig.4. FTIR-spectra of CoTiO₃-clay nanocomposites calcinated at 500 °C (a), 600 °C (b), 700°C (c) and 800 °C for 2 hours in 20%

Table 2. Assignment of bands observed in FTIR spectrum

Nano-Particle		Clay		Nano composite			
Reference	Experimental	Reference	Experimental	500°C	600°C	700°C	800°C
Ti-O Stretch 570-800cm ⁻¹	Ti-O Stretch 643.48cm ⁻¹	Si-O, Si-O-Al Stretch 600-800cm ⁻¹	660.26cm ⁻¹ 670.91cm ⁻¹	650.36cm ⁻¹ 760cm ⁻¹	646.77 cm ⁻¹	645.13 cm ⁻¹	650.05 cm ⁻¹
		Si-O, Si-O-Al Si-O-Si Stretch 900cm ⁻¹ 1700cm ⁻¹	970.93cm ⁻¹ 1640.84cm ⁻¹	978.03 cm ⁻¹	981.69 cm ⁻¹	980.20 cm ⁻¹	985.73 cm ⁻¹
		OH 3600cm ⁻¹ 3700cm ⁻¹	3405.57cm ⁻¹ 3548.27cm ⁻¹	3403.18 cm ⁻¹			

Figure 5 shows the typical SEM images of CoTiO₃-clay nano-composites. SEM observation of cobalt titanate powder indicates the nano-crystalline nature of particles is spherical. The nano-particles size is between 20-60 nm, these are agree with the result of XRD.

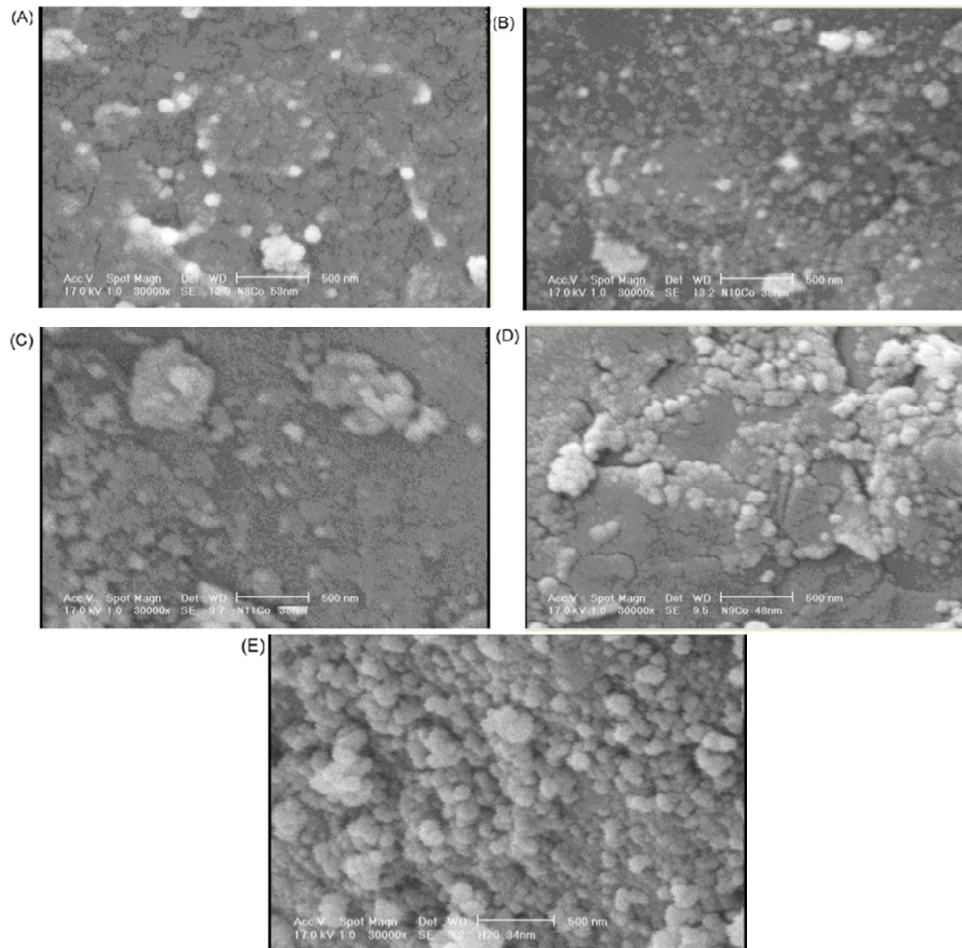


Fig. 5. SEM results of CoTiO₃/clay nano-composites calcinated at 500 °C (A) 600 °C (B) 700 °C (C), 800 °C (D) and CoTiO₃ nano-powder 600 °C (E) for 2 hours with 20%.

The SEM results show that all composites have agglomerated grain structure and the particle size of the samples by increasing of calcinations temperatures.

4. Conclusion

Nano-sized CoTiO₃ and a series of CoTiO₃-clay nanocomposites were synthesized via sol-gel process. In the prepared nanoparticle, the formation of rhombohedra cobalt titanate phase confirmed by X-ray diffraction. The SEM observation of CoTiO₃ powder indicates the nanocrystalline nature of particles is spherical and the nanoparticle size is between 20-60 nm, these are in agree with the result of XRD. X-ray diffraction patterns showed the presence and growth of CoTiO₃ nanoparticles in kaolinite. In the CoTiO₃-clay composites, CoTiO₃ nanocrystals are highly dispersed in the amorphous kaolinite matrix and Formation of Ti-O-Si bonds has been proved by FTIR spectra. In the SEM photograph, we observe the intercalation of nano-particle between the clay layers. It can be deduced from the results that the calcinations temperature govern on morphology, size and structure of the CoTiO₃ nanoparticles dispersed in kaolinite matrix. Finally the optimal heat treatment was at 600°C.

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