An intrigued Layered Oxide Structure of Thermoelectric Materials
1. **Title of the Project**  
   An intrigued Layered Oxide Structure of Thermoelectric Materials

2. **Applicant**  
   Arramel

3. **FOM Research Group**  
   G14

4. **Institute**  
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5. **Abstract**

   Renewed interest in promising thermoelectric materials (thermal gradient) is currently investigated. This interest originates from the conversion of heat into electricity which is known as Seebeck phenomena. It has been studied extensively to increase the performance of TE materials. NaCo$_2$O$_4$ was the first compound which is observed by Terasaki with a large value of thermopower +100 $\mu$V/K at 300K $^{[1]}$. The hole conductivity mechanism that occurs between Co$^{4+}$ ($S$=0.5) and Co$^{3+}$ ($S$=0) are likely driving the evolution of thermoelectricity in this particular compound. It is an interesting point to investigate the fundamental aspect of conducting holes among other transition metal oxide. Therefore, we describe the isomorphic compounds that are expected to have higher thermopower than layered cobalt oxide, above. Three new promising materials: Na$_4$CrO$_4$, RbCo$_2$O$_4$, and RbRh$_2$O$_4$ are introduced. Our expectation in general would be to increase thermopower coefficient compare to the existing TE materials. The implementation of TE device will follow shortly after realizing which compounds exhibit good and reliable parameters. This project offers an approach of TE materials between structural studies and their physical properties. Both contribute to emerging knowledge to solve waste heat problem in the future.

6. **Duration of the Project**

   Four years, starting from September 2007
7 Personnel

7.1 Senior Scientist

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7.2 Junior Scientist and Technician

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8 Cost Estimates

8.1 Personnel Positions
One PhD position for four years.

8.2 Running Budget
15k€ per year

8.3 Equipment
For implementation of structural studies, a high resolution of Transmission Electron Microscopy (Hitachi, H-1500) operated at 820kV is needed. This instrument is useful to determine the length of layered transition metal oxides within large construction of TE material framework.

8.4 Other Support
The project will be supported by the Zernike Institute for Advanced Materials and Rijksuniversiteit Groningen. The senior scientist and also the technician expected to guide and assist during the project.

8.5 Budget Summary (In k€)

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9. Research Programme

A. INTRODUCTION

Future development to re-use waste heat is quite interesting in these years. Since it may become one of the solutions of energy resources in the world. It can be obtained from industries output or even a combustion of gasoline which generate energy in the car. In addition, we can not escape ourselves that finding another source of alternative energy beside the petroleum or natural gas becomes prominent issue. We did not for sure until when that our stock of world petroleum oil can fulfill our needs within several decades. Therefore, an act to convert the energy output is considered as one of the alternative to deal the prediction scare of petroleum oil in the future.

One can imagine the large volume of waste heat is converted into another form of energy. For instance, it may become an electrical power forms. In 1950, this can be brought to life when the thermoelectric devices were introduced to the world. These instruments are extremely simple. It has no moving parts and no greenhouse gases application as well. The devices utilized two types of semiconductor “legs” that are connected in series [2]. Typical requirements of these conducting materials must have contains one positively charge carries (holes) and the other negative charge carriers (electrons). Normally, p- and n- type semiconductor have been widely known possessing these charge carries, respectively. In addition, the electrons and holes are carrying heat as well as electrical charge. There are two types of thermoelectric devices that can be distinguished from their different output. First type is concerning about how to convert the heat becomes electricity. These devices enable us to use the gradient temperature by applying heat to one junction that connects two different conducting materials. By doing this, the electron and hole are moving toward the heat source junction. These movements of charges enhance the buildup of current and consequently we can generate the electrical power at the end of integrated circuit. Common name has been given for this instrument which is a power generators device. NASA already used this principle to provide hundreds of Watts of electrical power for deep space probes such as Voyager I and II and the Cassini mission [3]. The second type is ”cooled circuit” by introducing the current into the system. In order to force both charge carriers (electrons and holes) moving away their parts to another section, thereby reduce the temperature at the active cooling junction (as shown in figure 1 in the next page).

Estonian-German physicist Thomas Johann Seebeck who discovered that if a heat is applied across the junction of two wires, then a current is generated [3]. In 1821, He discovered that a compass needle is deflected when it is placed in the vicinity of a closed loop formed from two dissimilar metal conductors if the junctions were maintained at different temperatures. He also observed that the magnitude of the deflection was proportional to the temperature difference and depend on the type of conducting material, and does not depend on the temperature distribution along the conductors [4]. This is the basis of thermocouples (material connected together in a electrical circuit). People are familiar with the name “Thermopower” or Seebeck effect.
The Seebeck phenomena can be characterized from the application of thermocouple where one junction is held at a constant temperature. Whereas other junction is treat as an open circuit to measure the change of temperature. From this it follows that \( \frac{dV}{dT} \) at one junction is independent of the temperature of the second junction. Thereby, we can define the Seebeck coefficient \( S \) as follows:

\[
S = \lim_{\Delta T \to 0} \frac{\Delta V}{\Delta T} = \frac{dV}{dT} \quad \ldots \quad (eqn \ 1)
\]

Where \( \Delta T \) is the difference in temperature between the two junctions of material \( a \) and \( b \). \( \Delta V \) is the resulting open circuit voltage. The following figure shows the schematic diagram of both Seebeck and Peltier phenomena.

If we applied an electrical source (i.e. battery) depicted on the figure 2. A current flows through the circuit and producing Joule heating \( (I^2R) \), but there is an additional thermal effect which known as Peltier effect. Heat could be lost or gained depend on...
the direction of the current through the junction between two materials. The Peltier coefficient $\pi$ is related from the below expression:

$$Q = \pi I \ldots \ (eqn \ 2)$$

Where $Q$ is the heat generated (or withdrawn) per second from the junction, and $I$ is the current flowing through the junction $[^5]$.  

Passing a known current as depicted on the schematic above, we can measure the Peltier coefficient by recording the change of temperature in time $[^6]$. As long as we know the rate of change of temperature and the heat capacity of the junction, this values will gives the rate at which heat is exchange with the surroundings. The Peltier coefficient is obtained after corrected with the Joule heating.

The refrigeration devices are expected to show promising benefit for the future. Since it can generate the cold system without any moving parts or bulk fluids [liquids or gases like chlorofluorocarbons (CFCs) or hydrochlorofluorocarbons (HCFCs)] $[^7]$. The majority problems that occurred in the conventional refrigeration systems are failure due to gas leaks or moving parts in generic compressors system. This problem may introduce some of the environmental problems. Therefore, thermoelectric devices were introduced because they avoided any toxic chemicals above. In addition, the appearance is rather simple, lightweight, and small. Moreover, they can be built under inexpensive way $[^7]$. In traditional approach, thermodynamic cycles involving compression and expansion of refrigerant gases (in familiar Freon) were used $[^8]$. In contrast, thermoelectric material did not depend on the gases, it is more relate to the characteristic of physical phenomena so called as the Peltier effect. In 1834, He described that thermal effects at the junction of dissimilar conductors arises when an electrical currents flows between the materials $[^6]$. However, He was not able to understand the full implications of his findings and later on Lenz concluded that there is heat adsorption or generation at the junctions depend on the direction of current flow.

Thermopower device can be made from two possible sources, metal or semiconductor thermocouple. The first material seems not promising since their only have relatively small voltages output. Due to the fact, that metals possess half-filled bands within its electronic structure. Therefore, metal contains an equivalent number of charge carrier electrons and holes. Since both are contributes to the induced thermoelectric thus canceling each others. Meanwhile, large voltages can be obtained from semiconductor-based thermocouples because of tend to have one dominant carrier per type: either $p$ or $n$ type semiconductor. As large thermoelectric material refers to have only one single charge carrier, it is more large possibility the group of semiconductor to produce large thermopower behavior.

Thermoelectric material can be determined by dimensionless parameter $\zeta T$, so called as figure of merit. Where $z$ is the first variable can be treat separately. Meanwhile T is referred to the temperature. This parameter is specific and unique for each considered material. The first variable ($z$) consists of several physical properties which is: Seebeck Coefficient ($S$), thermal conductivity ($\kappa$), and electrical resistivity ($\rho$).
In order to obtain higher Seebeck effect within a material, we can search for a material which possess high Seebeck coefficient (dimension is in Volt/Kelvin). In addition, it should have exhibit lower thermal conductivity and electrical resistivity as well. The latter component can be inversely quoted to have a material with high electrical conductivity. Further, we can calculate the efficiency for energy conversion in thermoelectric materials which is proportional to the product between Carnot efficiency and figure of merit. The equation no.4 explicitly defines both contributions are suitable to have higher efficiencies within the same material. If we able to introduce material with a wide range of operating temperature. As consequent, the difference between temperature at hot junction ($T_H$) and cold junction is large. In addition, we must note that that thermal conductivity comprises two components: electrical carrier contribution ($\kappa_e$) and lattice vibration (phonon, $\kappa_{ph}$).

However, if we take one example the world market sales of TE cooling devices is still small (about $80 million to $160 million per year). Most of the TE devices are being used as cooling laser diodes and electronic coolers for picnic baskets. The major problem which still faces and limits the application is with their low efficiencies. For the time being, our specification only considered to the figure of merit of material. The best thermoelectric materials commercially available today have $ZT \approx 0.9$. This is considered to be acceptable for certain application. Unfortunately this value is still far too low compete with the refrigerators in the kitchen. The expectation for a thermoelectric refrigerator would requires $ZT \approx 3$ at room temperature. However, the work of Venkatasubramanian and coworkers is attracted many people at the Materials Research Society Meeting in Boston. They were able to synthesize thin film of p-type Bi$_2$Te$_3$/Sb$_2$Te$_3$ semiconductor producing $ZT = 2.4$ at room temperature. These thin films have an unusual structure where a superlattice is formed by alternating layers of semiconductors. It appears this type of structure was able to induce the transport of current carrying electrons (and holes). In addition, it is blocking the transport of heat-carrying phonons as well. These two factors were raised $ZT$ drastically compared to its bulk semiconductor alloys. An application of nanoengineering was strongly control the above thin film layers formation. It turns out from their studies, a layers thickness or the size of the quantum dot (approximately 1 nm) contributed to tune $ZT$ values. This result are confirming to the idea that brought by Dresselhaus and her collaborators. For instance, PbTe was used as the active-layer material and the value of $ZT$ can reach 1.2 at room temperature.

## II. Motivation

The general task in the research of thermoelectric materials remains as a formidable challenge in how to increase their efficiencies. Therefore, pursuing the fundamental understanding and finding new material that exhibit large efficiency currently encouraged. As starting point, we may follow the terms of an ideal thermoelectric: A material which possessed an electron crystal and phonon glass behavior at the same time. This means that the mobile electrons are required to transport charge and
heat. On the contrary, phonons are expected to become disrupted at the atomic scale from transporting heat. The greatest possibility to fulfill this requirement is by minimizing the lattice thermal conductivity. For instance, the increase of phonon scattering mechanisms can be done by introducing an element with special requirements. They could be any heavy atoms, disorder, large unit cells or “rattling atoms”. The last term can be found by preparing material with particular kind of framework that enable to “rattle” one or more of its component. This step is realized to lower the lattice thermal conductivity without enhancing the electrical resistivity. Thereby, it may produce a high Seebeck coefficient.

In the past, the pursued of new thermoelectric material is concentrated on heavily doped semiconductor formed from heavy elements than the oxides. The latter is not favorable due to the reason that the metal exists in half-filled bands. Electrons and holes are in the equivalent in numbers. Since both contribute to the induced thermoelectric voltage thus cancelling each other’s contribution to that voltage and making it small. However from the finding layered cobalt oxides the story becomes completely different. The relationship between the heterostructure of small gap semiconductor and Na\textsubscript{0.5}CoO\textsubscript{2} has the same objective, which is minimizing the phonon component of thermal conductivity ($\kappa_{ph}$). In semiconductor by inserting loosely bound atoms or introducing voids or holes in the structure. It is expected to “rattle” inside these voids and thus scattering the phonons. This is effectively reducing the thermal conductivity. Further, the electronic factors must be addressed under standard model of semiconductor transport. The ZT value is monotonically increased as a function of two parameter energy gap ($E_G$) and B. The latter variable is determined by a number of materials parameters. In this analysis, we assumed that that the semiconductor carrier density has been adjusted to the optimum level either $n$- or $p$-type. Then, the band gap should be greater than kT (the thermal energy) by a factor of 10 in order to maximize ZT for a given B. Where B is a product of several component below\textsuperscript{[7]}.

$$B = N_V \mu m^{1.5}/\kappa_{phonon} \quad \text{(eqn 5)}$$

Where $N_V$ is the degeneracy of the band extrema near the Fermi level, $\mu$ is the electronic mobility, and $m$ is the band mass determined by the density of the state.

In other case of the bulk oxides, the same spirit is being applied how to decrease thermal phonon contribution within its structure. The approach would be determined to use large number of atoms (N) in the unit cell. Large N is considered to lower the fraction of vibrational modes (phonons) that carry heat efficiently (the acoustic modes) to 1/N.

The first and large thermoelectric power was obtained from a single crystal of NaCo$_2$O$_4$. Terasaki, et.al and his coworkers able to synthesized this bronze-type compound, which is normally expressed as A$_x$BO$_2$. It was first Jansen and Hoppe who had identified this material that x-value range from 0.5 to 1\textsuperscript{[13]} This oxides reveals strikingly result on its thermopower, the in-plane thermopower value reach 100 $\mu$V/K, at 300K\textsuperscript{[1]}. In addition, low electrical resistivity was observed 200$\mu$Ω cm at room temperature as well. One note to keep in mind, this material consists of forms 2D triangle lattice of CoO$_2$ layer (as shown in Fig.3.). This is quite different compared to the normal 2D square lattice of CuO$_2$ layer that observed in high temperature superconductor\textsuperscript{[14]}.
The sodium content may give an improvement to the thermoelectric properties of layered cobalt oxides. From the work of Motohashi, et.al[15] we can extract the important information that the value of $\rho$ is decreasing and the S value is increasing as the sodium content increases. For the illustrative result, the following graph shows the temperature dependence of those parameters.

Another example, IrSn$_{1.5}$Te$_{1.5}$ mixed anion skutterudites (formula AX$_{1.5}$Y$_{1.5}$, where A = Co, Rh or Ir, X = Ge or Sn and Y = S, Se or Te) have attracted much interest in science. They led to a material which exists with reduced bandgap and higher electrical conductivities. This material shows thermopower (S) with the value 160 $\mu$V/K at room temperature[16]. Unfortunately, high resistivity value reduces the power factor ($S^2/\rho$) of this compound. In the end, it is still too small for thermoelectric application.
Furthermore, in pursuing the good thermoelectric material, a layered rhodate oxide was successfully synthesized by Okada, et.al. They manage to produce the first synthesized misfit oxide without any cobalt component. The general design of new thermoelectric devices was based on the application of lattice misfit oxide. The material offers the route of combining CoO$_2$ blocks with charge reservoir block $^{[17]}$. The series of polycrystalline samples of (Bi$_{1-x}$Pb$_x$)$_{1.8}$Ba$_2$Rh$_{1.9}$O$_y$ ($x = 0, 0.1, 0.2$) were analyzed and showing thermopower 100 $\mu$V/K at 300K, which is nearly the same value for the thermoelectric layered cobalt oxides $^{[18]}$.

CuMO$_2$ ($M$ being a trivalent cation) with delafossite structure has received much attention as a promising candidate for p-type conducting transparent oxides $^{[19]}$. This oxide was considered to be the best candidates for a good thermoelectric material. It consist of hexagonal layered structure and it can be defined as the alternate stacking of edge-shared MO$_2^-$ octahedral layers. Moreover, O$^{2-}$-Cu$^{+}$-O$^{2-}$ dumbbell-shaped layered are perpendicular to the c- axis. Such layered structure can have the same advantages found in some conventional material Bi$_2$Te$_3$ and NaCoO$_2$. The large electrical conductivity ($\sigma$) supported with low $n$. Okuda and his coworker able to shows that CuCr$_{1-x}$Mg$_x$O$_2$ ($0 \leq x \leq 0.04$) exhibit large Seebeck coefficient ($S$) 350 $\mu$V/K at 300K for $x=0$ $^{[20]}$. However, the value of $\rho$ does not decreases so much with the increase of $x$ and remains in relatively large value (for instance, 0.0640 $\Omega$ cm in $x=0.03$), while the $S$ values is drastically change become 70 $\mu$V/K.

The other promising materials that people were investigated intermetallic alloys and heavy doped semiconductor. For instance, layered compounds of PbSb$_2$Te$_4$ and PbBi$_4$Te$_7$ has been investigated by Shelimova et.al, they introduced the idea to reduce the phonon thermal contribution by high z-elements compounds $^{[21]}$. This material was responsible for lowering its lattice thermal conductivity, which eventually will produce an effective scattering phonon mechanism contributed for heat conduction.

Despite all of the above examples, the big question still lies on how to design and finding new thermoelectric material. Especially the one predicted with large Seebeck coefficient and low electrical resistivity. Further, the challenge strongly encouraged how to minimize the phonon contribution and at the same time to increase the electrical conductivity as well.

### III. Primary Target Project

The goals of this future work contain the following points:

- Synthesized new and promising large thermoelectric material which constructed based on layered transition metal oxides.
- Characterization and measured physical properties of the proposed materials.

### IV. Description of the project.

Based on the previous description of layered structure, this proposal will extensively discuss certain issue which relates with the family of layered cobalt oxides. In particular, the group of ACo$_2$O$_4$ (the alkali cobalt bronze family where $A=$Na, K, Rb, and Cs). This group owns the equal number of Co$^{3+}$ and Co$^{4+}$ throughout the system. Low spin state are identified from the static and NMR measurement for 3d spins of Co ions $^{[22]}$. This system possessed hexagonal structure (P6$_3$22) with the alternative stacking of CoO$_2$ layer and A$_{0.5}$ planes along c (as depicted on Fig. 3). The first
subject is more concentrated on the substitution of the alkali metal in NaCo₂O₄. For other member of alkali groups, RbCo₂O₄ is expected to be metallic conductors as well. Nakamura successfully synthesized the polycrystalline forms. One of their results shows that the electrical resistivity is in order of 10⁻² Ω cm. This is quite promising value if we compare with the low value that own by Na₂Co₂O₄. Up till now, the study of relevant single crystal still not explored yet. Therefore, the anisotropy of RbCo₂O₄ remains unanswered and triggered us to understand about the outcome comparison between in-plane and out-plane thermoelectric behavior. The trend of Seebeck coefficient should be at least as large as recorded on its predecessor Na₂Co₂O₄ or even higher. This is expected to give significantly large contribution on the phonon scattering mechanisms. Thereby, it eventually will reduce the total thermal conductivity throughout all the framework of RbCo₂O₄. Our results are advisedly will add the general picture of thermoelectric behavior in the alkali bronze family.

To give solid foundation on the layered cobalt oxide, Terasaki greatly discussed about the electron configuration of cobalt ions [23] which behave uniquely. In particular, Co³⁺ and Co⁴⁺ in low spin state (as shown schematically below)

![Diagram](image)

**Fig 5. The electronic configuration of Co³⁺ (left panel) and Co⁴⁺ (right panel), respectively.**

Since tetravalent of Co⁴⁺ ion in the low spin state only have one hole in the t₂g state. This chemically unstable ion will likely exist around the vicinity of oxygen ligand hole. Thereby creating an intermediate state in such way contribute to have large entropy of k_B ln 6 arising from (t₂g)⁵ [23]. This term arises, as described by Koshibae, et.al which explained that an electrical conduction are realized by exchanging interaction between Co³⁺ and Co⁴⁺ [24]. As consequence, the large thermopower was observed in NaCo₂O₄ which is considerable close to the value of k_B (ln 6/e).

The term of “spin entropy” needs to be described more detail regarding its relation with thermopower buildup. This means that the spins are not staying completely in the lattice. Instead, it moves among the two ions and as it rapidly interchange from one point to another. Basically it resembles the same spirit in thermodynamically of expressing the ideal gas. In this case it is the spin behaves as our primary objects. The more disorder spins within a material, the larger thermopower would be expected. In strong correlated system such as the group of transition metal oxide, the electron-electron interaction is fashionably enhanced the thermopower value. Wang, et.al evidently proved that the suppression which experienced by the layered oxide Na₄Co₂O₄ are involving the application of an external magnetic fields. It seems that there is field dependence which indicated from thermopower (S) measurement under various temperatures. At low temperature, the in-plane thermopower was measured by the longitudinal magnetic field, and as result the trend of S values is monotonically
decreases as the field is increasing before it became zero in a field of 8 T\cite{25}. The field suppression can be understood from the strong correlation between two different ions Co$^{3+}$ and Co$^{4+}$. The hopping process are originates from holes belong to Co$^{4+}$ ($S=1/2$) which moves into Co$^{3+}$ ($S=0$). Therefore, this process implies that the transfer of a spin and holes are occurs at the same time.

This spin entropy contribution is suggested by Terasaki for the driving mechanism of thermoelectric properties. The argument was originates from the generalized of Heikes formula under Hubbard model. As their calculation results shown on the below expression, it contains the thermopower coefficient is largely determined from the concentration ration between Co$^{4+}$ and Co$^{3+}$ at their low spins state and the ratio of degeneracies both of them.

\[ Q = \frac{k_B}{e} \ln \left( \frac{g_3}{g_4} \frac{x}{1-x} \right) \ldots \text{(eqn 6)} \]

Where $Q$ is thermopower coefficient (the same as $S$), $k_B$ is Boltzmann constant, $e$ is the charge of electron, $g_3$ and $g_4$ is resemble the degerecy of spin for respective ions (3 for Co$^{3+}$ and 4 for Co$^{4+}$), the last one concern with the concentration of Co$^{4+}$ ions. From the above equation, we can relate the state of low spin Co$^{4+}$ involving large entropy of $k_B \ln 6$. it is indicates the large absolute value of the thermopower that can be realized when there exists unbalance of the spin and orbital degree of freedom between Co$^{3+}$ and Co$^{4+}$ sites. From these arguments and also the experimental evidence which is observed by Terasaki. Under this expression, Koshiba et.al described some of his calculations and pointed out that at the Co$^{3+}$ and Co$^{4+}$ low spin system. It was predicted to have the thermopower coefficient $154 \, \mu V/K$ which is quite comparable to the value that was found by Terasaki (in plane thermopower $100 \, \mu V/K$).

As for the remarks, this example shows us that the degeneracy of carriers together with the strong electron correlation within the layered cobalts oxide is the driving force of the large thermopower.

Another promising material that can be investigated is by replacing cobalt ion with Chromium (in particular Cr$^{4+}$). The proposed formula is Na$_4$CrO$_4$. Since they are belong to the same part in periodic table, which is in the transition metal oxide group. The similarity factor on the chemical of point of view hopefully work out the prediction in chromium systems to shows large thermoelectric properties. The study of layered chromium was initiated in the 1954 when Ruedorff\cite{26} introduced his crystal NaCrO$_2$. It contains the layered sodium which separated the octahedral CrO$_2$ oxides. Later on, Hoppe \textit{et al} \cite{27} described Na$_4$CrO$_4$ to be in triclinic fashion with the lattice parameter $a$, $b$ and $c$ is 8.597 Å, 5.698 Å, and 6.4 Å, respectively. The space group is classified to be P1\textit{-}. Further, the following figure illustrate the crystal structure.
As it shown above that the chromium ions is surrounded by three oxygens. Consequently, it will produce trigonal lattice symmetry which is almost comparable with the layered cobalt oxide. This case is quite intrigued to investigate whether or not they can possess thermoelectricity. Since most of the other groups (layered Cu, Ni, and Mn oxides) which belong to the same third periodic elements are being found with their low thermopower. In particular, Ni and Mn oxides show hopelessly high resistivity. Therefore question mark will be pointed to the chromium layered oxide. Do they behave differently from the above example? The driving force would resemble from the degeneracy level between Cr$^{3+}$ and Cr$^{4+}$. The latter ion is categorized to be unstable, therefore our expectation is considered that this degeneracy level would behave quite similar with the Co$^{3+}$-Co$^{4+}$ system. Regarding the issue of the phase stability, no further explanation can be withdrawn about this issue, since no related literature is found within the database described about the relevant phase stability.

In principle, another variation on the general formula can take place among this layered cobalt oxide. If we substitute both the sodium and cobalt ions at the same time, there are two choices that we must take into account, first is the chemical feasibility of those new elements to each other. Second aspect is considering its building block of “spin entropy” that controlling the origin of thermopower evolution. Our concern in this combination are perfectly clear, how to join these two aspect within one stable compound. Therefore we suggest our second material to be RbRh$_2$O$_4$. Rubidium has been considered as the promising member of alkali metal whose possessed larger ionic radii than sodium. It is expected to have large contribution to the transport properties, especially influencing the electron movement along the material. In addition, rhodium has been widely used to approach the necessity of finding new TE material. Compared to cobalt, this element has heavier weight of atom than cobalt. Most of them, currently investigated on the basis of complex structure such as in the rhodium misfit oxide Rh-based [Bi$_{1.95}$ Ba$_{1.95}$Rh$_{0.1}$O$_4$][RhO$_2$]$_{1.8}$. It is surprisingly shown a large thermopower $S$ of +95 $\mu$V/K at 300K$^{[28]}$. The coexistence of Rh$^{3+}$ and Rh$^{4+}$ in the RhO$_2$ layers suggesting the same explanation which occurred in conventional CoO$_2$ layers. From here, we predict profound result will come by modifying the above chemical composition of layered cobalt oxide. The formation of relevant single crystal hopefully will increase the richness of variety on the
investigation of TE materials. In the future prospects, it might bring more extended knowledge in thermopower generation.

In the rhodates system of RbRh$_2$O$_4$, I will deeply involve the topic of thermoelectric properties under two important aspects. The heavy element contribution and degenerate level of Rhodium in mixed valence state. Since no crystal data was found in ICSD website database which correspond to the related oxide. Therefore, I will approach the crystal structure that is already exists: NaRh$_2$O$_4$ compound. The following material is crystallizes under orthorhombic arrangement with the space group Pnma.

The crystal structure of NaRh$_2$O$_4$ was drawn above possess an orthorhombic fashion of their three components. Layered Na atoms is separated the two layered of Rhodium. The RhO$_6$ octahedra are connected by edge sharing within each chain, and the chains are tied to neighbors by sharing the corner oxygen. Moreover, the principal Rh-O-Rh angle in the chain is approximately 98°. The structural difference that observed compared to the NaCo$_2$O$_4$ compound is reflected to the chain type instead of layers structure of the sodium atoms. This material is interesting to explore about their physical properties. Since it possess the same electronic configuration of d-state with the layered cobalt oxides. Moreover it also shares the similar structural basis of the edge-sharing BO$_6$ octahedral in general ABO$_6$ structure (where A is the sodium and B is Cobalt or Rhodium). Based on the Slack concept that given a material with special character:” phonon-glass and electron-crystal“ We would like to specify the fist point if we can find a system which offers phonon to be disrupted in such way result to low thermal conductivity. Therefore, it is worthwhile to adopt a new combination of A site with more heavier element such as rubidium. The expectation by replacing the sodium with rubidium ions is enhancing the phonon scattering mechanism. Consequently, it is expected to reduce the thermal conductivity.

The stability of material has been tested under various physical measurements. No indication was reported to show that any structural transition occurs in this rhodate system. Some literature is presented an illustration of NaRh$_2$O$_4$ compound that exhibit electrical, thermal and transport properties at various temperature. One of this result is
given below, where the doping of calcium is being introduced to study the electrical and thermopower properties.

**Fig 8.** Temperature dependence of the electrical resistivity of the polycrystalline Na$_{1-x}$Ca$_x$Rh$_2$O$_4$. Inset: Comparison between the two plots of the data for CaRh$_2$O$_4$.

In Figure 8, the temperature and Ca concentration dependence of the electrical resistivity is shown. The resistivity of the compound NaRh$_2$O$_4$ is typical of a normal metal. This might relate to the mixed Rh valence character: formally 0.5 unpaired electrons per Rh contribute to the conducting state. As the data indicate, the Ca substitution converts the conducting state dramatically. The state gradually shifts to being poorly conducting with increasing Ca concentration, and the end compound CaRh$_2$O$_4$ is indeed electrically insulating. In other result, the Seebeck coefficient below 300 K for the solid solution is presented in Figure 9. The n-type carrier is indicated from the Seebeck coefficient determination which gives negative value. The Seebeck coefficient increases in magnitude as a function of Ca concentration and reaches a maximum at $x = 0.75$.

**Fig 9.** Thermoelectric power of the polycrystalline Na$_{1-x}$Ca$_x$Rh$_2$O$_4$.

We can not deny that there is always a bottle neck arise during the research. Finding new material would be interfered with the complexity or puzzling technical problem during formation of the precursor. As consequence, the curiosity on three proposed new layered oxides: RbCo$_2$O$_4$, NaCr$_2$O$_4$ and RbRh$_2$O$_4$ might result a large thermoelectric phenomena. However, we also have to think some modification regarding the structure as a counter step. If we facing the unstable compounds or lower value of thermopower in room temperature. Highly doping with other promising ions can be performed as one of the alternative to enhance the value of thermopower coefficient. A tremendous physical change can happen by imposed small discrepancies ionic radii of one component onto the system.
Our initial task will be concentrated to fabricate large and promising single crystals. The conventional solid state reaction will be introduced based on each corresponding compounds. Furthermore, characterization analysis of material is necessary to be done under x-ray diffraction pattern. The subsequent steps are combined with additional grinding between one scan to another, which eventually it will produce a powdered single phase material. Formation of single crystal growth will be specified into two routes: flux growth method and Optical Solvent Floating Zone technique. The crucial aspect of this research lies on how to produce good and preferred oriented single crystal. If we manage to develop a systematic way and come out with considerable size of pure single crystalline. It would embrace our life for the following physical characterization and measurement accordingly. Thermopower coefficient can be measured by preparing the sample contact based on the normal four probe geometry. It was measured under a steady–state technique that being held from range of 4.2 to 300 K in a liquid He cryostat. Physical Properties Measurement Systems (PPMS) will be useful to determine thermopower response. In addition, resistivity measurement can not be separated as complementary result to extract the transport properties of TE material. Typical measurement of resistivity will also carried out by four probe method as well.

Based on this general outline work, we may aims for a better performance of layered oxides which particularly put a foundation for future implementation on the TE-based devices. Hopefully our attempt will give contribution to the science regarding the issue increasing the efficiency matters. As consequence, releasing idea and growing the future prospect of application in thermopower generator or cooler technology application.

**V. Plan of Project.**

The research time will consume within 48 months of works. Herewith are the sequences of time table throughout four years (given in months). They contain subsequent events which describe general plan and short explanation on future programme. These diagrams are flexible and it may develop further during the research.

<table>
<thead>
<tr>
<th>Month No.</th>
<th>Research Activities</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-3</td>
<td>At the first stage, the research will be initiated on how to produce pure powdered form of promising TE materials. The preparation of all samples can be synthesized under conventional solid state reaction. The target single phase forms are expected for subsequent steps of research. Further, X-ray analysis is conducted to observe any impurities within several samples. We must take precaution during the synthesis especially dealing with impurity. Sometimes the precursors are not reacted completely and remains within target materials.</td>
</tr>
<tr>
<td>4-6</td>
<td>Attempted to growth single crystal, the synthesis of target materials are carried out by two different methods: Flux Method and Optical Floating Solvent Zone. Each material is plans to be synthesized approximately one month. The important preparative route that must be considered is finding an effective way to growth large and pure single crystal. In accompanied with a preferential growth of direction. This will be related on the following step such as the orientation or physical properties</td>
</tr>
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</table>
In order to check the crystalline forms, a crushed single crystal is mounted on BrukerD8 Diffractometer and scanned accordingly. We can emphasize that there is no impurities exists in the powder diffraction data by compared it with the reference or homolog system such as Na$_{x}$Co$_2$O$_4$ peaks. In addition, we can also learn about the structural parameters regarding the trend of bonding length among the predicted materials. This could give some indication in which system we should considered seriously. These studies can be performed under a software programme so called General Structure Analysis System (GSAS). In this software we will extract the lattice constant and other structural parameters as well. In addition, we also able to confirm the purity of crystal from the fitting of diffraction pattern compared with respective analogues compounds. Furthermore, we plan to use CAD4 Single X-ray Diffractometer to produce three different crystallographic planes for future electrical and physical measurement. Afterwards, we would able to orient the single crystal along certain direction.

The electrical properties such as resistivity will be measured by one integrated system. Namely, Model 6000 Physical Properties Measurement System (PPMS). We would like to compare from those three predicted materials, which one has a lower electrical resistivity that will influence the power law on figure of merit expression. Further impact by achieving this result is to construct the thermopower measurements (which will be carried out with the same instruments). These results are expected to give us future progress on the investigation of large thermopower materials. In addition, we can explore more detail about the substitution effect on cobalt of TE layered oxides. Some modification by replacing the cobalt ions (by Chromium or Rhodium) are encouraged to reproduce the same magnitude of thermopower coefficient as Na$_{x}$Co$_2$O$_4$ compound.

Further investigation about the structural studies can be precisely extracted under synchrotron radiation. The proposal of beam time will be sent to the corresponding facility research. By obtaining these important facts about the structures, we are aiming some relationship between the structure of material and thermopower behavior. Consequently, it will add to the future development on new thermoelectric materials with large thermopower coefficients.

Additional magnetic studies on thermoelectric properties maybe included as supplementary data. Therefore, Magnetic Properties Measurement system (MPMS) can be very useful to run this experiment. Conducting several variations on field or temperature dependence may help us to extract some information about the magnetic properties of the proposed materials.

To provide a better interpretation on the above physical results, we intended to measure the specific heat and Hall coefficient as well. This may also gives additional physical information on these TE materials. Further, we expected to increase our knowledge regarding the evolution of mechanism thermoelectric materials Because there is similarity among those two physical properties and thermopower. From one reference it has been shown that they share the same trend to increase
progressively when we raised the temperature at elevated ranges. Therefore it is of important to extract further the relationship between three different properties more extensively.

| 38-43 | To get insight into the practical application, we plan to use the successful materials into simple p-n thermopower devices. We consider that the target materials have similar p-type TE. Due to homolog Na$_x$Co$_2$O$_4$ to produce positive Seebeck coefficient, which means that the holes conduction are contributed for the origin of development on this particular compound. Therefore, we plan to use electrons doped Cd$_3$TeO$_6$ 1:1 ordered perovskite-type structure. This material previously discovered to have large negative thermopower -50 μV/K $^{[30]}$. The unique electronic properties of Cd$_3$TeO$_6$ are generated from the interaction electrons inside the structure. It consists of an ordered perovskide oxide with strongly deformed monoclinic (p2$_1/n$). Due to equivalent distance of Cd-O both in A and B sites site, the overlap of the 2$p$ orbitals of the oxide ions are occurs with 5$s$ orbitals of the B site and A sites as well. This implementation will be compared with the existing commercial TE device which is already known and commercially available in the market. We might think to construct small refrigerator systems that generated under Peltier effect using our materials. The efficiency of the TE-devices remains as primary factor to determine the performances of respective materials. |

| 44-48 | The plan for the last six months will be focused on writing publications and visiting several conferences in other city or country. At the same time, the plan would be followed by writing PhD thesis for the final fulfillment of the programme. |

10. Infrastructure.

The instruments which is planned to be used located in the group of Solid State Chemistry. The following equipment are listed that can be found in the laboratory for the research purposes.

- Standard laboratory apparatus for solid state reaction.
- Nabertherm Furnace.
- Bruker d8 Powder Diffractometer
- Apex and Cad4 Single Crystal Diffractometer.
- Physical Properties Measurement System (PPMS).
- Quantum Design Magnetic Properties Measurement System (MPMS)
- Replica of p-n type Thermoelectric Device.

11. Application Perspective in industry, other disciplines or society.

Combination between science and technology boundaries is approaching at their limit regarding the TE materials. In the sense of re-use waste heat that arouse in large number either on the industrial output or other unwanted heat sources. We intend to put some contribution regarding this issue by investigating new promising TE materials. Our expectation would lies on how to enlarge thermopower (or known as Seebeck) coefficient form existing large TE material, especially layered cobalt oxides.
Further implementation of TE devices are expected to bring huge contributions to provide good, stable, and reliable tools. Incorporating the large n-type of TE compounds (as previously described) hopefully can expand the performance of p-n type TE based oxide materials. It might provide a better comparison with the similar devices which are currently constructed based on semiconductor compounds. If this research results in producing a positive signature, we think to increase our implementation level by studying the reliability of target materials to build TE devices. A valuable point would depend on finding a good system device which possessed high performance on their efficiencies. Afterwards, we might put a construction in large industry scale to overcome the large waste heat problem for elevated process. The first building steps, it will concern how to make a good thermoelectric material and applicable for the industry part to develop it under large scale production.

12. References