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The Preparation of Cu - doped $Ca_3Co_4O_9$ Thermoelectric Materials

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Abstract. In this paper, $CaCO_3$, CoO, CuO as raw materials, using solid phase preparation of $Ca_3Co_4O_9$-based thermoelectric materials doping Cu. The $Ca_3Co_4O_9$-based thermoelectric material intermediates were prepared according to the stoichiometric ratio x=0.01, and the sintered crystals were prepared by using muffle furnace under different temperature setting conditions. X-ray diffraction (XRD) and Scanning electron microscopy (SEM) were used to analyze the crystallinity and morphology of the samples after sintering. The results show that the crystallinity of $Ca_3Co_4O_9$-based thermoelectric materials is best when sintered at 800-850℃, and the crystallinity of samples sintered at 850℃ is better than that at 800℃, The diffraction intensity ratio is stronger than 800℃.Continue to raise the temperature, $Ca_3Co_4O_9$-based thermoelectric materials phase transition to $Ca_3Co_2O_6$-based thermoelectric materials, When the sintering temperature is 1000℃, the product is Cu-doped $Ca_3Co_2O_6$-based thermoelectric materials.

1. Introduction

The thermoelectric material [1] is a functional material capable of converting thermal energy and electrical energy. With the increasing environmental problems, the energy crisis intensified. Oxide thermoelectric materials are a new type of thermoelectric materials [2]. In 1997, Japanese scholar Terasaki et al [3-4] discovered a single crystal transition metal oxide NaCo2O4 with abnormal thermoelectric properties during its research, thus breaking the understanding that oxides cannot be used as thermoelectric materials. Calcium cobaltite is a kind of oxide thermoelectric material, its structure and NaCo2O4 structure is similar, are layered structure, because the calcium cobalt oxide thermoelectric material in the work process of good oxidation resistance, thermal stability, non-toxic, thermoelectric superior performance and much attention [5-6]. The study of new thermoelectric materials has a strong practical significance in today's environmental pollution and energy crisis [7]. Thermoelectric materials have high economic value and can achieve the purpose of waste heat and waste heat recovery and utilization. It is an environment-friendly function material. In this paper, CaCO3, CoO, CuO as raw materials, the use of high temperature solid phase method, the successful synthesis of Cu doped Ca3Co4O9 thermoelectric materials. The crystallographic and surface morphology of the synthesized product were characterized by XRD and SEM.

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2. Experiment

The raw materials were CaCO3, CoO and CuO, and the mixture was transferred to the mortar according to the stoichiometric ratio of the doping amount x = 0.01, and the material was sintered for 15 min, The amount of the intermediate intermediate is substantially transferred to the crucible and sintered in a muffle furnace. The temperature of the sintering crystallization temperature in the muffle furnace is as follows:the time is 25℃ at room temperature; and the temperature is raised from room temperature to the maximum temperature of the calcined sample at 650℃ to 1000℃ for 120min, and calcined at 650℃ to1000℃ for 240min, The time required to cool to a room temperature of 25℃ from 1000℃ within120 min; and after the sample is cooled for 120 min, samples were taken from the muffle furnace. The structure of Cu-doped Ca3Co4O9 thermoelectric materials was analyzed by XRD. The microstructure of Cu-doped Ca3Co4O9 thermoelectric materials was analyzed by SEM.

3. Results and discussions

3.1. The XRD analysis of samples

Fig 1 shows the XRD patterns of Cu-Co-O thermoelectric materials doped with Cu. The graphs show the sample composition at different sintering temperatures. The XRD spectrum of Cu doped with x = 0.01 on the Ca-Co-O-based thermoelectric materials is analyzed. It can be found that when the sintering temperature is in the range of 650-850℃, the product is Cu-based Ca3Co4O9 material, when the temperature exceeds 900℃, Ca3Co4O9 began to decompose into Ca3Co2O6 thermoelectric materials.

Corresponding to the JCPDS (23-0110) spectrum, no other peaks appear. When the temperature was calcined at 800℃ for high temperature calcination, the composition was Ca3Co4O9 corresponding to the JCPDS (23-0110) spectrum. As can be seen from the figure, each peak is more dispersed, and the overall diffraction intensity is not strong. When the temperature was at 850℃, the composition was Ca3Co4O9 corresponding to the JCPDS (23-0110) spectrum. It can be seen that the diffraction strength of the sample sintered at 850℃ is stronger than the diffraction intensity of the sample sintered at 800℃, indicating that the sample has better crystallinity at 850℃, the optimum synthesis temperature of Ca3Co4O9 thermoelectric materials was 850℃. When the sintering temperature were 900℃ and 1000℃, the sample composition is Ca3Co2O6 corresponding to the JCPDS (51-0311) spectrum, indicating that the Ca3Co4O9 sample undergoes decomposition reaction with temperature, which also indicates that the best temperature of synthesizing Ca3Co4O9 thermoelectric materials was at 800℃-850℃with solid phase .And it can be seen from the figure that the diffraction intensity of Ca3Co2O6 is relatively high. When the sintering temperature is 900℃, several miscellaneous peaks appear in the XRD spectrum, and the corresponding product composition is not found corresponding to the Ca3Co2O6 standard. The results show that the hybrid peak is cobalt oxide (CoO). To investigate whether the oxide impurities at the higher temperature can be completely converted into Ca3Co2O6 thermoelectric materials, when the temperature was 1000℃. The results show that Ca3Co2O6 corresponding to the JCPDS (51-0311) spectrum. It can be seen from the spectrum that the diffraction curve does not appear at the peak of the XRD spectrum of the sample sintered at 900℃. All the diffraction peaks correspond to Ca3Co2O6 composition, which shows that the high temperature at 1000℃ The Ca3Co4O9 thermoelectric material has been completely transformed into Ca3Co2O6 thermoelectric material under sintering.

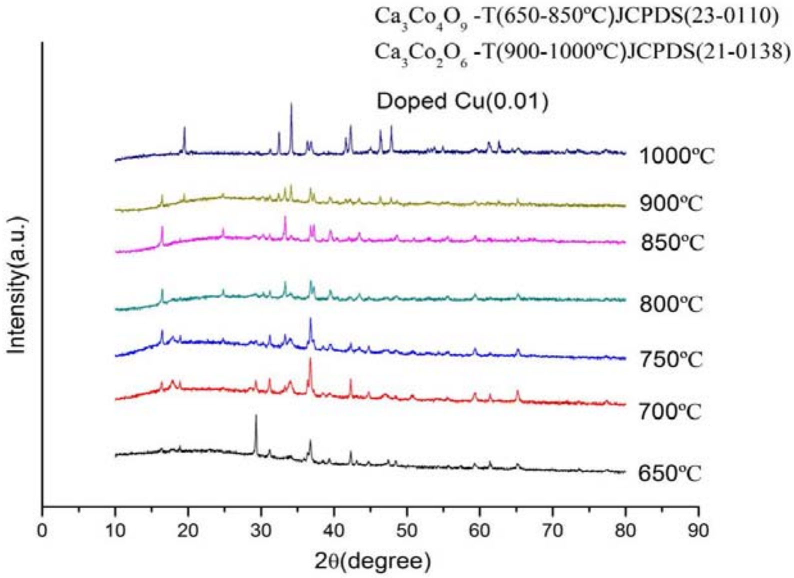
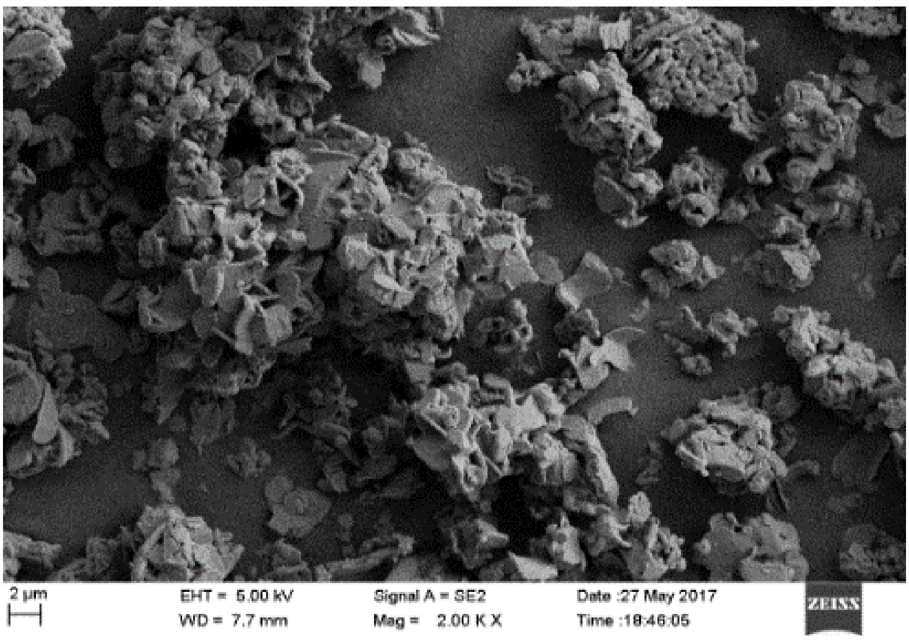


Figure 1. The XRD diffraction pattern of sample Ca3Co4O9

3.2. The SEM analysis of sample

Fig 2 (a, b) for the Cu-doped sample Ca3Co4O9 at different magnification of the SEM image, we can see from the figure the microscopic dimensions of the sample are micron level. Fig 2-a shows the morphology of the Ca3Co4O9 thermoelectric material obtained at a magnification of 2 k times. The image shows that the sample Ca3Co4O9 obtained at this magnification has a size of about 200 nm, a sheet shape and a large number of pores, Its lattice thermal conductivity is low, the thermoelectric value is higher. For a more clear observation of its morphology, the SEM magnification is further amplified to 10k times, as shown in Fig 2-b. After amplification, the sample size can be seen more clearly 200nm, for the uniform sheet structure, which shows that through the solid phase method can be synthesized homogeneous Ca3Co4O9 thermoelectric materials.



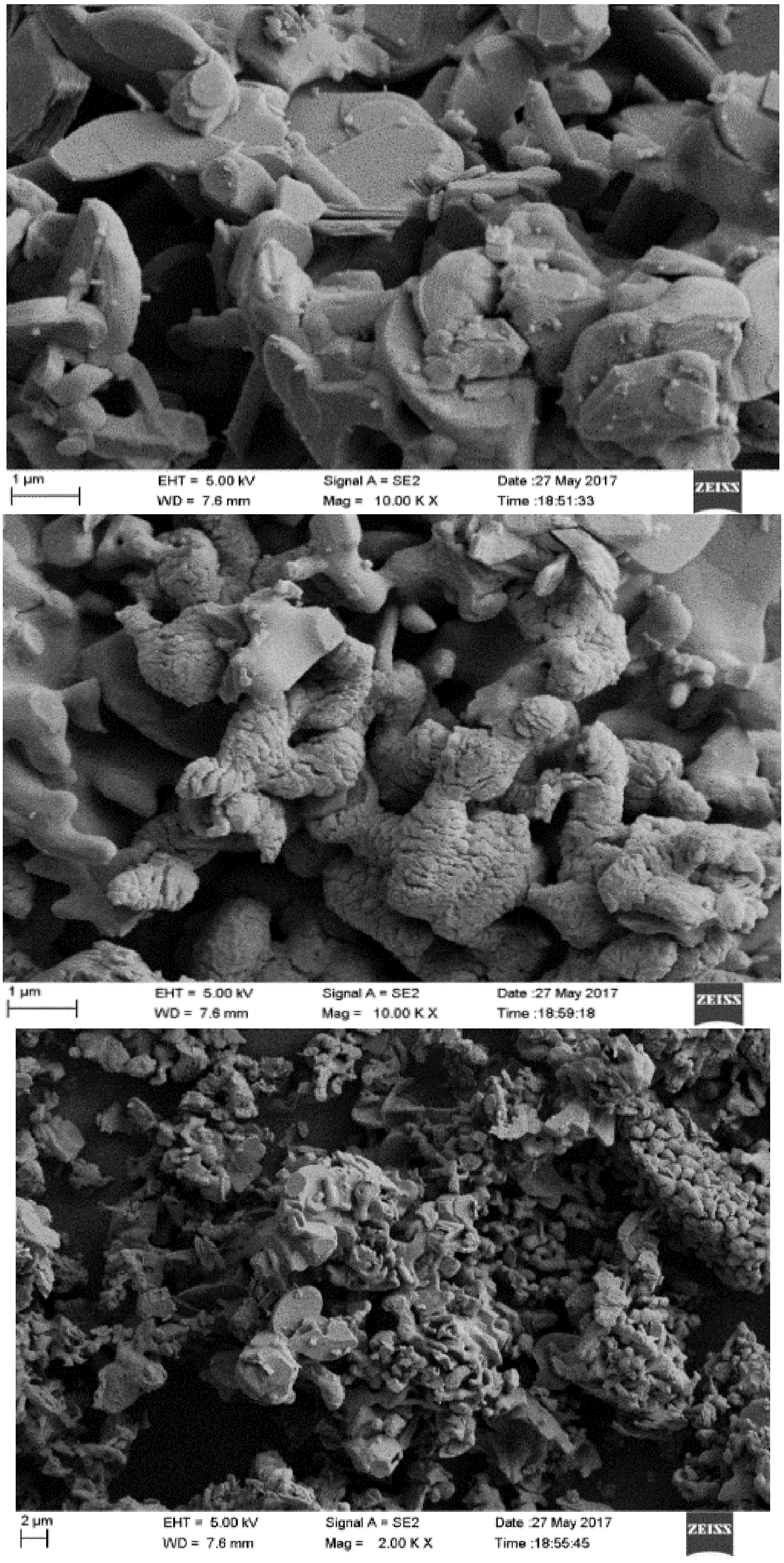


Figure 2. The SEM Spectrum of the sample Ca3Co4O9

4. Conclusion

In this paper, Cu-doped Ca3Co4O9 thermoelectric materials were synthesized by high temperature solid-state method. The results show that when the amount of Cu doping is x = 0.01, the optimum sintering temperature range is 800℃-850℃. When the sintering temperature is 850℃, the sintering temperature is 850℃ When the sintering temperature is 1000℃, Ca3Co4O9 is completely transformed into Ca3Co2O6, and the temperature of Ca3Co4O9 is changed to Ca3Co2O6. The sample obtained by sintering at the best sintering temperature of 850℃ is a sheet-like porous microstructure. When the temperature is raised to 900 ℃, the formation of the stacking phenomenon is caused by the transformation of Ca3Co4O9.

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