

## **Effect of annealing time and annealing atmosphere on infrared emissivity property of $Zn_{1-x}Co_xO$ by solid state reaction**

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**Keywords:** Infrared emissivity; annealing time; annealing atmosphere; Co-doped ZnO

### **Abstract**

The  $Zn_{1-x}Co_xO$  powders were synthesized by solid-state reaction at different annealing time and annealing atmosphere. The effects of annealing time and annealing atmosphere on the structure, morphologies and infrared emissivities have been investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-visible absorption spectroscopy and IR-2 dual-band infrared emissometer. The results indicate that the  $Zn_{1-x}Co_xO$  samples have hexagonal wurtzite structure while the peaks of the secondary phase, Co, were observed when sintering at  $N_2$  atmosphere. The annealing time and annealing atmosphere have important impacts on the microstructure and the infrared radiation properties of  $Zn_{1-x}Co_xO$  nanopowders. UV-visible absorption spectra showed that Co ions substituted the Zn ions in the ZnO lattices. And the infrared emissivity depends on the microstructure, grain size and lattice vibration.

### **Introduction**

Zinc oxide has wide band gap energy (3.3 eV) at room temperature and high excitonic binding energy (60 meV) [1]. As an important n-type semiconductor material, ZnO has received extensive attention because of its remarkable optical, magnetic, and electrical properties [2-3]. The doping of transition metal elements is one of the most important methods to modify the electronic structure and characteristics of the host material [4-5]. Among all of the transition metals, Co has been frequently employed because of its variable oxidation state, large magnetic and high solubility limit in ZnO. In the past several years, many studies in Co-doped ZnO are focused on its magnetic properties [6-7], however, the properties of variable emissivity are neglected. Nevertheless, the properties of emissivity have different applications in different fields. The materials with low infrared emissivity (LIE) materials can decrease the probability for the military equipment being detected by infrared detector [8-9]. High emissivity in high temperature can be used in furnaces lining, supersonic aircraft and other fields, to save energy or to decrease the temperature by radiation [10]. The variable emissivity coatings have great application prospects to spacecraft thermal control [11].

In this paper, we conducted a simple solid-state reaction to synthesize  $Zn_{1-x}Co_xO$  nanopowders successfully and studied the influence of annealing time and annealing atmosphere on the crystal structures, morphologies as well as infrared emissivity.

### **Experimental details**

The doped oxides  $Zn_{1-x}Co_xO$  were prepared by solid-state reaction. Raw ZnO powders (9.798g) and  $Co_3O_4$  powders (0.202g) were mixed before calcination. This mixture was gently ground in an agate mortar for homogenisation.

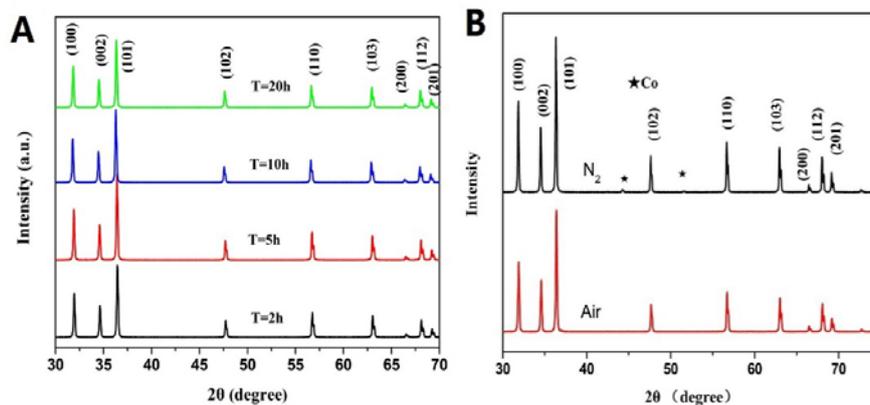
The obtained powders were annealed at 1000 °C in air for different hours (2h, 5h, 10h and 20h, respectively) and anneal at 900 °C for 2h under dynamic nitrogen and air atmosphere respectively, with a heating rate of 4 °C/min until reach the annealing temperature. After annealed, the powders were allowed to cool to room temperature gradually in furnace. Finally, the pre-treated  $Zn_{1-x}Co_xO$

powders with different annealing time and atmosphere were obtained.

The crystalline phases of the  $Zn_{1-x}Co_xO$  powders were examined by x-ray diffraction using  $CuK\alpha$  radiation (XRD Rigaku, D/max-RA) from  $20^\circ$  to  $80^\circ$  ( $2\theta$ ). The microstructures of samples were observed by scanning electron microscopy (SEM, FEI SIRION-100). The absorption spectrum was recorded by a Shimadzu 2450 UV-VIS spectrophotometer and the investigated wavelength ranged from 200 to 800 nm. The infrared emissivity in the range of 3–5  $\mu m$  in different temperature was detected by an infrared emissometer (IR-2 dual-band emissometer, Shanghai Institute of Technical Physics, CAS, China).

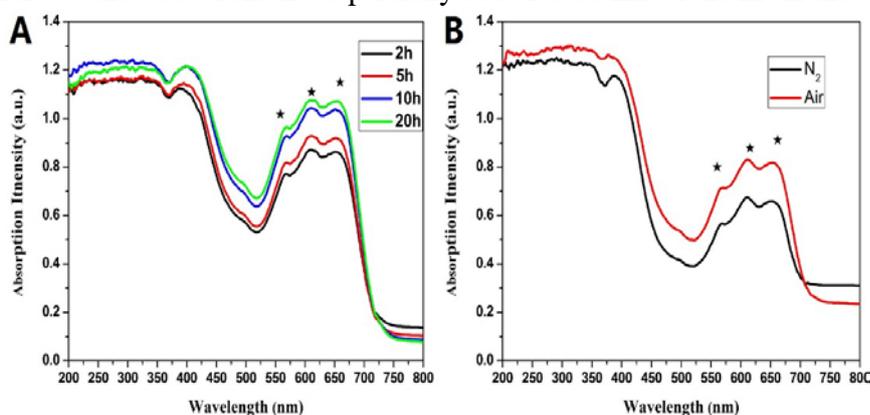
## Results and discussion

**X-ray diffraction spectrums (XRD).** The XRD spectrums of  $Zn_{1-x}Co_xO$  nanoparticles are shown in Fig.2. As can be seen in Fig.2, the diffraction peaks match well with the standard values of pure ZnO (JCPDS card no.36-1451). It indicates that all samples possess a wurtzite (hexagonal) zincite crystal structure with a more preferential orientation along the c-axis perpendicular. However, a small amount of impurity peaks or secondary phase of Co are observed when the samples anneal in  $N_2$  in Fig. 2 (B). This is because that  $Co_2O_3$  could be reduced to cobalt in nitrogen atmosphere at a high temperature.



**Fig. 1.** XRD patterns of  $Zn_{1-x}Co_xO$  nanoparticles. **A**, annealed at  $1000^\circ C$  in air for 2h, 5h, 10h, 20h; **B**, annealed at  $900^\circ C$  for 2h in air and  $N_2$ , respectively.

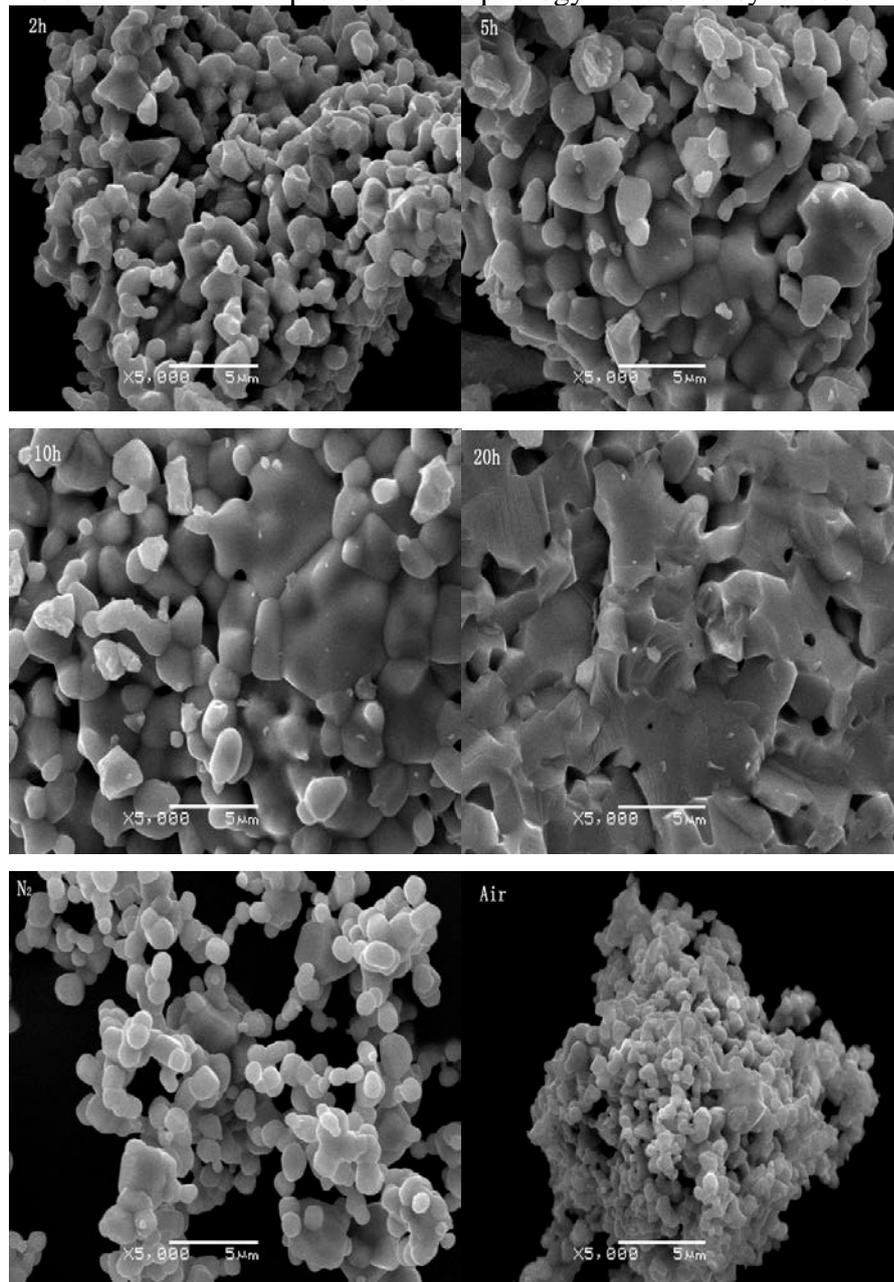
**UV-vis absorption spectra.** Fig.2 exhibits UV-vis absorption spectra of  $Zn_{1-x}Co_xO$  powders. The absorption coefficient in visible light region increases with the increasing of annealing time as shown in Fig.2 (A) and the absorption coefficient of samples annealed in air is larger than that of annealed in  $N_2$  as shown in Fig.2 (B). There are three absorption peaks at 565 nm, 610 nm, and 660 nm can be observed. These absorptions are attributed to the d–d transitions of the  $Co^{2+}$  ions. These absorption peaks indicate that  $Co^{2+}$  ions have partially substituted  $Zn^{2+}$  ions in all the samples [12].



**Fig.2.** UV-visible absorption spectra  $Zn_{1-x}Co_xO$  nanoparticles. **A**, annealed at  $1000^\circ C$  in air for 2h, 5h, 10h, 20h; **B**, annealed at  $900^\circ C$  for 2h in air and  $N_2$ , respectively.

**Scanning electron microscopy (SEM).** Fig.3 shows the morphology of  $Zn_{1-x}Co_xO$  at various

annealing time and atmosphere with the same magnification. From the SEM image of the  $Zn_{1-x}Co_xO$  powders with different annealing time, it can be observed that the samples consist of spherical particles and construct a loosely porous structure when the annealing time is 2h, the grain size of powders appears to increase and gradually merge into each other with the increasing of annealing time, and the block grains are formed when the annealing time reaches 20h. It is believed that the increasing of grain size is due to the effects of the liquid phase sintering process. And the liquid phase helps facilitate ion diffusion and enhances the grain growth mechanism during sintering process [13]. The grain growing up could bring about the loss of specific surface area. It is obvious that grains are spherical and porosity when annealed in  $N_2$  while the particles are irregular and close together when annealed in air. The SEM implies that the annealing time and atmosphere plays an important role in the technical process of morphology-controlled synthesis.

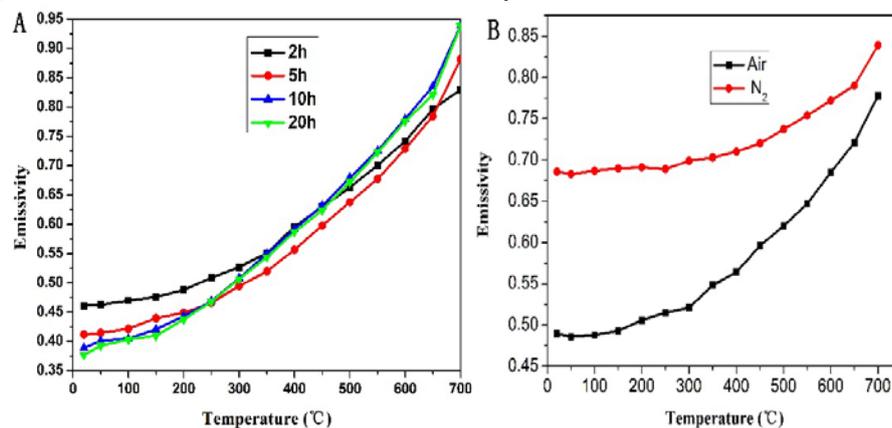


**Fig.3.** SEM image of the  $Zn_{1-x}Co_xO$  powders with different annealing time and different annealing atmosphere.

**Infrared emissivity analysis.** Fig. 4 shows the emissivity values at the wavelength of 3-5 $\mu$ m of all the  $Zn_{1-x}Co_xO$  samples at various test temperatures from 20 °C to 700 °C, with an interval of 50 °C. It can be seen that, the infrared emissivity of all the  $Zn_{1-x}Co_xO$  samples increase with the increasing of test temperature. The infrared radiation of the materials in 3 ~ 5 $\mu$ m band is mainly related to the

electronic transition behavior within of the crystal. As is known to all, rotation and vibration of molecules and atoms would increase with the increasing of test temperature. These changes could enhance the lattice vibrational absorption, and accordingly result in the enhancement of the infrared emissivity.

Form the Fig.4 (A), it can be seen that, the infrared emissivity decrease with the increasing of annealing time from 2h to 20h when at room temperature 20 °C. This phenomenon may be caused by different morphology. Nanoparticles with large specific surface area such as sphericity could enhance the infrared radiation absorption [14]. When the sample is loosely porous spherical structure loosely particles, most of the infrared radiation would have been absorbed and only little radiation can be reflected. When the grain size of powders appears to increase and gradually merge into each other with the increasing of annealing time, and the block grains are formed. The infrared radiation absorption decreases and infrared reflection increases and consequently result in a lower emissivity. This can also explain why the infrared emissivity of samples annealed in N<sub>2</sub> is higher than that of annealed in air. Besides, when the test temperatures from 20 °C to 700 °C, the changes of infrared emissivity at annealing time of 2h, 5h, 10h and 20h is about 0.369, 0.470, 0.551 and 0.562, respectively, which indicate that the changing rates of infrared emissivity has increased with the increasing of annealing time. When the samples annealed in air, the changing rates of infrared emissivity is larger than that of annealed in N<sub>2</sub> obviously.



**Fig.4.** Infrared emissivity values of Zn<sub>1-x</sub>Co<sub>x</sub>O samples. **A**, annealed at 1000 °C in air for 2h, 5h, 10h, 20h; **B**, annealed at 900 °C for 2h in air and N<sub>2</sub>, respectively.

## Conclusions

In summary, the Zn<sub>1-x</sub>Co<sub>x</sub>O powders were prepared by solid-state reaction. The Zn<sub>1-x</sub>Co<sub>x</sub>O samples have hexagonal wurtzite structure while the peaks of the secondary phase, Co, were observed when sintering at N<sub>2</sub> atmosphere. The annealing time and annealing atmosphere have important impacts on the microstructure of Zn<sub>1-x</sub>Co<sub>x</sub>O nanopowders. UV-visible absorption spectra proved that Co ions exist in a tetrahedral crystal field in the +2 state without destroying the wurzite crystal structure of ZnO. Loosely porous spherical particles could lead to higher emissivity while block grains lose together could lead to lower emissivity. In addition, the changing rates of infrared emissivity has increased with the increasing of annealing time. When the samples annealed in air, the changing rates of infrared emissivity is larger than that of annealed in N<sub>2</sub>. The Zn<sub>1-x</sub>Co<sub>x</sub>O powders as a novel kind of variable emissivity material may have great potential applications in spacecraft thermal control.

## Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (Grant Nos: 51403102), the Natural Science Foundation of Jiangsu Province, China (Grant Nos: BK20140811), Fundamental Research Funds for the Center Universities (Grant Nos: NS2014058)

and a Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

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