

CaCo_{1-x}Ru_xO_y: Role of Ru/Co Ratio on Its Transport Properties

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ABSTRACT

Calcium cobaltites, especially Ca₃Co₄O₉ with a misfit layered structure, are promising thermoelectric materials due to their suitability for high temperature applications and low densities. The existence of low spin-state electronic configurations for both Co³⁺ (*t*_{2g}⁶) and Co⁴⁺ (*t*_{2g}⁵) species is one of the key parameter to explain the large thermopower values. Ruthenium oxide, with a layered structure, exhibits strong electron-electron correlation and the extended nature of their 4*d* electrons enhances orbital overlapping which is expected to influence the transport characteristics of CaCo_{1-x}Ru_xO_y (CCR) samples, by affecting the spin state of the 3*d* Co ions. The effect on thermopower and electrical resistivity due to partial substitution of Co by Ru ions, up to 0.33 moles, from 300 to 600 K was investigated. A sharp decline in resistivity and in thermopower was observed until a transition ion ratio (*TIR*), (Ru/(Ru + Co)), of 0.5 is reached, beyond which both the properties became less sensitive to *TIR*. These variations in the transport properties are explained by the presence of 4*d* Ru in close proximity to the Co, which could influence the spin and oxidation state of Co ions. The Co rich and Ru rich samples exhibit very distinct microstructures and phase assemblages.

KEYWORDS

Calcium Cobaltite; Ruthenium Oxide; Calcium Ruthenate; Transport Properties; Thermoelectric Properties; Seebeck Coefficient; Resistivity

1. Introduction

Ceramic materials comprising transition metal oxides exhibit a number of unusual and technologically important phenomena, such as high temperature superconductivity in cuprates, colossal magnetoresistance in manganites, and superior thermoelectric properties in layered cobaltites [1,2]. Among these materials, the layered cobaltite with the composition Ca₃Co₄O₉ exhibits metallic conductivity and extraordinarily large positive thermopower (*S* = 125 μV/K), which demonstrates that dominant carriers in Ca₃Co₄O₉ are holes [3]. Ca₃Co₄O₉ has a two-dimensional (2*d*) layered structure, which consists of alternating stacks of CaO-CoO-CaO rock salt type and CdI₂-type

hexagonal CoO₂ layers along the *c* axis [1,4-7]. Both subsystems have identical *a* and *c* but different *b* parameters. The misfit between the two subsystems leads to an incommensurate spatial modulation along the *b* axis. The Ca₃Co₄O₉ system exhibits very complicated magnetic and transport properties due to this complex crystal structure [8]. Although the compound has two crystallographically distinct Co ion sites, electric conduction mainly occurs within the CoO₂ sheets because the other Co ion site is situated in the highly oxygen-deficient Ca₂CoO_{3.4} subsystem [5].

Another example of cobalt oxides, the one dimensional (1-*d*) cobaltite, Ca₃Co₂O₆, is also very attractive for its magnetic properties [1]. The rhombohedral structure of this phase [1] consists of [Co₂O₆] chains running along

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the *c* axis of the hexagonal cell. In each chain, one CoO₆ octahedron alternates with one CoO₆ trigonal prism. In these compounds the oxygen stoichiometry controls the redox or mixed valence state of the Co ions. Maignan *et al.*, [9] demonstrated that in polycrystalline compounds (sintered in air under similar conditions), the oxygen stoichiometry increases with the size of the lanthanide ion.

Compounds containing RuO₂ (commonly called ruthenates) have been observed to exhibit strong electron-electron correlation and a number of physical properties such as metal-insulator transition and antiferromagnetism in Ca₂RuO₄ [10,11], ferromagnetism in SrRuO₃, and Sr₄Ru₃O₁₀ [12,13], superconductivity in Sr₂RuO₄ [14] and metamagnetism and magnetoresistivity in Ca₃Ru₂O₇ [15]. Among the layered ruthenates, the physical properties of Ca₂RuO₄ and CaRuO₃ have been investigated earlier [16-18]. Another family of compounds with the general composition CaMO₃ (M=Ru and Fe) has evoked considerable interest on account of their unusual magnetic properties which indicate paramagnetic behavior down to 30 mK [19-22]. This compound, CaRuO₃, is composed of an array of corner-shared RuO₆ octahedra and it is assumed that the degree of tilting and rotation of these octahedra within their ideal cubic-perovskite structure governs the magnetic and also the transport properties. In CaRuO₃, a narrow itinerant 4*d* band is formed through hybridization of Ru-*t*_{2g} and O-2*p* orbitals. The 4*d* bandwidth thus formed sensitively depends on degree of hybridization [23] which also determines the mobility of carriers, leading to electric conduction.

To optimize the carrier concentration and to improve the electrical transport of calcium cobaltite, one approach is to partially substitute Ca with alkali metals, alkaline earth metals, or rare-earth metals [24]. Another route towards improvement of the transport properties is the partial substitution of other 3*d* transition metals for Co [25]. The spin state of a transition metal ion, such as Co, is determined by the competition between the crystal field and intra-atomic Coulomb repulsion energy. Among the 3*d* transition metal elements, Co has both intra-atomic Coulomb energy and crystal field energy. The variation in spin and oxidation states of cobalt oxide allows them to be influenced by other 3*d* or 4*d* transition ions. The *d*-shells of 4*d* transition metal ions are more extended than their 3*d* counterparts. This extended nature of 4*d* electrons enhances orbital overlapping which is expected to influence the transport and thermopower characteristics by affecting the spin state of the 3*d* Co ions. As discussed earlier, the spin state of Co ions has a large influence on the thermopower of these cobaltites.

In the present investigation, transport properties such as resistivity and thermopower of CaCo_{1-x}Ru_xO_y (CCR) have been determined as Co is substituted by Ru ions (up

to 33 mol%), keeping CaO invariant at 50 mol%. Two samples (CCR-3 and CCR-4) were also prepared by replacing Co by Ca and Ca by Ru, respectively. X-ray diffraction (XRD) analysis, supported by electron microscopic investigation, has been presented to aid in the understanding of the variation in transport properties as a function of composition. The evolution of the structure as a function of *TIR* has been studied as the structure changes from needle shaped crystals for Co rich compositions to planar structure for Ru rich compositions. The thermopower and resistivity data have been discussed in the light of the general properties exhibited by calcium-cobaltites and CaRuO₃.

2. Experimental Procedure

Samples with the general composition CaCo_{1-x}Ru_xO_y, with *x* varying from 0.06 to 0.33, were prepared, as listed in **Table 1**. For compositions CCR-1, -2, -5 and -6, CaO was kept invariant at 0.5 moles and a gradual equimolar substitution of Co by Ru was made with Ru varying between 0.06 and 0.33. The composition represented by CCR-4 is a variation of CCR-6 in which an equimolar replacement of CaO by RuO₂ was made while the compound designated CCR-3 is a variation of CCR-2 with an equimolar substitution of CoO by CaO.

All the CaCo_{1-x}Ru_xO_y samples were prepared, using reagent grade CaCO₃, CoO and RuO₂, following a three-stage mixing protocol to ensure compositional homogeneity. In the first step, stoichiometric amounts of CaCO₃, CoO and RuO₂ were weighed using a Metler balance to an accuracy of 1 mg and mixed thoroughly by grinding them in an alumina mortar and pestle. The mixture was subsequently calcined in a muffle furnace, in ambient atmosphere, at 873 K for 4 hours, at a heating rate of 200 K/hr. in an alumina crucible. The calcined mixture was ground/mixed in a mortar and pestle and it was re-calcined in the same alumina crucible at a higher temperature (1073 K) using the same heating and cooling protocol. The purpose of repeated calcinations is to completely remove moisture and all the combustion products, especially the CO₂ gas generated by the decomposition of CaCO₃. After the second calcination step the samples were homogenized one last time, again by grinding in a mortar and pestle. This homogenized sample was then formed into pellets, 1 cm in dia and ~5 mm in thickness, by dry-pressing in a hydraulic press under an applied load of 35 MPa. These pellets were sintered at 1173 K for 10 hours on a fresh alumina substrate using the same heating protocol and were cooled to room temperature at a rate of 100 K/hr. The purpose of this elaborate procedure for sample preparation was to achieve reproducibility and compositional homogeneity of the samples which was confirmed by XRD and x-ray fluorescence spectroscopy (XRF) measurements.

Table 1. Composition and transport properties of CaCo_{1-x}Ru_xO_y Samples.

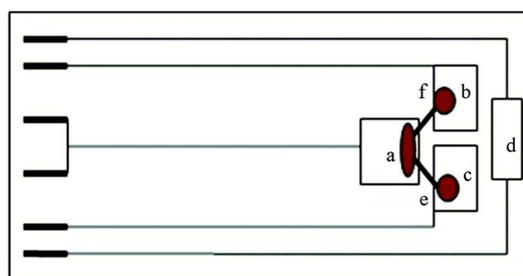
Sample ID	Molar Composition			Resistivity at 600 K (ρ) ($\Omega\cdot\text{m}$)	Seebeck Coefficient at 600 K (S) ($\mu\text{V}/\text{K}$)	Power Factor (S^2/ρ) ($\text{Wm}^{-1}\text{K}^{-2}$)	Ru/(Co+Ru) Ratio
	CaO	CoO	RuO ₂				
CaR-5 ²⁷	0.54	0.00	0.46	7.50×10^{-5}	37	1.83×10^{-5}	1.00
CCR-1	0.50	0.17	0.33	1.42×10^{-4}	36	9.11×10^{-6}	0.66
CCR-2	0.50	0.25	0.25	2.23×10^{-4}	39	6.86×10^{-6}	0.50
CCR-3	0.56	0.19	0.25	4.7×10^{-4}	30	1.96×10^{-6}	
CCR-4	0.45	0.45	0.10	6.94×10^{-4}	127	2.31×10^{-5}	
CCR-5	0.50	0.38	0.12	5.65×10^{-4}	136	3.29×10^{-5}	0.24
CCR-6	0.50	0.44	0.06	8.24×10^{-4}	187	4.24×10^{-5}	0.12
CC-1 ²⁸	0.47	0.53	0.00	1.11×10^{-3}	151	2.08×10^{-5}	0.00

Several identical pellets of each CaCo_{1-x}Ru_xO_y composition were prepared as described above. One such pellet would be crushed into powder for XRF analysis for confirmation of its composition and the same powder would then be used as the sample for XRD analysis (Thermo ARL-X'tra Diffractometer), using Cu-K α radiation. XRD data were analyzed by a commercial software (Jade) in the pattern-matching mode to identify the phase composition of the samples. Another pellet would be mounted using epoxy resin and then surface polished for microstructural and compositional analyses using scanning electron microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) analysis (JEOL, JXA-35A) to verify the homogeneity of the prepared samples and detect if multiple phases were present in the samples.

Electrical conductivity was measured by the van der Pauw's four-probe method [26].

The sintered CaCo_{1-x}Ru_xO_y samples were ground and polished to be coplanar with a thickness of about 1 - 2 mm. A fully computerized apparatus, capable of scanning between 82 and 700 K (H-50 and K-20 systems, MMR Technologies, Mountain View, California) was employed for this purpose and these resistivity measurements were conducted in a dark chamber, maintained at 8 - 10 mtorr vacuum, under ohmic conditions. The procedure used for electrical resistivity measurement on similar samples has been described in detail elsewhere [27]. In all, twenty four resistivity measurements were performed at each temperature and the average of these values comprises each of the resistivity data presented in **Table 1**. The error in temperature measurement was determined at ± 0.5 K and the error margin of conductivity measurements is estimated at $\pm 7\%$.

Thermopower (Seebeck coefficient) of the CaCo_{1-x}Ru_xO_y samples was measured with a computerized apparatus (SB-100 and K-20, MMR Technologies, Mountain View, California) and **Figure 1** shows a sche-

**Figure 1.** Schematic of seebeck coefficient measurement system. a—heat sink, b & c—heat source, d—heater, e—reference constantan wire, f—sample.

matic description of this experimental setup. The procedure used for thermopower measurement on similar samples has been described in detail elsewhere [27]. The error in temperature determination was estimated at ± 0.1 K and that of thermopower measurement is determined at $\pm 10\%$. It is important to ensure good thermal contact (not just electrical contact) between the sample/reference wire and the heat sink/source copperpads.

3. Results and Discussion

Compositions of the six CaCo_{1-x}Ru_xO_y(CCR) samples prepared have been verified by XRF and are listed in **Table 1**. As discussed earlier the compositions represented by CCR-3 and -4 are variations of CCR-2 and -6 respectively in which an equimolar replacement of CaO by RuO₂ or CoO by CaO was made. The measured properties of these samples (CCR-3, -4) are shown in *italics* in **Table 1** and as diamonds in the figures to distinguish them from the rest of the compositions.

When $TIR = 0$, the sample composition is basically that of binary calcium cobaltite (CC-1, [28]). The sample composition turns out to be the binary calcium ruthenate (CaR-5), when $TIR = 1$. All the regular CaCo_{1-x}Ru_xO_y samples (CCR-1, -2, -5 and -6) fall between these two

end members. In the following the properties of binary calcium ruthenate (CaR-5, [27]) and binary calcium cobaltite (CC-1) will be compared with the ternary CaCo_{1-x}Ru_xO_y compositions.

The resistivity data of the CaCo_{1-x}Ru_xO_y samples are presented in **Figure 2** as a function of temperature ($\ln \rho$ vs $1000/T$), which shows that the resistivity decreases with increasing temperature, 300 to 600 K. The resistivity values of the CaCo_{1-x}Ru_xO_y samples measured at 600 K provided in **Table 1** and **Figure 3** depict the effect of Ru substitution, in the form of *TIR*, on the resistivity of the CaCo_{1-x}Ru_xO_y system. The resistivity of CaR-5, the binary calcium ruthenate [27] is less than that of CC-1 which is the binary calcium cobaltite [28]. A monotonic reduction in resistivity is expected, in non-metallic systems, and observed as RuO₂ is added to the samples and the composition moves from CC-1 to CaR-5. This monotonic reduction in resistivity with Ru addition is in line with results found in literature for similar systems [29]. The explanation offered being that the charge carriers in these systems are the electrons occupying the *d*-orbitals of Ru and Co ions and even though Ru and Co are both transition ions, the outer orbital of the former comprises *4d* electrons whereas that of Co is occupied by *3d* electrons. *4d* orbitals have larger overlapping characteristics than their *3d* counterparts and result in greater mobility of the charge carriers. As a result the resistivity decreases with increasing proportion of RuO₂ in the composition. The resistivity decreases from $8.24 \times 10^{-4} \Omega\cdot\text{m}$ for CCR-6 (*TIR* = 0.12) to $1.42 \times 10^{-4} \Omega\cdot\text{m}$ for CCR-1 (*TIR* = 0.66).

Comparing the resistivities of CCR-4 and -6, it was observed that replacement of Ca by Ru ions reduces resistivity, which can be explained by the extended nature of the Ru *4d* electron orbitals and this reduction in resistivity is in line with the results found in literature for similar systems, for example calcium manganites [1,29]. Conversely, comparing the resistivities of CCR-2 and -3, it was observed that replacement of Co by Ca increases the resistivity and this increase in resistivity is expected since alkaline earth ions have rather constrained outer orbitals compared to those of *3d* transition ions such as Co.

Samples which have a *TIR* ≥ 0.5 , CCR-1 and -2, have resistivity values similar to that of CaR-5, pure calcium ruthenate as can be seen from **Table 1** and **Figure 3**. Similar behavior is observed in calcium ruthenates when either Ca is replaced by other alkaline earths or the Ru ions by lanthanides [29]. The other two samples CCR-5 and -6 have higher resistivity and closer to that of CC-1 composition.

The thermopower data of the CaCo_{1-x}Ru_xO_y samples (CCR-1, 2, 5 and 6) are presented in **Figure 4** as a function of temperature, which shows that for all the compo-

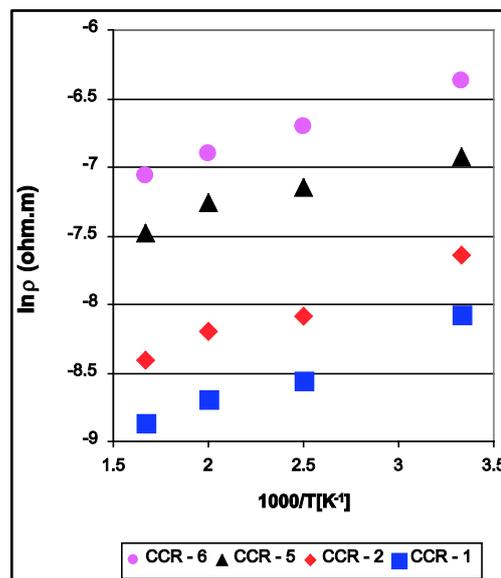


Figure 2. Electrical resistivity of ternary CaCo_{1-x}Ru_xO_y samples as a function of temperature with resistivity decreasing with increasing temperature for all the samples.

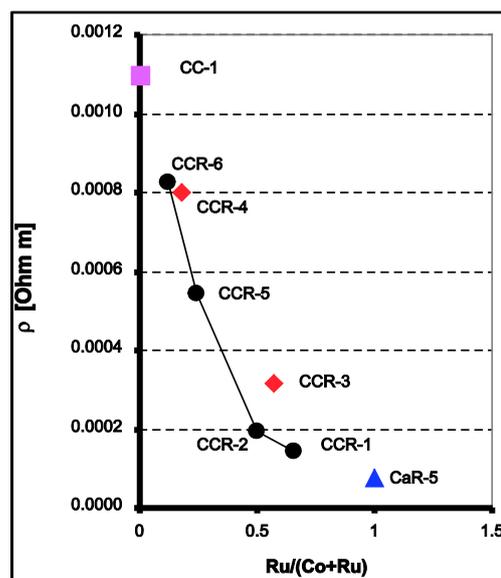


Figure 3. Electrical resistivity, at 600 K, of ternary CaCo_{1-x}Ru_xO_y samples as a function of *TIR* showing a decrease in resistivity with increasing *TIR*.

sitions *S* increases with increasing temperature, in the range of 300 to 600 K. The CaCo_{1-x}Ru_xO_y samples with *TIR* ≥ 0.5 do not show any significant change in *S* with temperature over the 300 K range, while the ternary samples with *TIR* < 0.5 do exhibit an increase in *S* with temperature over the same temperature range. The Seebeck coefficient at 600 K, (**Table 1** and **Figure 5**) shows a monotonic decrease as the RuO₂ content is increased and *TIR* increases from 0.12 to 0.66. The thermopower of binary calcium cobaltite (CC-1) is 151 $\mu\text{V/K}$ [28] and

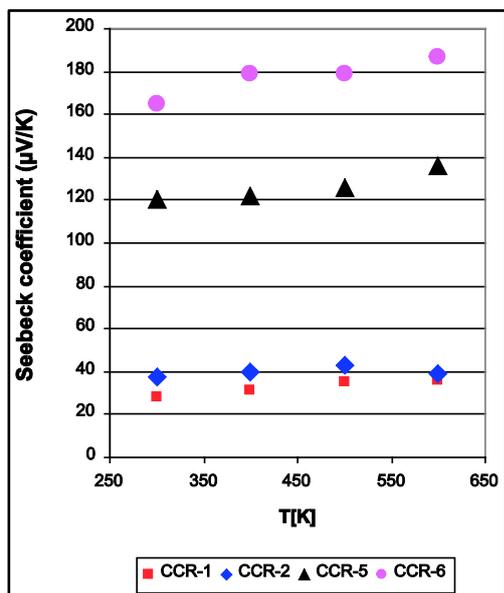


Figure 4. Seebeck Coefficient of ternary CaCo_{1-x}Ru_xO_y samples as a function of temperature showing that increase in S temperature decreases with increasing Ru content.

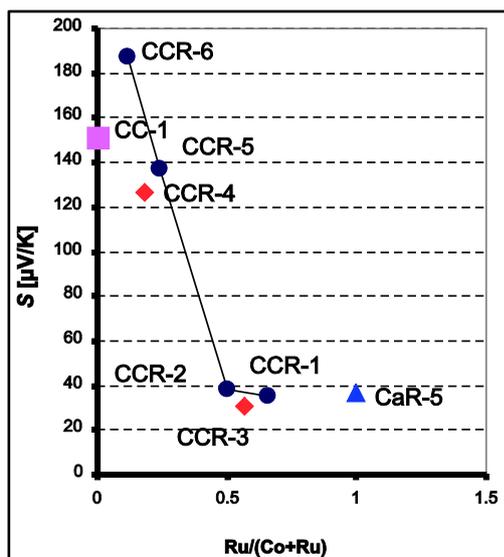


Figure 5. Thermopower, at 600 K, of CaCo_{1-x}Ru_xO_y samples as a function of TIR with S decreasing with TIR.

that of binary calcium ruthenate (CaR-5) is 37 $\mu\text{V/K}$ [27]. As cobalt ions are progressively replaced by ruthenium to form the CaCo_{1-x}Ru_xO_y series, thermopower is observed to decrease monotonically. However if the thermopower of CC-1 and CCR-6 are compared it was observed that the thermopower increases from 151 to 187 $\mu\text{V/K}$. Unlike the trend observed in resistivity, the thermopower of CaCo_{1-x}Ru_xO_y system exhibits a maximum, even though any variation in resistivity is reflected in a similar variation in thermopower in most semiconductors. However, if only the CaCo_{1-x}Ru_xO_y (ternary) composi-

tions are considered, the resistivity and Seebeck coefficient vary as expected in a semiconducting system. For the CaCo_{1-x}Ru_xO_y compositions (Table 1) while the resistivity decreases from 8.24×10^{-4} to 1.42×10^{-4} $\Omega\cdot\text{m}$, the Seebeck coefficient also decreases from 187 to 35 $\mu\text{V/K}$ in the same composition range. Comparing the Seebeck coefficients of CCR-4 and -6, it is observed that replacement of Ca by Ru ions reduces the Seebeck coefficient by a factor of 1.5. Similarly comparing the Seebeck coefficients of CCR-2 and -3, it was observed that replacement of Co by Ca also reduces the Seebeck coefficient, but not significantly.

The two samples CCR-1 and CCR-2 have very similar Seebeck coefficients 38 and 35 $\mu\text{V/K}$ respectively, while the binary calcium ruthenate (CaR-5) has a thermopower of 37 $\mu\text{V/K}$. This behavior of thermopower is similar to that of resistivity discussed earlier for these two samples. This insensitivity of thermopower to RuO₂ concentration in the calcium ruthenate samples agrees with previously reported data [27,30]. The invariance of thermopower signifies that the electronic structure and especially the density of states of these ceramics (e.g. SrRuO₃ and CaRuO₃) are unaffected not only by the various substitutions, but also by the type of the other cations (apart from Ru) constituting the ceramic. The Seebeck coefficient of the other two samples, CCR-5 and -6 varies with composition from 127 to 187 $\mu\text{V/K}$.

The power factor, S^2/ρ , (or $S^2\sigma$, where σ is the conductivity) of the four CaCo_{1-x}Ru_xO_y compositions (CCR-1, 2, 5 and 6) is depicted as a function of temperature in Figure 6. The samples with $TIR < 0.5$ exhibit an increase in the power factor as the temperature is increased from 300 to 600 K, while the samples with $TIR \geq 0.5$ also show an increase in power factor but not to the same extent as the earlier group. The power factor of the CaCo_{1-x}Ru_xO_y samples at 600 K varies within a rather small range [Figure 7]: 8.6×10^{-6} to 4.3×10^{-5} $\text{Wm}^{-1}\text{K}^{-2}$. The combined effect of S and ρ on the power factor as brought about by compositional changes is listed in Table 1 and Figure 7. Compared to the data available in the literature for substitution of Co in calcium cobaltites by other transition metal ions, such as Fe, Ni, Mn etc., this reduction in the power factor of CaCo_{1-x}Ru_xO_y compositions is not meager. Comparing the power factors of the binary calcium cobaltite (CC-1) and the CaCo_{1-x}Ru_xO_y sample with the highest Ru concentration (CCR-1, TIR of 0.66) it was observed that the power factor diminishes by a factor of 2.8. This decrease is higher than the observation of Yao *et al.*, [24] who observed a reduction of power factor by a factor of only 0.5 to 1.1 when Fe, Ni, Mn or Cu was substituted for Co. Even though this decrease is not substantially higher compared to their result, it could be due to the fact that Ru is a 4d transition metal compared to the 3d transition

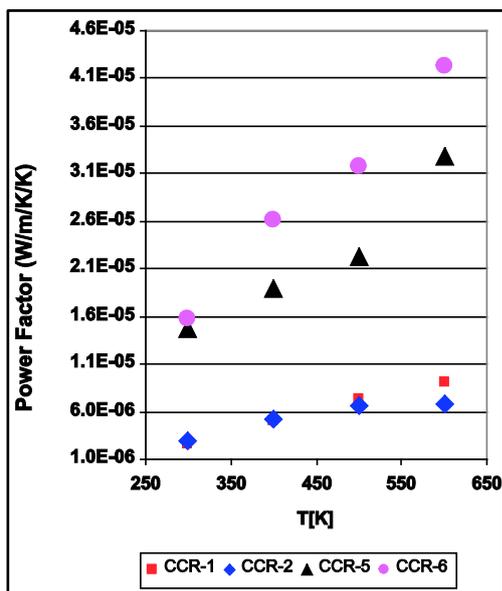


Figure 6. Powerfactor of CaCo_{1-x}Ru_xO_y samples as a function of temperature with powerfactor decreasing with temperature for all the samples.

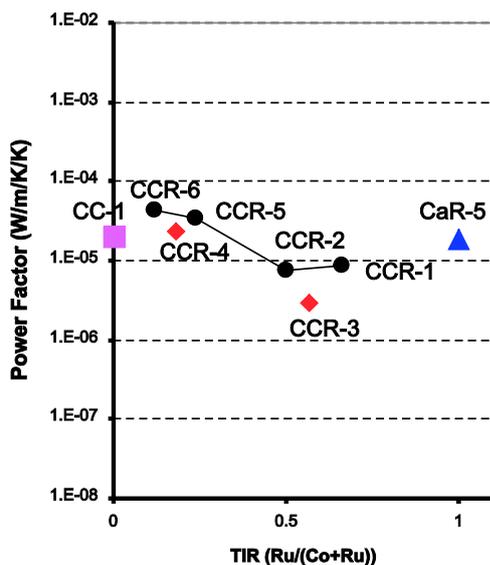


Figure 7. Powerfactor, at 600 K, of CaCo_{1-x}Ru_xO_y samples as a function of TIR shows that change in powerfactor is less than an order of magnitude.

metals, Fe, Ni, Mn and Cu, that Yao *et al.*, used. As a result of the decrease in the thermopower (Figure 6) caused by Ru-substitution of Co ions, the power factor (S^2/ρ) is found to be reduced, though only by less than an order of magnitude, diminishing its value as a prospective thermoelectric material. However, its value as an electrode material is significantly enhanced.

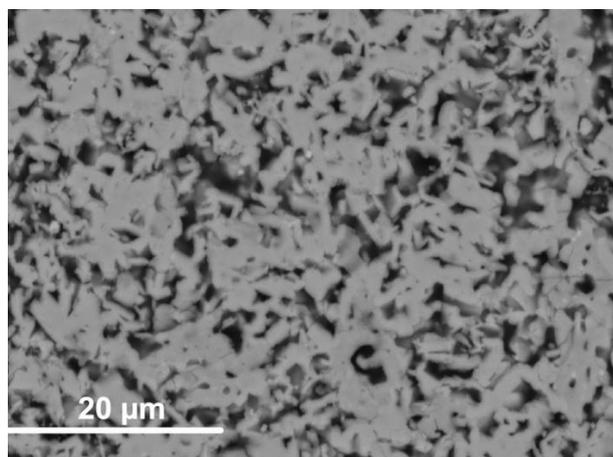
Scanning electron microscopy/EDS analyses performed on the CaCo_{1-x}Ru_xO_y samples reveal that substitution of Ru for Co in the range of compositions (Table 1)

does not lead to the formation of a significant second phase. However, a minority phase (~1% - 2%) has been observed in most samples. The small size of this phase (~1 micron) renders it difficult to precisely determine its composition. Apparently, Ru ions have replaced Co in the major phase or vice versa depending on the composition (Figure 8(a) and Figure 9(a)). However, depending on the composition, two distinctly different microstructures have been observed. The majority phase assumes a needle shaped structure, for compositions having $TIR < 0.5$, such as those observed in samples CCR-5 and CCR-6 (Figure 8(a)). This microstructure is not very different from that of CC-1, the binary calcium cobaltite, as can be observed from Figure 8(b). These compositions (CCR-5 and -6) exhibit higher resistivities as well as higher Seebeck coefficients (Table 1, Figures 4-7) compared to the compositions with $TIR \geq 0.5$. For CCR-1 and -2 which have a $TIR \geq 0.5$, the microstructure contains plate-like crystals as presented in Figure 9(a) (CCR-2). Binary calcium ruthenate (CaR-5), in which the only phase is CaRuO₃, was also demonstrated [27] to have a similar plate-like microstructure, as depicted in Figure 9(b). Compositions with $TIR \geq 0.5$ (CCR-1 & -2) exhibit similar (lower) resistivities and Seebeck coefficients.

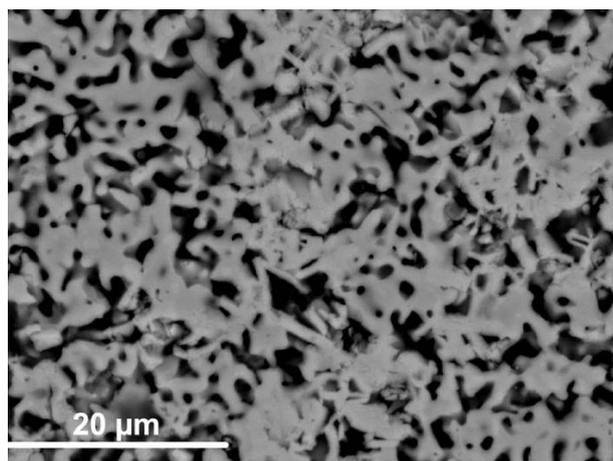
X-ray diffraction patterns of the four CaCo_{1-x}Ru_xO_y samples (CCR-1, 2, 5 and 6) are provided in Figures 10 and 11 along with that of CaR-5 and CC-1 to study the evolution of the phases with increasing TIR . CCR-1 and -2, which have a $TIR \geq 0.5$, have CaRuO₃ as the major phase with CoO and CaO being the minor phases while CaR-5, the binary calcium ruthenate, has only the CaRuO₃ phase as can be observed from Figure 10. The XRD patterns of CCR-6 and -5, which have a $TIR < 0.5$, exhibit the predominance of the Ca₉Co₁₂O₂₈ phase with minor amounts of Ca₃Co₂O₆ (CCR-6) or CaRuO₃ (CCR-5) along with CaO as seen from Figure 11. Ca₃Co₂O₆ and Ca₂Co₂O₅ are the major and minor phases respectively in the CC-1 composition as shown in Figure 11.

Based on the above, it can be proposed that the CaCo_{1-x}Ru_xO_y samples on either side of the central line ($TIR = 0.5$) have similar microstructures, phase assemblage, resistivities and Seebeck coefficients.

Ru has been identified as a unique dopant [29] in ceramic compounds containing transition ion oxides because the electronic structure of Ru, similar to that of the 3d transition metal ions (TI), favors the interactions between the TI and Ru and improves metallicity. This metallicity enhancement with Ru addition has been reported [29] in CaMnO₃ where the ferromagnetic properties of RuO₂ seem to contribute to conductivity enhancement as compared to non-magnetic cations such as Nb and Mo. It was concluded that when CaMnO₃ was doped with Ru, ferromagnetic interactions and thus metallicity were en-



(a)

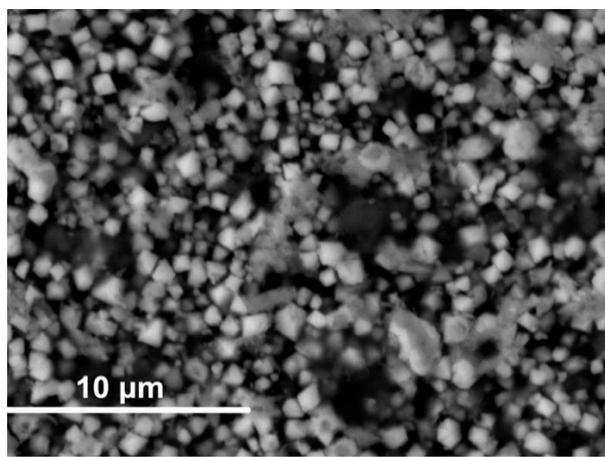


(b)

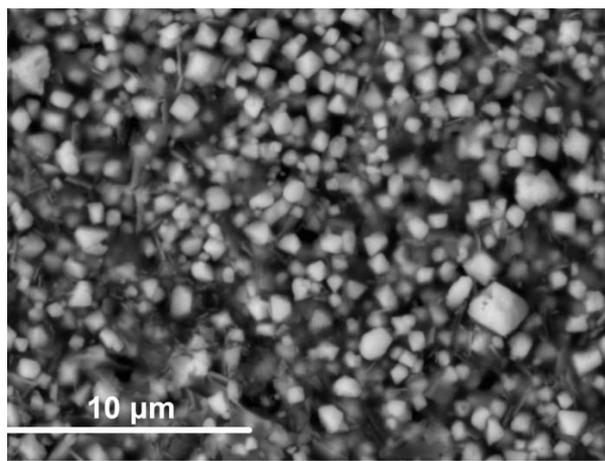
Figure 8. (a) SEM micrograph of the CCR-6 sample, which exhibits microstructure and transport properties similar to the binary calcium cobaltite (CC-1) shown in (b) SEM micrograph of the microstructure of CC-1 sample (binary calcium cobaltite), showing acicular structure.

hanced because of superexchange interactions between Mn and Ru and, furthermore, the e_g electron of Ru⁴⁺ actively participated in the transport phenomena. As the 4*d* orbitals of Ru ions are more extended than its 3*d* counterparts, enhanced orbital overlapping (with TI 3-*d* and oxygen 2-*p* orbitals) takes place, resulting in higher conductivity. The effect of equimolar substitution of cobalt ions by ruthenium on the thermopower also proves the enhanced metallic properties of the ceramic. As a result of this increasing metallicity of the ceramic, the thermopower decreases monotonically.

The effect of Ru-substitution on the thermoelectric properties of CaCo_{1-x}Ru_xO_y samples has been found to be similar to those observed earlier [24] in Ca₃Co_{4-x}Cu_xO_{9+δ}, where Cu substitution for Co ions resulted in the decrease of electrical resistivity and themopower. It was demonstrated that substitution of Cu for Co took place in



(a)



(b)

Figure 9. (a) Microstructure of the CCR-2 sample which has calcium ruthenate as the major phase and has microstructure and transport properties similar to the binary calcium ruthenate shown in (b) Microstructure of CaR-5 [27] showing plate like structure of binary calcium ruthenate.

the Ca₂CoO₃ layer, while substitution by Fe, Ni or Mn took place in CoO₂ layer [24]. Since the CoO₂ layer is the conducting path in these cobaltites, such a “defect” would present itself as a scattering center for the carriers as it would block the passage of the latter, thereby increasing the resistivity and the activation energy for conduction. However, a substitution (Cu for Co) in the Ca₂CoO₃ layers would not disturb the conduction path and the activation energy would remain constant or was even found to be lowered. In Ca₃Co₄O_{9+δ} compounds, the effective carriers are holes, as evidenced from the positive thermopower. Usually, the Co ions are trivalent or tetravalent in the Ca₂CoO₃ layers and the Cu ion is divalent in CuO. The substitution of Cu for the Co in the Ca₂CoO₃ layer increases the hole concentration and leads to an increase in conductivity [24]. In the case of Ru, an

insensitivity of transport properties to compositional variation and also have microstructure, electrical resistivity and thermopower values similar to that of the binary CaR-5. The members of CaCo_{1-x}Ru_xO_y series with $TIR < 0.5$ have a different microstructure, higher resistivity and higher thermopower compared to the members with $TIR > 0.5$, but similar to that of the binary CC-1 composition. The power factor, however, does not change appreciably with TIR , changing by less than an order of magnitude. These ternary CaCo_{1-x}Ru_xO_y samples may be used for applications where lower resistivity is required, like electrode materials.

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