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Significant Development of the Thermoelectric Materials in Effect of Hot-Pressing Process on Ca3Co4O₉

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Abstract: *This work explores the prospects for a further enhancement of the thermoelectric properties of Ca_3Co4O_9 with hot-pressing. The modified hot-pressing process resulted in highly textured and dense ceramics. This paper describes the synthesis process to make dense pellets from the Indian made hot press system. This paper reports a novel composite-based processing route for improving the electrical performance of Ca_3Co4O_9 thermoelectric (TE) ceramics. In this study, highly textured ceramics of Ca_3Co4O_9 were fabricated by solid state methods and hot-pressing (HP) was used to increase the density and reduce porosity from pellets so that we get dense thermoelectric materials for measurements. Thermoelectric $Ca_3Co_4O_9$ Calcium Cobalt Oxide 820mm circular pellets have been prepared successfully by the Hot pressed method, expectedly sintered, and their thermoelectric properties, in which the density is approximately the same as the theoretical value. XRD of Sintered pellets well matched with JCPDS data. FESEM images show the compactness of circular pellets where porosity is reduced between molecules, excellent for thermoelectric measurements.*

Keywords*:* Ceramics; Oxides; Hot-pressing; Texture; Electrical properties, $Ca3Co4O_9$, $Ca3Co2O_6$, Two-step sintering, Thermoelectric property, Mixture

Introduction

Nowadays, there is a great need for competitive renewable energy sources and devices, and many efforts are being put into their large-scale research, development, and innovation. Among the various existing types and in the context of the present environmental challenges, thermoelectric (TE) generation stands out as one of the most promising options allowing for direct conversion of waste heat into electrical power [1-4], with no unwanted byproducts or side effects. Fossil fuels, utilized as popular energy supplies in recent years, have resulted in global warming and a severe energy crisis. Thermoelectric (TE) materials can achieve conversion between waste heat and electricity, providing an eco-friendly, sustainable energy source. To realize large-scale production, TE applications require affordable and effective TE technologies; these depend critically on the TE properties of candidate materials [5].

The thermoelectric era presents a promising opportunity to recover waste heat emitted from industrial sectors and convert it into electricity [6]. This requires an efficient TE material that is smooth enough to operate in the air and maintain stability at high temperatures [7-15]. Transition metal oxides have attracted significant interest since the discovery of high-temperature superconductivity in layered cuprates. Increased attention has been focused on cobalt oxides due to their high thermopower.

The $Ca_3Co_4O_9$ compound is considered to be one of the most promising p-type TE oxides to date, suitable for waste heat recovery applications in air, at high temperatures [16]. The main challenges for this material are related to its strong anisotropic electrical properties induced by the 'misfit layered' crystal structures and its relatively low bulk density and weak mechanical strength (caused by the big difference between the maximum *stability temperature of the $Ca_3Co_4O_9$ phase and the corresponding solidus temperature). These issues severely limit its use in power generation applications and technologies [17]*

Thermoelectric materials with high energy conversion efficiency are highly required for both electric power and waste heat recovery as well as the refrigeration of electronic devices. Recently, oxides have attracted increasing attention as high-temperature thermoelectric materials for power device because of their oxidation resistance, high thermal stability and reduced toxicity, and oxide systems such as Na_xCoO_2 and $Ca_3Co_4O_9$ [10-15]. It has been theoretically verified that artificial super lattice quantum-well materials, which consist of conducting and insulating layers stacked alternately, should give higher thermoelectric value [18-19]. Synthetization process is very important to achieve high thermoelectric properties. In this paper, we have described the synthesis process to make dense pellets from Indian made hot press system.

In this study, highly textured ceramics of Ca3Co4O_9 were fabricated by solid state methods, and hot-pressing (HP) was used to increase the density and reduce porosity from pellets so that we get dense thermoelectric materials for measurements. Considering that calcium cobalt oxide has two possible crystal phases with markedly different characteristics, we have prepared sintered mixtures of $CaCO_3$ and Co_3O_4 and comprehensively investigated the effect of their mixture ratio on the crystal phase and thermoelectric properties.

1. *Synthesis and Characterization details*

The $Ca_3Co_4O_9$ polycrystalline samples were prepared by conventional solid-state synthesis method $CaCO_3$ and Co_3O_4 starting precursors in the stoichiometric ratio were mixed in dry conditions and calcined in air at 1150K for 24 h to permit the decomposition of the carbonate, and then form the 349 phase. The obtained mixture was reground and treated in a vacuum (10^{-3} bar) in the hot-pressed Sintering apparatus (Model: Insamrat system, Hyderabad) graphite die with an inner diameter of 20 mm. The density of the prepared samples was measured by Archimedes Principle. $Ca_3Co_4O_9$ thermoelectric (TE) oxide ceramics were successfully prepared by hot pressed Sintering process. The effects of the uniaxial pressure (86 MPa), and the dwell temperature (1123K) were investigated. Microstructure analyses have revealed strong enhancements of the bulk density as the pressure level and the applied temperature during the hot press process are increased [20-21]

2. *Results and Discussion*

2.1 *Synthesization of Hot-pressed $Ca_3Co_4O_9$ ceramics Pellets*

$Ca_3Co_4O_9$ ceramics with different concentrations were synthesized by hot-pressed method using high purity AR grade $CaCO_3$, and Co_3O_4, powders as starting materials. The precursors were weighed in the stoichiometric ratios to obtain the nominal composition of $Ca_3Co_4O_9$. Here S0 denotes pure in Table 1. Density measurement by Archimedes principle shows that 99 percent same with theoretical values as shown in table 1. Operating parameters needed for the control panel are shown in Table .2. The circular pellets of thickness 10 mm and diameter 20 mm were obtained, and were polished to remove stray graphite foil, and were subsequently heated at 723K temperature for one hour before other characterizations.

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Table .1: *Un -doped $Ca_3Co_4O_9$ samples*.

Un Doped	Nominal Composition	Abbreviation	Density G/CM^3
Un-doped	$Ca_3Co_4O_9$	S0	**4.6352**

Table 2: *Operating (externally by the help of user) parameter for Hot-press*

Time (min) /Parameter	Temperature (K)	Volt (V)	Current (A)	LVDT (mm)	Pressure (MegaPascal)
1	323	1.81	210	104.7	57.82
3	546	3.37	410	104.8	57.82
5	773	4.10	520	104.9	80.95
7	910	4.735	610	104.6	80.96
8	1027	4.78	640	104.5	80.95
9	1131	4.58	629	106.2	80.94
10	1136	4.57	615	107.6	80.95
11	1138	4.55	630	107.5	80.96
12	1139	4.55	600	107.4	80.97
15	1144	4.56	625	106.3	80.95
16	1148	4.55	630	106.3	80.94
17	1149	4.54	620	105.7	86.78
18	1149	4.55	630	105.5	86.75
20	1150	4.56	610	105.2	86.79
30	1150	4.55	625	105.3	86.77
40	1151	4.54	645	105.2	86.78
50	1151	4.54	640	105.2	86.78

The calcined powder so obtained was hot- pressed by an indigenous process (developed by Insamrat Systems, Hyderabad, India) by means of hydraulic cylinders. The hot press consists of the following major sub assemblies, vaccum chamber and its supporting structure, vaccum pump assembly, hydraulic power pack assembly, electrical power pack assembly, cooling pump and cooling tower assembly and main controle CPU.The calcined powders (10 grams) was loaded into the graphite die and held between two plungers; which was further loaded into the machine and placed between the top and the bottom ram (piston rod) of hydraulic cylinder with help of graphite discs. One the sample was loaded, vacuum chamber was closed, maintained at vacuum pressure 10^{-3} bar . Employing joule's law of heating, current was passed through the two rams to further heating of the sample at rate of 650K/min till the temperature 1150K was reached. The sample was held at the temperature for 30 minutes. It is observed that to achieve heating rate of 350^{0}C/min in a die of internal diameter 20mm, amount of current required is 635 Ampere. Later the sample was cooled at a rate of 573K/min which led to decrease in the current flow. When the temperature of the sample cools down to 373K, the vacuum is broken by applying N2 gas and the rams was separated from the samples which was *then collected. In between, we manage the temperature as shown in table 2 and table 3 explains how the machine operate with the user values systematically. The circular pellets of thickness 10mm & diameter 20mm, so obtained are polished to clear out the stray graphite foil, and then heated at 723K temperature for one hour to be use them for other characterizations. Internal parameter of hot press are also shown in table 3 which shows that everything fine under the machine [22-23]. We have observe the internal parameter of hot press so that every parameter works smoothly according to user specification values.*

Table 3: *Operating (Internally) parameter for Hot-press*

Observation Time/Parameter	**Start-00min**	**20 min**	**30 min**	**40 min**	**50min**	**60 min**	**One hou 10 min**	**One hou 20 min**	**One hou 30 min**
Cooling Water Pr	3 Kg	3 kg	3	3	3	3	3	3	3
Hydraulic Pr(Bar)	10 bar	10	10	10	10	10	10	10	10
Ram Load, Tons(Mega Pascal)	57.83	57.82	86.74	86.76	86.74	86.74	86.77	86.74	86.77
Die diameter,mm	20	20	20	20	20	20	20	20	20
Vaccum mbar	3.2^{-3}	3.3^{-3}	3.3^{-3}	3.2^{-3}	2.2^{-3}	1.2^{-3}	1.1^{-3}	1.1^{-3}	3.1^{-3}
Temp Top Ram(T1)(Kelvin)	305	305	313	328	353	393	448	483	553
Temp Top Ram(T4)	305	305	330	370	370	393	448	483	553
Temp CW Inlet	Normal	N	N	N	N	N	N	N	N
Temp CW Outlets	N	N	N	N	N	N	N	N	N
Top Ram Inlet(K)	303	303	303	303	303	303	303	310	310
Top Ram Outlet	300	300	300	300	300	300	300	300	300
Bottom Ram Inlet	300	300	300	300	300	300	300	300	300
Bottom Ram Outlets	300	300	300	300	300	320	320	320	320
Die Temps(T2)(K)	303	313	390	449	677	801	975	1023	1043
Pyrometer Temperature(K)	533	543	543	573	583	603	690	718	733

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After various optimization parameter trials, this is the best parameter that is suit for making dense Calcium cobalt oxide pellets for thermoelectric measurements. Figure 1 shows the dense pellets obtained from the Hot press machine.

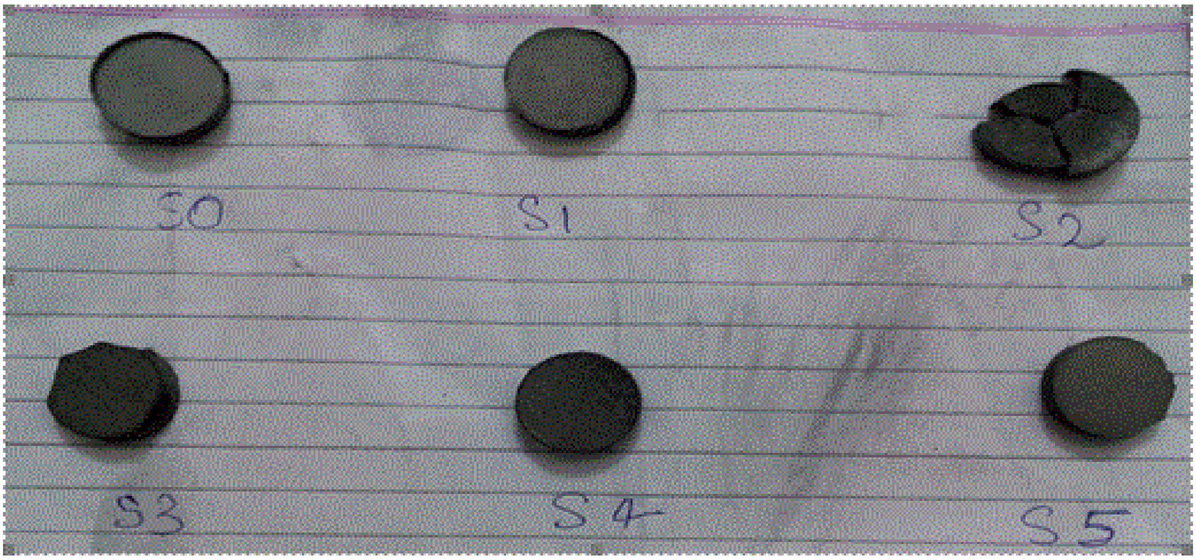

Figure 1: *$Ca_3Co_4O_9$ pellets (20mm circular) obtained from Hot-press.*

2. 2 X-ray diffraction analysis

Fig. 2 shows the X-ray diffraction (XRD) patterns of the pure S0 pellets sample. All the observed diffraction peaks of the sample matched with JCPDS card number 023-0110 of $Ca_3Co_4O_9$ confirming pure phase formation for Ca3Co4O_9. Moreover, no unwanted peaks observed in the diffraction peak means that no unwanted reaction has taken place during hot press machine.

Phase identification was performed through powder X-Ray Diffraction (XRD) analyses, for various Ca3Co4O_9 based samples (ground into powder) and for precursors (after the organic phases burn-out and after the 3-step thermal treatment), at RT, using a PHILIPS X'PERT system with CuKα radiation (Cuα = 1.54060 Å), with 2θ angles ranging between 5 and 90 degrees and a step and exposure time of 0.02°2θ and 3 s, respectively [24-26]. The XRD and TE coefficient plots were constructed using the Origin Pro software (2019b (9.65)).

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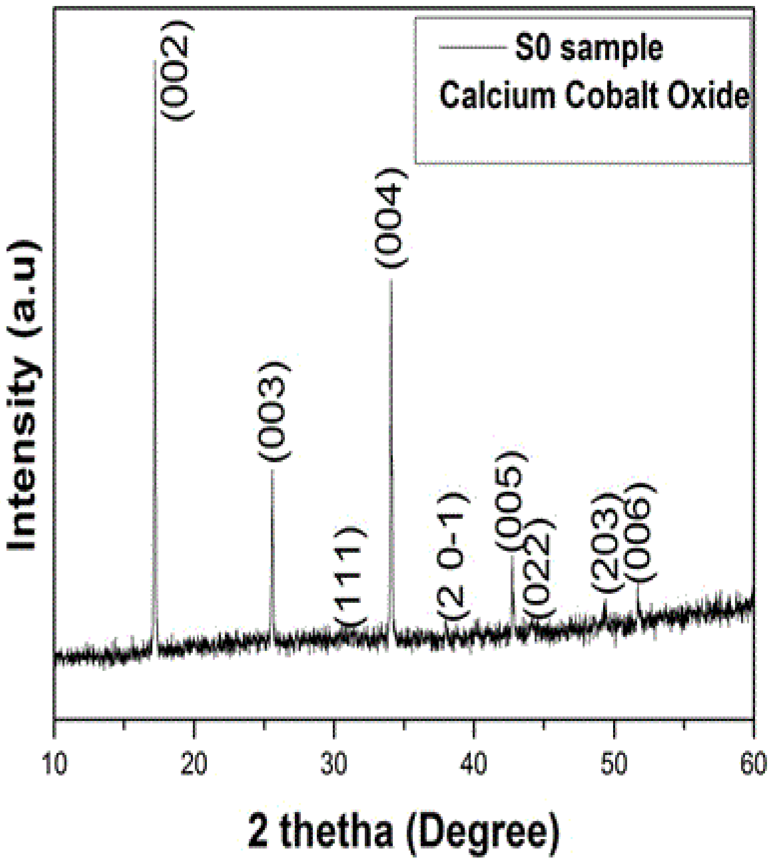

Figure 2: *XRD patterns of the Hot- Press pellets of Calcium Cobalt Oxide*

2.2 FESEM Image

Fig. 3 demonstrates the FESEM images of the typical microstructures of the fractured surfaces for hot pressed samples of the pure Ca3Co4O$_9$*. Closed packed compact disk like grains of various sizes are observed which are scattered in all orientations. Morphological characterization of fractured samples coated with carbon was performed using scanning electron microscopy (SEM, Hitachi SU-70 instrument, Aveiro, Portugal), complemented by energy-dispersive spectrometry (EDS, Bruker Quantax 400 detector).*

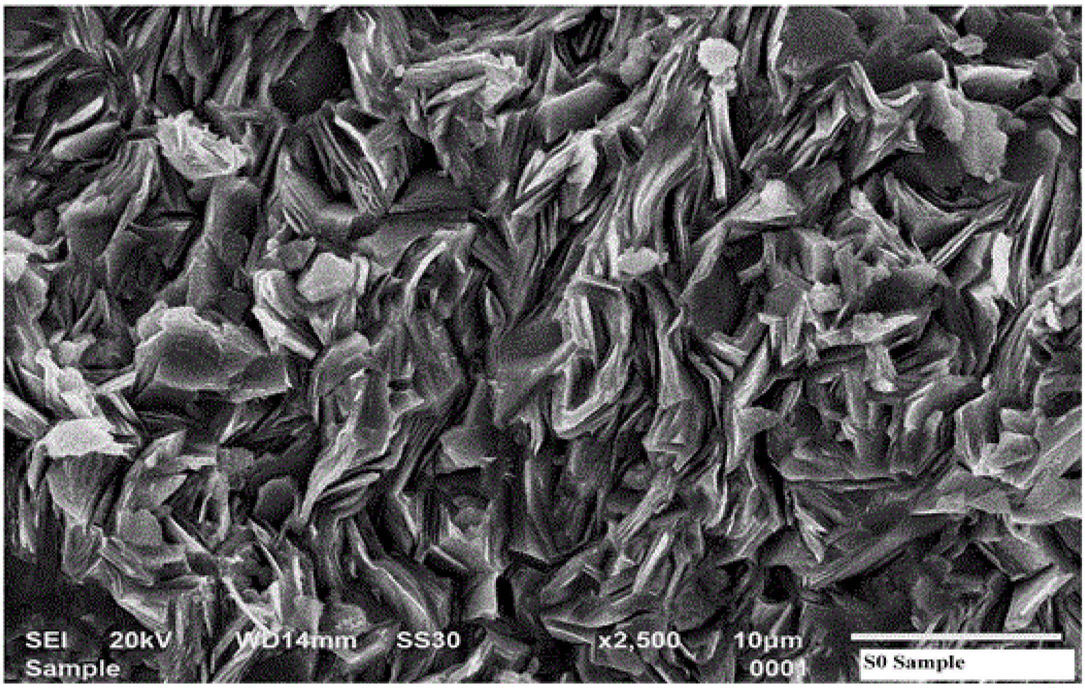

Figure 3: *SEM image of the surfaces of the pellet samples S0*

3.0 Conclusion

This work demonstrates how high-performing Ca3Co4O9 thermoelectric materials can be produced through a modified hot-pressing process combined with doping. Microstructural studies have revealed significant grain orientation, relatively large grain sizes, and low porosity. Density measurements confirmed the high density of samples.

Thermoelectric $Ca_3Co_4O_9$ Calcium Cobalt Oxide 20mm circular pellets have been prepared successfully by the Hot pressed method, expectedly sintered, and their thermoelectric properties, in which density is approximately the same as the theoretical value. XRD of sintered pellets closely matches the JCPDS data. FESEM images demonstrate the compactness of circular pellets, where porosity is reduced between molecules, which is excellent for thermoelectric applications measurements.

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