SYNTHESIS AND CHARACTERIZATIONS OF $Ca_9Co_{12}O_{28}$ COMPOUND

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ABSTRACT

The $Ca_9Co_{12}O_{28}$ compound was synthetized by solid state reaction (SSR) method. Thermo gravimetric analysis (TGA), differential thermal analysis (DTA), X-Ray Diffraction (XRD), and bulk density were employed. The precursor had the minimum weight loss at the temperature range of about 700-950 $^{\circ}$C. The XRD detected pattern phase transition according to thermal analysis, in which the calcine sample was studied at 850°C and the sinter samples at 850°C and 900°C for 24 hr, respectively. Full Width at Half Maximum (FWHM) was calculated for the crystallite size of the sinter sample. By about 360 nm at 850°C, the crystallite sizes increased with increasing temperature and phase transition changed with increasing temperature. The bulk density decreased with rising temperature.

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INTRODUCTION

Global warming from greenhouse has dramatically increased and and there have been attempt to reduce these effect. People have investigated harvest heat energy which has an important role in the development of alternative energy. One approach is thermoelectric materials. Thermoelectric can convert heat to power generation and convert electricity to refrigeration. Thermoelectric materials are composed of n-type and p-type materials. They are combined harmoniously as well as operation has transfered of electron and hole by heat flux. The Seebeck effect is basic of power generation, where voltage difference (ΔV) is proportion with temperature gradient (ΔT) as relation Seebeck coefficient (S) (S = $\Delta V/\Delta T$). The thermoelectric performance can be detected by dimensionless figure of merit (ZT = $S^2\sigma T/\kappa$, σ is resistivity and κ is thermal conductivity). Thermoelectric materials as high ZT indicate high thermoelectric efficiency. Calcium Cobalt Oxide compound material has received much attention in recent years due to its p-type materials, low cost and convenient precursor preparation. M. Shikano and R. Funahashi [1] investigated the $Ca_3Co_4O_9$ p-type material, and found that the $Ca_3Co_4O_9$ had high ZT about 0.87 at 700°C [1]. They indicated that $Ca_3Co_4O_9$ has high thermoelectric performance. Additionally, the ZT value of thermoelectric materials depended on reduction of thermal conductivity due to phonon scattering within lattice boundary [2]. S. Chakraborty et al. [3] showed that thermal conductivity of lattice contribution had decreased with reducing grain size of silicon germanium alloy. The thermal conductivity of $Ca_3Co_4O_9$ nano-powder reduced with increasing temperature, which was prepared by heat treatment from a mixture of $CaCO_3$ and Co_3O_4 at 920°C with several hours [4]. However, precursor sample preparation has various methods. Y. Song and C.W. Nan [5] prepared the $Ca_3Co_4O_9$ by poly acrylamind gel and spark plasma sintering and found high Seebeck coefficient and electrical conductivity value. J. Nan et al. [6] synthesized $Ca_3Co_4O_9$ by citrate gel processes. J.X. Zhang et al. [7] synthesized the $Ca_3Co_4O_9$ powder by

citrate sol gel method and investigated the $Ca_3Co_4O_9$ nanoparticle. These upper procedures indicated that the $Ca_3Co_4O_9$ particles were arranged finely as the higher density and electrical conductivity.

Recently, the investigation of Lu^{3+} has substituted Ca^{3+} in a series of $Ca_{3-x}Lu_x Co_4O_9$ (x = 0, 0.1, 0.2 and 0.4), Seebeck coefficient and resistivity have increased and thermal conductivity (κ) has decreased, they could be show the dimensionless Figure of merit (ZT) about 0.032 which better than $Ca_3Co_4O_9$ (about 0.007) [8]. In addition, S. Li et al. [9] investigated the $Ca_9Co_{12}O_{28}$ with adjacent $Ca_3Co_4O_9$ phases, in which they found that electrical conductivity of about 84 Scm^{-1}, Seebeck coefficient of about 118 mVK^{-1} and thermal conductivity of about 1.73 $Wm^{-1}K^{-1}$ at $700^{\circ}C$ as well as the $Ca_9Co_{12}O_{28}$ has well efficiency for thermoelectric material [9]. Both of $Ca_3Co_4O_9$ and $Ca_9Co_{12}O_{28}$ are thermoelectric materials and appropriate for thermoelectric p-type which oxides thermoelectric material had durable at high temperature. The $Ca_9Co_{12}O_{28}$ could be various preparation method for which the preparation should concentrate on convenience and low cost. Therefore, $Ca_9Co_{12}O_{28}$ structure is interesting that the transformation of phases and crystallites when increase temperature increasing.

The purposes of this paper were to report the synthesis of $Ca_9Co_{12}O_{28}$ powders by SSR method and to investigate the weight loss by thermal decomposition analysis. We prepared calcine and sinter of the $Ca_9Co_{12}O_{28}$ samples powder for detected the characterization by XRD patterns, the borderline diffraction patterns can be used for calculation of crystallite size, including the bulk density for mechanical properties study, which in this synthesis was used solid state reaction.

MATERIALS AND METHODS

In this experiment setup, we prepared the $Ca_9Co_{12}O_{28}$ ceramic powder by SSR method, using the powder precursor of $CaCO_3$ (Lot 7, QREC New Zealand) and Co_2O_3 (Lot 71020, Sigma-Aldrich Laborchemikalien), mixed with weight proportion and grinded by ceramic balls in ball mill.

The detection of TGA and DTA were used with the $Ca_9Co_{12}O_{28}$ powder for 0.5 mg. The temperature of the bath rate $5^{\circ}C/min$ increased from room temperature to $1000^{\circ}C$ in air

atmosphere. The calcination was elevated contaminate, which we used an electric furnace for heat at $800^{\circ}C$ for 10 hr in air, the calcine powder pressing uniaxial at 500 MPa into bulk size $2\times2\times0.3$ cm^3. The bulk samples were heated at the rate of $20^{\circ}C/min$ at $850^{\circ}C$ for 12 h, and another one at $900^{\circ}C$ for 12 hr in air, cooling down slowly to room temperature according to the thermal inertia of heat in furnaces for protection cracking of the samples [10]. We investigated the bulk density after sintered by using deionized water as liquid together with Archimedes method density.

Phase characteristic detected by X-ray diffraction (XRD) with Cu Kα1 (λ = 1.54056), voltage 40 kV, current 30 mA, scan speed 2.0 degree/min and scan range 5-60 degree, XRD could be analyzed the sample powder of calcine and sinter, as well as could be calculated the crystallite size (L) of $Ca_9Co_{12}O_{28}$. We calculated the grain size average of spherical crystallites by FWHM, a peak characteristic diffraction or proportion of the area with height x-ray diffraction as in the following:

$$L(2\theta) = \frac{K\lambda}{\beta\cos\theta} \qquad (1)$$

where K is Scherrer constant is 1.05 , λ is the wave length, β is a volume average of the crystal thickness in the direction normal to the reflection planes (integral breadth for this article), Θ is the diffraction angle [11, 12].

Even though these methods are suitable for estimation of microstructure materials, the diffraction feature analysis is well structure and popular in the investigations of polycrystalline samples [13] and compound materials.

RESULTS AND DISCUSSION

1. TGA and DTA Investigation

The TGA and DTA are detected the $Ca_9Co_{12}O_{28}$ precursor; the curve forms are shown in Fig.1. The weight loss step can be observed upon heating the three steps at room temperature until $1000^{\circ}C$. The first step was observed at the temperature lower than $600^{\circ}C$, which found that the weight loss about 5% as well dehydration of precursor can be predicted. The second part was observed between the temperature range of $600^{\circ}C$ to $700^{\circ}C$, which was composed of a complex series of decomposition processes. In this part is hard weight loss of 25% for precursor, the TGA results indicated that the thermal decomposition

of anhydrous, CO_2 and contamination in precursor, were eventually attributed to the reaction of $CaCO_3$ and Co_2O_3 in air atmosphere. Moreover, between range $700°C$ to $950°C$, it is known that precursor not suffering from weight loss change, as well as confirming that the formation of the $Ca_9Co_{12}O_{28}$ in this temperature range for preparation calcine and sinter. The weight loss above $950°C$, the TGA curve shows weight loss about 3% and related a small decomposition of precursor, which indicated that finally the $Ca_9Co_{12}O_{28}$ phase had changed to another phase.
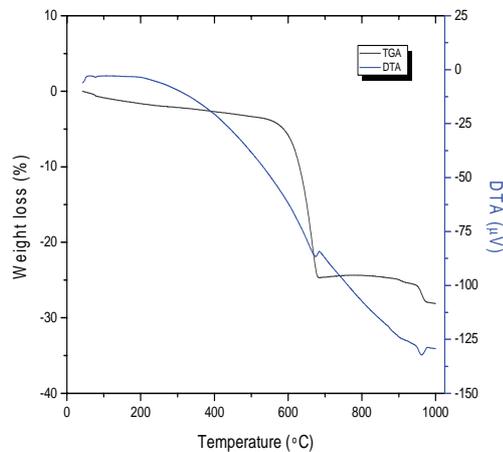

Fig.1. TGA-DTA curves of the $Ca_9Co_{12}O_{28}$ precursor

The DTA curve of $Ca_9Co_{12}O_{28}$ obtained at air atmosphere is shown in Fig. 1 (blue line). The DTA curve present at room temperature to $670°C$ range, the observed high expand endothermic effect correlated with the combustion of contamination in precursor corresponding to a rapid weight loss by 25% in TGA curve, the exothermic effect appearing as a small plateau at $690°C$ can be correlated with the change of water crystalline together with slightly decomposition obtained by hydrolysis of precursor. The DTA curve indicates that temperature range $700-950°C$ had endothermic effect, of which the reaction was attributed to $CaCO_3$ and Co_2O_3; the $Ca_9Co_{12}O_{28}$ was correlated with decomposition. The curve above $950°C$ indicates exothermic effect that can be ascribed to the thermal reduction of Co_2O_3 to CoO [14]. Eventually, the endothermic effect was located at $950°C$ for mixture of $CaCO_3$ and Co_2O_3, which the both of $CaCO_3$ and Co_2O_3 are compound of $Ca_9Co_{12}O_{28}$ and $Ca_2Co_2O_5$ [15].

2. XRD Analysis

The $Ca_9Co_{12}O_{28}$ precursor was calcined at $800°C$. This temperature was elevated the contamination in the $Ca_9Co_{12}O_{28}$ phase, which could be observed the weight loss according to TGA results. The XRD patterns were detected the powder precursor and powder calcine at $800°C$ for 10 h are shown in Fig. 2.

This article reveals a mixture by solid state reaction of $CaCO_3$ and Co_2O_3 are obtained to $Ca_9Co_{12}O_{28}$ precursor, which the peaks not match standard peaks of $Ca_9Co_{12}O_{28}$, the observation of the $Ca_9Co_{12}O_{28}$ peak calcine at $800°C$ for 10 h is appeared a peaks different precursor peaks, which the calcination is elevated the contamination of precursor., In addition, the TGA curve and the DTA curve had intersection at temperature range about $750°C$, the endothermic has effected calcine for 10 hr. Moreover, it is convenient and economic at calcination for 10 hr, Furthermore, the thermal analysis result of sinter at $850°C$ and $900°C$ in air atmosphere by XRD were accompanied by the intensities of the diffraction had increased in lines as shown in Fig. 2. The diffraction peaks position of sinter at $850°C$ for 24 h indicated that the mixture of $CaCO_3$ and Co_2O_3 as well as match with the standard JPDS card (021-0139) of $Ca_9Co_{12}O_{28}$ had according with the previously paper results [16].

Table 1. The crystallite sizes result of $Ca_9Co_{12}O_{28}$ precursor, calcine and sinter

Precursor 25°C (nm)	Calcine 10 h 800°C (nm)	Sinter 24 h	
		850°C (nm)	900°C (nm)
591	240	363.5	4428

Additionally, Fig. 2 shows the diffraction patterns of sinter samples. The observed peak positions are different from with calcine sample peak, which only intensities of peaks are different. The intensity of (001) peaks are initiated peaks for detected to the other (*hkl*) peaks condition, the (001), (002), (003), (004), (200), (020), (202) and (203) plane on base of $Ca_3Co_4O_9$ indicated a strong preference of $Ca_9Co_{12}O_{28}$ pellets, the sinter samples powder detecting by XRD pattern, the sinter results showed that peaks are shifted and disappeared which indicated that the $Ca_9Co_{12}O_{28}$ at $900°C$ had deflected of structure and the phase changed and oriented of (200), (020), (202) and (203) plane, which the intensity had decreased at $900°C$ which believed

that the $CaCO_3$ phases are loosed by heat. Moreover, these results can be believed that a texture structure inducing to uniaxial pressing as the previously reported [17, 18], these showed that the solid state reaction method depends on appropriate calcine and sinter temperature.
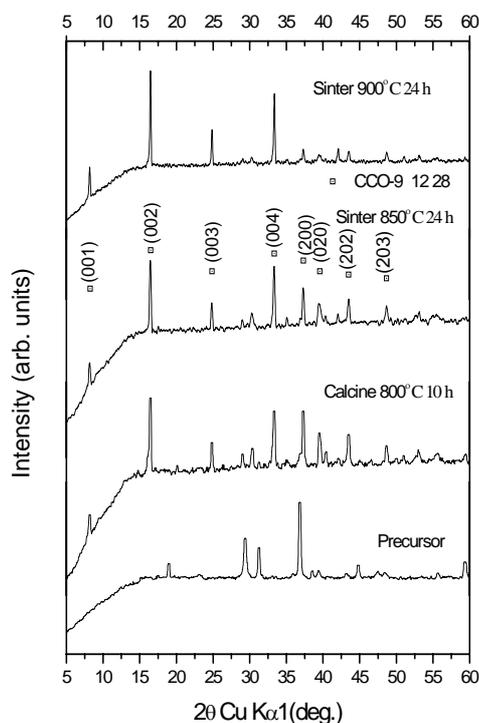

Fig. 2. The XRD patterns calcine at $800^{\circ}C$ for 10 h and sinter at $850^{\circ}C$, $900^{\circ}C$ for 24 h of $Ca_9Co_{12}O_{28}$

The broader lines of x-ray diffraction indicate the presence of the crystallite sizes, the $Ca_9Co_{12}O_{28}$ powder calcine at $800^{\circ}C$ and sinter at $850^{\circ}C$ and $900^{\circ}C$, the crystallite sizes calculated from suitable of the diffraction peaks as follow equation (1) shown in Table 1. The diffraction lines of precursor powder are predicted crystallite sizes about 591 nm, the calcine at $800^{\circ}C$ about 240 nm, the crystallite sizes are decreased solid state interaction together with decomposition of $CaCO_3$ and Co_2O_3 are accumulated to the other phase, which these phase are similar to the $Ca_9Co_{12}O_{28}$ pattern, in addition to the calcination at $800^{\circ}C$ could be simultaneously dehydration and elevate contaminations, it's indicated that the crystallite sizes according with TGA-DTA analysis. Moreover, the decreasing of crystallite

size will be effected to the easier accumulation, as well as the boundary grain accumulated of $Ca_9Co_{12}O_{28}$ crystallite.

Moreover, the diffraction patterns of $Ca_9Co_{12}O_{28}$ sinter at $850^{\circ}C$ for 24 h are calculated the lattice parameters $a = 4.8656$ Å, $b = 4.58799$ Å and $c = 10.6417$ Å, $\beta = 82.36$ degree. The calculation of crystallite sizes of $Ca_9Co_{12}O_{28}$ sinter at $850^{\circ}C$ for 24 h has greater than the crystallite sizes of calcine due to the particles of $CaCO_3$ and Co_2O_3 are accumulated to $Ca_9Co_{12}O_{28}$ crystals have been effected to the FWHM, which the FWHM is calculated degree at $2\Theta = 44.6^{\circ}$ the crystallite sizes about 363 nm are shown in Table 1. The crystallite sizes of $Ca_9Co_{12}O_{28}$ sinter at $900^{\circ}C$ for 24 h has about 4428 nm, which the crystallite sizes has been increased extremely with increasing temperature range $850^{\circ}C$ to $900^{\circ}C$ due to a temperature increased to the accumulation of particle, as well as the XRD results in Fig. 2 showed the intensity of sinter at $900^{\circ}C$ is higher than intensity of sinter at $850^{\circ}C$, however, the pattern of boarder line and phase are shifted, the phase intensities of (200), (020), (202) and (203) plane has been lower than standard peaks of $Ca_9Co_{12}O_{28}$. These effected to are investigated the choice of sinter temperature properly.

3. Bulk Density

Mechanical properties in regard to electrical conductivity, if the bulk density is high, also electrical conductivity will be high. The density of $Ca_9Co_{12}O_{28}$ bulk is detected the sinter samples at $850^{\circ}C$ and $900^{\circ}C$ for 24 h are decreased from 4.431 g/cm^3, 4.426 g/cm^3 respectively, which correspond-ding to 89.9% and 89.8% of the theoretical density on base of $Ca_3Co_4O_9$ [15] respectively, these results are indicated that weight loss of $Ca_9Co_{12}O_{28}$ has been decreased over $800^{\circ}C$ which according with TGA analysis and the elements of $Ca_9Co_{12}O_{28}$ are loosed at $900^{\circ}C$ as shown in XRD sinter results, meanwhile, the volume of bulks changed with increasing temperature, in this results are found that the solid state reaction of $Ca_9Co_{12}O_{28}$ be adequate at $850^{\circ}C$.

CONCLUSION

The $Ca_9Co_{12}O_{28}$ compound was synthesized by solid state reaction method, which this study on $Ca_3Co_4O_9$ base. The calcination temperature at $800^{\circ}C$ for 10 hr and sinter at temperature $850^{\circ}C$ and $900^{\circ}C$ for 24 hr success led at $850^{\circ}C$ for 24

hr are investigated. The TGA-DTA analysis and the XRD patterns are shown characterization results of $Ca_9Co_{12}O_{28}$. The bulks densities are investigated the mechanical property with dependence on sinter temperature. The temperature has been increased with significant to effect on $Ca_9Co_{12}O_{28}$ structure, in addition to, the $Ca_9Co_{12}O_{28}$ sample are sinter at $850^{\circ}C$ for 24 h, which investigation will be appropriate for thermoelectric properties in the future work.

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