CaCo$_{1-x}$Ru$_x$O$_y$: Role of Ru/Co Ratio on Its Transport Properties

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**ABSTRACT**

Calcium cobaltites, especially Ca$_3$Co$_4$O$_9$ 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 Co$^{3+}$ ($t_{2g}^6$) and Co$^{4+}$ ($t_{2g}^5$) species is one of the key parameters 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$_x$O$_y$ (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 Ca$_3$Co$_4$O$_9$ exhibits metallic conductivity and extraordinarily large positive thermopower ($s = 125$ µV/K), which demonstrates that dominant carriers in Ca$_3$Co$_4$O$_9$ are holes [3]. Ca$_3$Co$_4$O$_9$ has a two-dimensional (2$d$) layered structure, which consists of alternating stacks of CaO-CoO-CaO rock salt type and CdI$_2$-type hexagonal CoO$_2$ 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 Ca$_3$Co$_4$O$_9$ 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 CoO$_2$ sheets because the other Co ion site is situated in the highly oxygen-deficient Ca$_3$CoO$_{3.4}$ subsystem [5].

Another example of cobalt oxides, the one-dimensional (1-$d$) cobaltite, Ca$_3$Co$_2$O$_6$, is also very attractive for its magnetic properties [1]. The rhombohedral structure of this phase [1] consists of [Co$_2$O$_6$] chains running along
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 Ca₃RuO₄ [10,11], ferromagnetism in SrRuO₃, and Sr₂Ru₂O₁₀ [12,13], superconductivity in Sr₂RuO₄ [14] and metamagnetism and magnetoresistivity in Ca₃Ru₂O₇ [15]. Among the layered ruthenates, the physical properties of Ca₃RuO₄ and CaRuO₃ have been investigated earlier [16-18]. Another family of compounds with the general composition CaMØ₃ (M=Ru and Fe) has evolved 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 4d band is formed through hybridization of Ru-t₂g and O-2p orbitals. The 4d 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 3d 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 3d 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 3d or 4d transition ions. The d-shells of 4d transition metal ions are more extended than their 3d counterparts. This extended nature of 4d electrons enhances orbital overlapping which is expected to influence the transport and thermopower characteristics by affecting the spin state of the 3d 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 CaCo₁₋ₓRuₓO₃ (CCR) have been determined as Co is substituted by Ru ions (up to 33 mol%), keeping CaO invariant at 50 mol%. Two compounds (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 CaCo₁₋ₓRuₓO₃, 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 CaCo₁₋ₓRuₓO₃ 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 muffine 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 crucible at (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\textsubscript{1-\textit{x}}Ru\textsubscript{\textit{x}}O\textsubscript{\textit{y}} Samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Molar Composition</th>
<th>Resistivity at 600 K (ρ)</th>
<th>Seebeck Coefficient at 600 K (S)</th>
<th>Power Factor (S\textsuperscript{2}/ρ)</th>
<th>Ru/(Co+Ru) Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaR-5\textsuperscript{27}</td>
<td>0.54 0.00 0.46</td>
<td>7.50 x 10\textsuperscript{-5}</td>
<td>37</td>
<td>1.83 x 10\textsuperscript{-3}</td>
<td>1.00</td>
</tr>
<tr>
<td>CCR-1</td>
<td>0.50 0.17 0.33</td>
<td>1.42 x 10\textsuperscript{-4}</td>
<td>36</td>
<td>9.11 x 10\textsuperscript{-6}</td>
<td>0.66</td>
</tr>
<tr>
<td>CCR-2</td>
<td>0.50 0.25 0.25</td>
<td>2.23 x 10\textsuperscript{-4}</td>
<td>39</td>
<td>6.86 x 10\textsuperscript{-6}</td>
<td>0.50</td>
</tr>
<tr>
<td>CCR-3</td>
<td>0.56 0.19 0.25</td>
<td>4.70 x 10\textsuperscript{-4}</td>
<td>30</td>
<td>1.96 x 10\textsuperscript{-6}</td>
<td>0.50</td>
</tr>
<tr>
<td>CCR-4</td>
<td>0.45 0.45 0.10</td>
<td>6.94 x 10\textsuperscript{-4}</td>
<td>127</td>
<td>2.31 x 10\textsuperscript{-5}</td>
<td>0.66</td>
</tr>
<tr>
<td>CCR-5</td>
<td>0.50 0.38 0.12</td>
<td>5.65 x 10\textsuperscript{-4}</td>
<td>136</td>
<td>3.29 x 10\textsuperscript{-3}</td>
<td>0.24</td>
</tr>
<tr>
<td>CCR-6</td>
<td>0.50 0.44 0.06</td>
<td>8.24 x 10\textsuperscript{-4}</td>
<td>187</td>
<td>4.24 x 10\textsuperscript{-3}</td>
<td>0.12</td>
</tr>
<tr>
<td>CC-1\textsuperscript{28}</td>
<td>0.47 0.53 0.00</td>
<td>1.11 x 10\textsuperscript{-3}</td>
<td>151</td>
<td>2.08 x 10\textsuperscript{-3}</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Several identical pellets of each CaCo\textsubscript{1-\textit{x}}Ru\textsubscript{\textit{x}}O\textsubscript{\textit{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\textalpha 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\textsubscript{1-\textit{x}}Ru\textsubscript{\textit{x}}O\textsubscript{\textit{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]. The error in temperature measurement was determined at ±0.5 K and the error margin of conductivity measurements is estimated at ±7%.

Thermopower (Seebeck coefficient) of the CaCo\textsubscript{1-\textit{x}}Ru\textsubscript{\textit{x}}O\textsubscript{\textit{y}} samples was measured with a computerized apparatus (SB-100 and K-20, MMR Technologies, Mountain View, California) and Figure 1 shows a schematic 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 ±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\textsubscript{1-\textit{x}}Ru\textsubscript{\textit{x}}O\textsubscript{\textit{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 RuO\textsubscript{2} 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 \textit{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 \textit{TIR} = 1. All the regular CaCo\textsubscript{1-\textit{x}}Ru\textsubscript{\textit{x}}O\textsubscript{\textit{y}} samples (CCR-1, -2, -5 and -6) fall between these two compositions.
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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\textsubscript{1-x}Ru\textsubscript{x}O\textsubscript{y} compositions.

The resistivity data of the CaCo\textsubscript{1-x}Ru\textsubscript{x}O\textsubscript{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\textsubscript{1-x}Ru\textsubscript{x}O\textsubscript{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\textsubscript{1-x}Ru\textsubscript{x}O\textsubscript{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 RuO\textsubscript{2} 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 RuO\textsubscript{2} in the composition. The resistivity decreases from $8.24 \times 10^{-4}$ $\Omega \cdot m$ for CCR-6 (TIR = 0.12) to $1.42 \times 10^{-4}$ $\Omega \cdot m$ 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 $\geq$ 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\textsubscript{1-x}Ru\textsubscript{x}O\textsubscript{y} samples (CCR-1, 2, 5 and 6) are presented in Figure 4 as a function of temperature, which shows that for all the compositions $S$ increases with increasing temperature, in the range of 300 to 600 K. The CaCo\textsubscript{1-x}Ru\textsubscript{x}O\textsubscript{y} samples with TIR $\geq$ 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 RuO\textsubscript{2} content is increased and TIR increases from 0.12 to 0.66. The thermopower of binary calcium cobaltite (CC-1) is 151 $\mu$V/K [28] and...
that of binary calcium ruthenate (CaR-5) is 37 μV/K [27].

As cobalt ions are progressively replaced by ruthenium to form the CaCo$_{1-x}$Ru$_x$O$_y$ 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 μV/K. Unlike the trend observed in resistivity, the thermopower of CaCo$_{1-x}$Ru$_x$O$_y$ 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$_x$O$_y$ (ternary) compositions are considered, the resistivity and Seebeck coefficient vary as expected in a semiconducting system. For the CaCo$_{1-x}$Ru$_x$O$_y$ compositions (Table 1) while the resistivity decreases from $8.24 \times 10^{-4}$ to $1.42 \times 10^{-4}$ Ω m, the Seebeck coefficient also decreases from 187 to 35 μV/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 μV/K respectively, while the binary calcium ruthenate (CaR-5) has a thermopower of 37 μV/K. This behavior of thermopower is similar to that of resistivity discussed earlier for these two samples. This insensitivity of thermopower to RuO$_2$ 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. SrRuO$_3$ and CaRuO$_3$) 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 μV/K.

The power factor, $S^2/\rho$, (or $S^2/\sigma$, where $\sigma$ is the conductivity) of the four CaCo$_{1-x}$Ru$_x$O$_y$ 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$_x$O$_y$ samples at 600 K varies within a rather small range [Figure 7]: $8.6 \times 10^{-6}$ to $4.3 \times 10^{-5}$ W m$^{-1}$ K$^{-2}$. The combined effect of $S$ and $\rho$ 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$_x$O$_y$ compositions is not meager. Comparing the power factors of the binary calcium cobaltite (CC-1) and the CaCo$_{1-x}$Ru$_x$O$_y$ 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 4$d$ transition metal compared to the 3$d$ transition...
Figure 6. Powerfactor of CaCo$_{1-x}$Ru$_x$O$_y$ 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$_x$O$_y$ 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 ($S^2/\rho$) 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$_x$O$_y$ 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 CaRuO$_3$, 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$_x$O$_y$ 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 CaRuO$_3$ as the major phase with CoO and CaO being the minor phases while CaR-5, the binary calcium ruthenate, has only the CaRuO$_3$ 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 Ca$_3$Co$_2$O$_6$ phase with minor amounts of Ca$_9$Co$_{12}$O$_{28}$ (CCR-6) or CaRuO$_3$ (CCR-5) along with CaO as seen from Figure 11. Ca$_3$Co$_2$O$_6$ and Ca$_2$Co$_2$O$_5$ 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$_x$O$_y$ samples on either side of the central line ($TIR = 0.5$) have similar microstructures, phase assembly, 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 3$d$ 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 CaMnO$_3$ where the ferromagnetic properties of RuO$_2$ seem to contribute to conductivity enhancement as compared to non-magnetic cations such as Nb and Mo. It was concluded that when CaMnO$_3$ was doped with Ru, ferromagnetic interactions and thus metallicity were en-
enhanced because of superexchange interactions between Mn and Ru and, furthermore, the $e_g$ electron of Ru$^{4+}$ 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$_x$O$_y$ samples has been found to be similar to those observed earlier [24] in Ca$_2$Co$_{4-x}$Cu$_x$O$_9$+$\delta$, where Cu substitution for Co ions resulted in the decrease of electrical resistivity and thermopower. It was demonstrated that substitution of Cu for Co took place in the Ca$_2$CoO$_3$ layer, while substitution by Fe, Ni or Mn took place in CoO$_2$ layer [24]. Since the CoO$_2$ 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 Ca$_2$CoO$_3$ layers would not disturb the conduction path and the activation energy would remain constant or was even found to be lowered. In Ca$_2$Co$_{4-x}$O$_{9+\delta}$ compounds, the effective carriers are holes, as evidenced from the positive thermopower. Usually, the Co ions are trivalent or tetravalent in the Ca$_2$CoO$_3$ layers and the Cu ion is divalent in CuO. The substitution of Cu for the Co in the Ca$_2$CoO$_3$ layer increases the hole concentration and leads to an increase in conductivity [24]. In the case of Ru, an
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Recently, it has been demonstrated by Tran and others [31], using x-ray photoemission spectroscopy and a cluster model calculation, that considerable hybridization of the Cu 3d and Ru 4d orbitals exist in CaCu\textsubscript{1-x}Ru\textsubscript{x}O\textsubscript{y} and render the Ru 4d electrons highly itinerant. In our system, it was found that equimolar substitution of Co (3d) by Ru (4d) reduces the resistivity as well as the thermopower of the system. This reduction in resistivity and thermopower supports the contention of Tran et al. [31] and indicates that Co 3d and Ru 4d orbitals do overlap and render the Ru-substituted CaCo\textsubscript{1-x}Ru\textsubscript{x}O\textsubscript{y} samples more conductive (metallic). Thus the decrease in resistivity and thermopower may be ascribed to the superior overlapping of the O 2p, Co 3d and Ru 4d orbitals as compared to the binary calcium cobaltite system facilitating transport of the carriers.

It was observed that when Co was substituted by various 3d transition metals such as Fe, Ni, Mn or Cu (to the extent of 0.6 moles), the maximum power factor variation was 0.5 times the value before substitution [24]. In the present investigation where Ru was substituted for Co (to the extent of only 0.33 moles), the power factor variation observed is from 2 (up) to 2.4 (down) times the value observed before substitution. As the 4d orbitals of Ru ions are more extended than its 3d counterparts, like that of Fe, Ni, Mn or Cu, enhanced orbital overlapping (with Co 3d and oxygen 2p orbitals) takes place, resulting in higher conductivity. This enhanced orbital overlapping also reduces the band gap, resulting in the reduction of thermopower [32]. Thus increased metallicity due to enhanced orbital overlapping explains the higher reduction/increase in the power factor of Ru substituted calcium cobaltite samples compared to the other 3d transition metal, such as Fe, Ni, Mn or Cu, substituted calcium cobaltite samples.

4. Conclusion

Effective substitution of Co by Ru ions in the calcium-cobalt-ruthenium oxide system (CCR), represented by the general formula CaCo\textsubscript{1-x}Ru\textsubscript{x}O\textsubscript{y}, with x varying from 0.06 to 0.33, has been demonstrated without the formation of a substantial second phase. Both thermopower and resistivity of the CaCo\textsubscript{1-x}Ru\textsubscript{x}O\textsubscript{y} samples decrease sharply until a TIR, (Ru/Co + Ru ratio), of 0.5 is reached, beyond which they are insensitive to the TIR. The Seebeck coefficient varies from 187 $\mu$V/K, at a TIR of 0.12, to 35 $\mu$V/K, at a TIR of 0.66, while the resistivity decreases from $8.2 \times 10^{-4}$ to $1.4 \times 10^{-4}$ $\Omega$·m in the same TIR range. The decrease in thermopower and resistivity is suggested to be caused by efficient orbital overlapping of the 4d Ru orbitals with Co 3d and oxygen 2p orbitals. Based on the transport properties, the members of the CaCo\textsubscript{1-x}Ru\textsubscript{x}O\textsubscript{y} series having higher TIR (≥0.5) are found to behave similar to the calcium ruthenates, i.e. relative...
insensitivity of transport properties to compositional variation and also have a different microstructure, electrical resistivity and thermopower values similar to that of the binary CaR-5. The members of CaCo₃₋ₓRuₓO₇ 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 CaCo₃₋ₓRuₓO₇ samples may be used for applications where lower resistivity is required, like electrode materials.

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REFERENCES


CaCo$_1$$_x$Ru$_x$O$_y$: Role of Ru/Co Ratio on Its Transport Properties


