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Synthesis and Properties of Nano-Perovskite $Mg_{0.5}Nd_{0.5}CoO_3$ by Co-Precipitation Technique

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The nano-perovskite $Mg_{0.5}Nd_{0.5}CoO_3$was prepared by co-precipitation technique using $Nd(NO_3)_3·6H_2O$, $Mg(NO_3)_2·6H_2O$ and $Co(NO_3)_3·6H_2O$ as main raw materials and the effects of calcination temperatures on the lattice parameters, particle sizes and micro stress of the perovskite were studied by X-ray diffraction and transmission electron microscopy. The results show that the $Mg_{0.5}Nd_{0.5}CoO_3$ have formed after calcination at 700 °C and the finishing temperatures of synthesizing perovskites is at 800 °C. After calcination at 800 °C, the lattice parameter of the perovskites $Mg_{0.5}Nd_{0.5}CoO_3$ is 7.54367 Å and the average sizes is 17.5 nm. The lattice parameter and the average sizes of the perovskite have declining trends with increasing temperatures, but the average sizes of the perovskite maintain almost unchanged with increasing temperatures and there is no micro stress in the perovskite. The average lattice parameters of the perovskite $Mg_{0.5}Nd_{0.5}CoO_3$ is lower than the lattice parameter of the perovskite $NdCoO_3$.

Keywords: Perovskite, Nanoparticles, Co-precipitation, X-ray diffraction.

INTRODUCTION

The general chemical formula of perovskite oxide materials is ABO_3, where A site, on the corners of the lattice, is usually an alkaline earth metal or rare earth elements; B site, on the center of the lattice, could be transition metal elements. If the values of tolerance factor t [$t = (R_A + R_O)/(2^{0.5} (R_B + R_O)]$, where R_A, R_B and R_O represent the effective ionic radii of A and B site elements and oxygen, respectively] is in the range of 0.75-1.00, many metallic elements are stable in the perovskite structure[1-3]. Due to huge variety in composition and structure, the perovskite materials exhibit a lot of interesting physical, chemical and catalytic properties and become research hotspots in the field of materials chemistry, solid-state chemistry and physics[4]. Researchers have studied the pyroelectricity[5-8], sensitivity[9-11], catalytic[3,10,12], superconductivity[13], magnetism[14,15] and the effects of dopant on properties of perovskite to use as advanced functional materials[16,17], such as electrode materials, chemical sensors, oxygen-permeating membranes, thermoelectric devices and catalyst, *etc.*[18-20].

There are many factors to influence the properties of perovskite. One of the main factors is doping effects on the A site of the perovskite, dopant on the A site can change the average ionic radius on this site and introduce defects for charge compensation, further influence the properties and applications of perovskite[21]. Another main factors are the particle sizes and lattice parameters. In this work, we induce Mg ion on the A site of perovskite $NdCoO_3$ to prepare perovskites $Mg_{0.5}Nd_{0.5}CoO_3$ and investigate that the effects of calcination temperatures on the lattice parameters, particle sizes and micro stress of perovskite $Mg_{0.5}Nd_{0.5}CoO_3$.

EXPERIMENTAL

In the experiments, we used chemical pure $Nd(NO_3)_3·6H_2O$, $Mg(NO_3)_2·6H_2O$ and $Co(NO_3)_3·6H_2O$ as main raw materials.

Precursors $Mg_{0.5}Nd_{0.5}CoO_3$ was prepared from the mixed of $Nd(NO_3)_3$, $Mg(NO_3)_2$ and $Co(NO_3)_3$ solutions by co-precipitation technique. The synthesis process is as follows: (1) starting solutions of $Co(NO_3)_3$ (0.005 mol L^{-1}), $Mg(NO_3)_2$ (0.005 mol L^{-1}) and $Nd(NO_3)_3$ (0.005 mol L^{-1}) were prepared by dissolving a certain amount of $Nd(NO_3)_3·6H_2O$, $Mg(NO_3)_2·6H_2O$ and $Co(NO_3)_3·6H_2O$ in deionized water, respectively. (2) 100 mL of $Co(NO_3)_3$, 50 mL of $Mg(NO_3)_2$ and 50 mL of the $Nd(NO_3)_3$ solutions basing on the required stoichiometric amounts of $Mg_{0.5}Nd_{0.5}CoO_3$ were mixed in a bottom flask and stirred for 0.5 h. (3) 1 M solution of $NaOH/Na_2CO_3$ (molar ratio of 1/1) was added dropwise to the flask until pH reached 9.5-10 under intense stirring. The residue was repeatedly filtered out and washed several times by using deionized water in order to ensure pH = 7 and then washed three times by ethyl alcohol and dried at 100 °C for 24 h in an oven. (4) Precursors $Mg_{0.5}Nd_{0.5}CoO_3$

were calcined at 500, 600, 700, 800, 900 and 1000 °C for 3 h with heating rate of 4 °C min^{-1} in a furnace and then gradually cooled to room temperature in the furnace to gain the calcined samples.

Phase composition and microstructure: The phase composition, grain sizes, micro stress and lattice parameters of the calcined samples were analyzed by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

RESULTS AND DISCUSSION

Calcination experiments: The XRD patterns of precursors $Mg_{0.5}Nd_{0.5}CoO_3$ after calcination at 500-1000 °C is shown in Fig. 1. Fig. 1 showed that there is no formation of perovskite $Mg_{0.5}Nd_{0.5}CoO_3$ after calcination at 500 °C. But after analysis of XRD patterns, we know that the amorphous $Mg_{0.5}Nd_{0.5}CoO_3$ phase appears after calcination at 600 °C and a mass of cubic type perovskite $Mg_{0.5}Nd_{0.5}CoO_3$ (Reference code: 00-025-1064) have formed after calcination at 700 °C. After calcinations at 900 and 1000 °C, we find that the crystal phase is also perovskite and there is not any new diffraction peaks and characteristic peak (220) intensity of perovskite maintains almost the same. The results indicate that crystalline perovskite phase has formed at 700 °C and the formation of perovskite has finished after calcination at 800 °C.

Lattice parameters: The relationship among interplanar distance, Miller indices and lattice parameters of the perovskite with cubic structure can be expressed as follows:

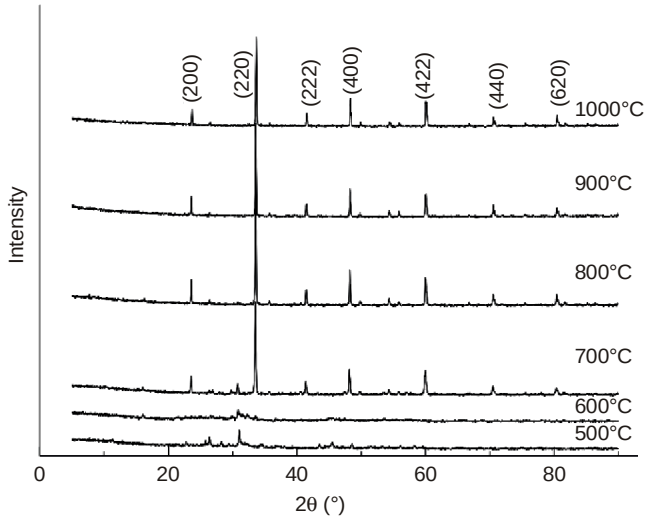

Fig. 1. XRD patterns of precursors $Mg_{0.5}Nd_{0.5}CoO_3$ after calcination at 500-1000 °C

$$(1/d_{hkl})^2 = (h^2 + h^2 + l^2)/a^2 \quad (1)$$

where h, k and l are Miller indices of crystal planes (hkl); d_{hkl} is the interplanar distance (Å); a is the lattice parameter (Å).

In order to decrease the error, we choose high angle Miller indices (620), (440) and (422) to calculate lattice parameters. Results show that the average lattice parameters of the perovskite are 7.54367, 7.54217 and 7.54103 Å at 800, 900 and 1000 °C, respectively. It indicates that the lattice parameters of the perovskite appears a little decrease with increasing temperatures. As is well known, higher heat treatment temperature has great influence on the formation of perovskite, crystallinity and densification process of the synthesized materials before over-sintering will be improved with increasing temperature, then the synthesized materials tend to undergo a series of transitions to progressively higher symmetry and stability[22,23]. So the lattice parameters of the perovskite appear a little decrease with increase of calcination temperatures. At the same time, the rusults show that the values of the average lattice parameters is lower than the lattice parameter (7.5460 Å) of the perovskite $NdCoO_3$ (Reference code: 00-025-1064). It is because that the Mg^{2+} ion radius (about 65 pm) lower than that of Nd^{3+} ion radius (about 99.5 pm).

Sizes and micro stress: From the Fig. 1, we find that the characteristic of XRD patterns fit well with Gaussian distribution. So we can gain the average particle sizes and micro strain of the synthesized perovskite according to the eqn. 2. In order to decrease the effect of error on the particle sizes, we choose low angle Miller indices (200), (220), (222) and (400) peaks of the perovskite to calculate the particle sizes. First, we can get Bragg angles (θ) and full width at the half maximum (B) of the diffraction peaks from the XRD patterns of the perovskite synthesized at 800-1000 °C, then gain the physical width (β) basing on the $\beta = (B\text{-}b)^{0.5}$ (where b is the intrinsic width of the instrument, about 0.075 nm). Subsequently, we can draw the relationship line between $(\sin\theta/\lambda)^2$ and $(\beta \cos\theta/\lambda)^2$ (Fig. 2), and then gain the intercepts $(1/L^2)$ from the figure, further calculate that the average particle sizes are 17.5, 17.3 and 18.2 nm at 800, 900 and 1000 °C, respectively. Results indicate that the average particle sizes of the perovskite are very small and the average particle sizes maintain almost unchanged with increasing temperatures. In addition, from the negative value $(16\varepsilon^2)$ of the slope we know that there is no micro strain in the perovskites. So we know that here is no micro stress (ρ) in the perovskite basing on the equation $\rho = E\varepsilon$ (where E is the modulus of elasticity).

$$(\beta \cos\theta/\lambda)^2 = 1/L^2 + 16\varepsilon^2 (\sin\theta/\lambda)^2 \quad (2)$$

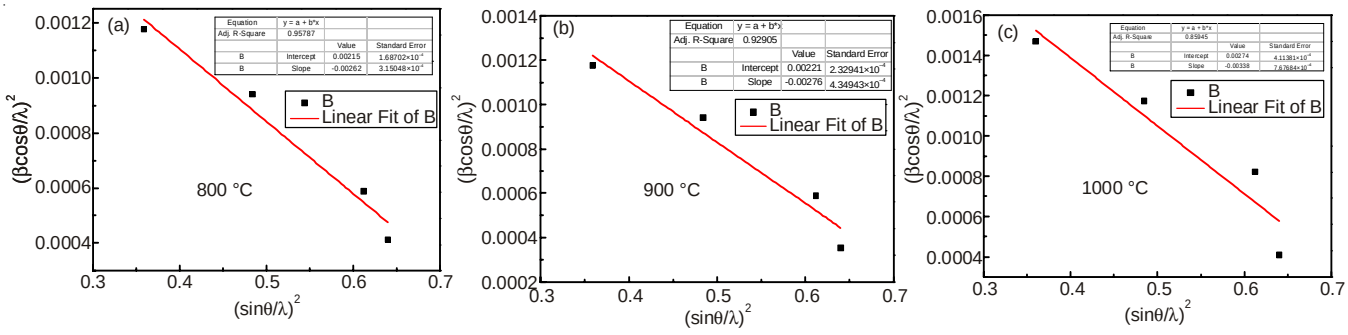

Fig. 2. Relationships between $(\sin\theta/\lambda)^2$ and $(\beta\cos\theta/\lambda)^2$ about the perovskite synthesized at 800, 900 and 1000 °C

where θ = Bragg angle (rad); β = physical width of diffraction peak (rad); λ = wavelength of diffraction (0.154056 nm); L = average particle size (nm); ε = microstrain (%).

Fig. 3 shows the typical TEM micrograph of the perovskite $Mg_{0.5}Nd_{0.5}CoO_3$ obtained after calcination at 800 °C. From the figure we know that the most sizes of the perovskite are in the range of 120-200 nm. The particle sizes of perovskite watched by TEM is larger than the average size of 17.5 nm gained by XRD measurement. It indicates that the particle sizes watched by TEM micrograph is not a single crystal, but is composed of agglomerate nano-crystallites.

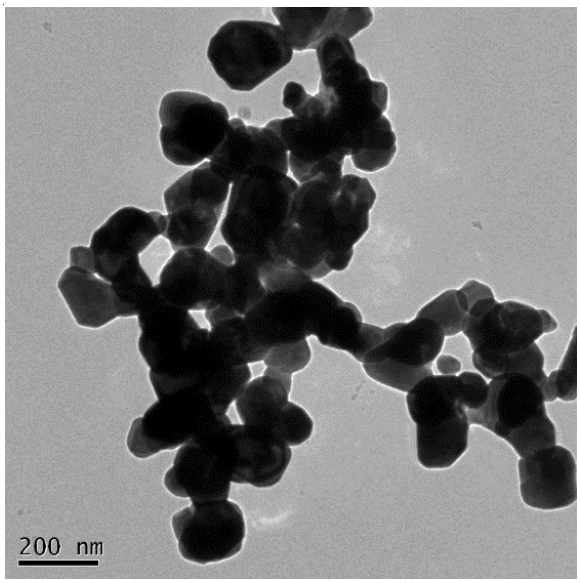

Fig. 3. TEM micrograph of the perovskite $Mg_{0.5}Nd_{0.5}CoO_3$ obtained after calcination at 800 °C

Conclusions

• The nano-perovskite $Mg_{0.5}Nd_{0.5}CoO_3$ can be synthesized by co-precipitation technique. The perovskite $Mg_{0.5}Nd_{0.5}CoO_3$ has formed after calcination at 700 °C and the finishing temperatures of synthesizing the perovskite is at 800 °C.

• After calcination at 800 °C, the average lattice parameters of the perovskite is 7.54103 Å and the average particle sizes of the perovskite is 17.5 nm.

• The lattice parameters of perovskite $Mg_{0.5}Nd_{0.5}CoO_3$ have a little decrease with increase of calcination temperatures, but the average particle sizes of perovskite $Mg_{0.5}Nd_{0.5}CoO_3$ maintain almost unchanged with increasing temperatures and there is no microstress in the perovskite. The average lattice parameters of perovskite $Mg_{0.5}Nd_{0.5}CoO_3$ is lower than the lattice parameter of perovskite $NdCoO_3$.

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