Synthesis of Ca₃Co₄O₉ and CuAlO₂ Ceramics of the Thermoelectric Application Using A Reaction- Sintering Process

Y. C. LIOU*, W. C. TSAI, W. Y. LIN and U. R. LEE

Department of Electronic Engineering, Kun Shan University, Tainan 71003, Taiwan, R.O.C.
*email: ycliou@mail.ksu.edu.tw

ABSTRACT

Synthesis of Ca₃Co₄O₉ and CuAlO₂ ceramics for thermoelectric application using a reaction-sintering process were investigated in this study. Without any calcination involved, the mixture of raw materials was pressed and sintered directly. Decomposition of Ca₃Co₄O₉ at 926°C limited a sintering temperature above 926°C. Ca₃Co₄O₉ formed as the major phase and some minor phases Co₃O₄, CaCO₃ and Ca₂Co₂O₅ were also found in Ca₃Co₄O₉. A maximum density value 2.46 g/cm³ was found at 900°C/6 h sintering. Very weak peaks of unreacted Al₂O₃ were detected in CuAlO₂. Density of CuAlO₂ ceramics reached a maximum value 4.1 g/cm³ at 1350°C/2 h. The reaction-sintering process has proven a simple and effective method in preparing Ca₃Co₄O₉ and CuAlO₂ ceramics for thermoelectric application.

KEYWORDS: Ca₃Co₄O₉, CuAlO₂, thermoelectric, reaction-sintering process

1. INTRODUCTION

It is well known that thermoelectric power generation could convert thermal energy directly to electrical energy via the Seebeck effect. The performance of thermoelectric materials can be evaluated by the figure of merit Z=S²σ/k, where S, σ, and k are the Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively. Increasing the temperature difference improves the conversion efficiency of the thermoelectric system. High temperature operation also raised conversion efficiency of thermoelectric system. Increasing attention has been put on oxide ceramics as thermoelectric materials because they are very suitable for long term use at high temperature in air.

Some oxide systems have been investigated, such as In₂O₃-MOₓ (M=Cr, Mn, Ni, Zn, Y, Nb, Sn) [1], NaCo₂O₄ was reported to have a high figure of merit ZT=1.04×10⁻⁴K⁻¹W⁻¹m⁻¹ at 1073K for single crystal and polycrystalline CuAlO₂, respectively [15]. Therefore, it is a promising material for thermoelectric energy conversion. Various methods have been tried to prepare the CuAlO₂ ceramics including the conventional solid-state reaction [16, 17], and ion exchange [18].

In previous studies, our group had prepared Pb(Mg₁/₃Nb₂/₃)O₃ (PMN) and Pb(Fe₁/₂Nb₁/₂)O₃ (PFN) ceramics via a simple and effective reaction-sintering process [19, 20]. PbO and Nb₂O₅ were mixed with Mg(NO₃)₂ or Fe(NO₃)₃ then pressed and sintered directly into PMN and PFN ceramics with the calcination step bypassed. These are the first successful synthesis of perovskite relaxor ferroelectric ceramics without having to go through the calcination step in the conventional solid state route or in the columbite/wolfamite route (two calcination steps were involved). PMN ceramics with a density 8.09 g/cm³ and dielectric constant 19,900 (1 kHz) were obtained. Other Pb-based complex perovskite ceramics were also produced by this reaction-sintering process successfully. In recent studies, some microwave dielectric ceramics such as BaTi₄O₁₂, Ba₅(Mg₁/₃Nb₂/₃)O₁₅, Sr₅(Nb₂O₇)₂, Ca₃Co₄O₉, CuAlO₂, and NiNb₂O₆ were also prepared successfully via this reaction-sintering process [21-25]. In this study, synthesis of Ca₃Co₄O₉ and CuAlO₂ ceramics using a reaction-sintering process were investigated.

2. EXPERIMENTAL PROCEDURES

All samples in this study were prepared from reagent-grade powders: CaCO₃ (99.9%), CoCO₃·xH₂O (99.9%), CuO (99%), and Al₂O₃ (99.5%). Appropriate amounts of raw materials for Ca₃Co₄O₉ and CuAlO₂ were milled in acetone with zirconia balls for 12 h separately. After they had been dried and pulverized, they were formed into pellets 12 mm in diameter and 2-3 mm thick. The pellets were then heated at a rate 10°C/min and sintered in a covered alumina crucible for 2-6 h in air at temperatures ranging between 850-900°C for Ca₃Co₄O₉...
Y. C. Liou, W. C. Tsai, W. Y. Lin, U. R. Lee

and 1200-1350°C for CuAlO₂. We analysed the sintered pellets using X-ray diffraction (XRD) to check the reflections of the phases. Microstructures were analysed using scanning electron microscopy (SEM). The density of the sintered pellets was measured using the Archimedes method.

![XRD patterns of Ca₃Co₄O₉ ceramics sintered at (A) 870°C and (B) 900°C for 2 h.](image1)

**Fig. 1** XRD patterns of Ca₃Co₄O₉ ceramics sintered at (A) 870°C and (B) 900°C for 2 h.

![SEM photos of as-fired Ca₃Co₄O₉ pellets sintered at 870°C for 2 h (A), 4 h (B), and 6 h (C); 900°C for 2 h (D), 4 h (E), and 6 h (F).](image2)

**Fig. 2** SEM photos of as-fired Ca₃Co₄O₉ pellets sintered at 870°C for 2 h (A), 4 h (B), and 6 h (C); 900°C for 2 h (D), 4 h (E), and 6 h (F).
3. RESULTS AND DISCUSSION

3.1 Ca$_3$Co$_4$O$_9$

Fig. 1 shows the XRD profiles of Ca$_3$Co$_4$O$_9$ ceramics sintered at 870°C and 900°C for 2 h. Reflections of Ca$_3$Co$_4$O$_9$ match with those in ICDD PDF # 00-023-0110, formed as the major phase. Co$_3$O$_4$, CaCo$_2$O$_4$, and Ca$_2$Co$_2$O$_5$ minor phases were also found in these pellets. Sopicka-Lizer et al. reported that Ca$_3$Co$_2$O$_6$ of ~25% content was found in Ca$_3$Co$_4$O$_9$ powder calcined at 850°C/20 h and almost pure Ca$_3$Co$_4$O$_9$ could be obtained at 900°C/20 h calcination. At 950°C/20 h calcination, ~33% Ca$_3$Co$_2$O$_6$ formed due to the decomposition of Ca$_3$Co$_4$O$_9$ [26]. While in Ca$_3$Co$_4$O$_9$ prepared via citrate sol-gel method, Zhang et al. obtained pure Ca$_3$Co$_4$O$_9$ powder at 750-900°C calcination for 2 h. Almost complete transformation to phase was observed at 950°C/2 h calcination [27]. Therefore, the reaction-sintering process is a simple and effective process to prepare Ca$_3$Co$_4$O$_9$ ceramics even the calcination stage was bypassed.

SEM photos of as-fired Ca$_3$Co$_4$O$_9$ pellets sintered at 870°C and 900°C for 2-6 h are shown in Fig. 2. Porous pellets formed due to the low sintering temperatures. Grains of size less than 6 μm were observed. The shrinkage percentage for Ca$_3$Co$_4$O$_9$ pellet increased from 10-12% at 850°C to 13-14% at 900°C as shown in Fig. 3. Density of Ca$_3$Co$_4$O$_9$ was found in a range of 2.0-2.2 g/cm$^3$ at 850-900°C sintering as illustrated in Fig. 4. Density of 2.46 g/cm$^3$ (52.6% of the theoretical value 4.677 g/cm$^3$) was obtained at 900°C/6 h sintering. This implies sintering temperatures below 900°C are not high enough to obtain dense Ca$_3$Co$_4$O$_9$ ceramics. Decomposition of Ca$_3$Co$_4$O$_9$ at 926°C limited a sintering temperature above 926°C. Addition of sintering aids or a prolonged soak time may lead to more dense pellets at a same sintering temperature. We are now investigating the effect of these factors.

3.2 CuAlO$_2$

XRD profiles of CuAlO$_2$ sintered at 1200°C and 1250°C for 2 h are shown in Fig. 5. Reflections of CuAlO$_2$ match with those in ICDD PDF # 00-035-1401 can easily be identified. Very weak peaks of unreacted Al$_2$O$_3$ were also detected. Therefore, reaction-sintering process is proven useful in preparing CuAlO$_2$ thermoelectric ceramics even the calcination stage in conventional solid oxide route has been bypassed. Park et al. reported the reaction of CuO and Al$_2$O$_3$ occurred at 1069-1095°C [16]. There were only 13-18 minutes for the reaction of CuO and Al$_2$O$_3$ during the heating up period from 1069°C to 1200-1250°C at a rate 10°C/min in reaction-sintering process. This is too short to complete the reaction. Park et al. found weak peaks of CuO instead of Al$_2$O$_3$ in CuAlO$_2$ after calcined at 800°C/2 h and then sintered twice at 1200°C/20 h [16]. Different second phase formed in CuAlO$_2$ via different process.
SEM photos of as-fired CuAlO$_2$ are shown in Fig. 6. Pores can be easily seen. It was noted that grains with two different morphologies were found. Smaller grains of 2-5 μm are Al$_2$O$_3$ and larger grains are CuAlO$_2$. This can be confirmed by the EDS results in Fig. 7. Park et al. reported elongated grains were observed and increased with sintering temperature [16]. Shrinkages were found only 3-6% in 1350°C/2-6 h sintered CuAlO$_2$ pellets. This is reasonable since there was no material lost during the reaction. All constituents CuO and Al$_2$O$_3$ reacted and remained. Fig. 8 shows density of CuAlO$_2$ sintered at various temperatures. Low density 2.6 g/cm$^3$ was measured in pellets sintered at 1200°C and increased slightly at increased temperature. It is noted a density 4.1 g/cm$^3$ (80.4% of the theoretical value 5.097 g/cm$^3$) was obtained at 1350°C/2 h sintering. Park et al. obtained CuAlO$_2$ with density 3.741 g/cm$^3$ and 3.818 g/cm$^3$ after 20 h sintering at 1160°C and 1200°C, respectively [16]. Therefore, dense CuAlO$_2$ ceramics could be obtained after sintering at high temperature for short soak time.

**4. CONCLUSIONS**

Reaction-sintering process can efficiently transform the mixture of raw materials into Ca$_3$Co$_4$O$_9$ and CuAlO$_2$ ceramics even if the calcination stage is bypassed. Ca$_3$Co$_4$O$_9$ formed as the major phase and some minor phases Co$_3$O$_4$, CaCo$_2$O$_4$, and Ca$_2$Co$_2$O$_5$ were also found. A maximum density value 2.46 g/cm$^3$ was found at 900°C/6 h sintering. Decomposition of Ca$_3$Co$_4$O$_9$ at 926°C limited a sintering temperature above 926°C. Very weak peaks of unreacted Al$_2$O$_3$ were detected in CuAlO$_2$. Density of CuAlO$_2$ ceramics reached a maximum value 4.1 g/cm$^3$ at 1350°C/2 h. The reaction-sintering process has proven a simple and effective method in preparing Ca$_3$Co$_4$O$_9$ and CuAlO$_2$ ceramics for thermoelectric application.
Fig. 7 EDS of the smaller grain in CuAlO$_2$ sintered at 1300$^\circ$C for 2 h.

5. REFERENCES


8. JCPDS Card, 21-139.


12. S. Li, R. Funahashi, I. Matsubara, H. Yamada, K. Ueno and S. Sodeoka, “Synthesis and thermoelectric properties of the new oxide ceramics Ca$_{3-x}$Sr$_x$Co$_4$O$_{9+\delta}$ ($x = 0.0-1.0$)”, Ceram. Int., Vol. [27], (2001), 321-324.


