Unusually Small Thermal Expansion of Ordered Perovskite Oxide CaCu$_3$Ru$_4$O$_{12}$ with High Conductivity

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Abstract: We measured the coefficient of thermal expansion (CTE) of conducting composite ceramics 30 vol.% CuO-mixed CaCu$_3$Ru$_4$O$_{12}$ together with CaCu$_3$Ru$_4$O$_{12}$ and CuO. Although conducting ceramics tend to show higher CTE values than insulators, and its CTE value does not match with other ceramic materials, the CTE of CaCu$_3$Ru$_4$O$_{12}$ (7–9 $\times$ 10$^{-6}$/K) was as small as those of insulators such as CuO (9 $\times$ 10$^{-6}$/K), alumina (8 $\times$ 10$^{-6}$/K), and other insulating perovskite oxides. We propose that the thermal expansion of CaCu$_3$Ru$_4$O$_{12}$ was suppressed by the Cu-O bond at the A-site due to the Jahn–Teller effect. This unusually small CTE of CaCu$_3$Ru$_4$O$_{12}$ compared to other conducting oxides plays a vital role enabling successful coating of 30 vol.% CuO-mixed CaCu$_3$Ru$_4$O$_{12}$ thick films on alumina substrates, as demonstrated in our previous study.

Keywords: ceramics heater; conducting oxide; perovskite; thermal expansion

1. Introduction

The coefficient of thermal expansion (CTE) and matching the thermal expansion between different materials are important factors when processing brittle ceramic materials that require high sintering temperatures. Currently, in order to use the heat resistance and functions of ceramic materials, devices containing heterogeneous ceramics with ceramic/ceramic or metal/ceramic interfaces have been actively developed using cofiring [1,2], printing [3,4], and coating [5–10] processes in various industrial fields, including energy [11–13], automotive [14,15], and healthcare [16,17]. Since the target ceramic materials are rarely well-sintered at the desired position when sintered with other materials, the thermal expansion needs to be tailored by optimizing the process, adding complementary materials, or controlling the composition of the ceramic [18,19]. In the case of devices using functional materials, such as perovskite oxides with CTE values often higher than those of other oxides, their thermal expansion behavior has been extensively investigated. When the perovskite composition is modified by the addition of other materials for thermal expansion matching, the properties of the original material may be degraded.

We have focused on the conducting oxide CaCu$_3$Ru$_4$O$_{12}$ [20–24] as an alternative conducting material to replace Pt in various high-temperature electrical devices, such as gas sensors [16] and solid oxide fuel cells [25], and have studied its physical properties and processing [26,27]. CaCu$_3$Ru$_4$O$_{12}$ is an ordered perovskite oxide, the crystal structure of which is shown in the schematic diagram in Figure 1a.
The resistivity is lower than 1 m·Ω·cm, even at 500 °C, and the temperature dependence shows metallic behavior, which is rarely seen in oxides, as shown in Figure 1b (black plot). Although CaCu$_3$Ru$_4$O$_{12}$ is difficult to sinter, we overcame this drawback by adding CuO as a sintering additive, which enabled the fabrication of dense bulks and thick films on alumina substrates [26]. The temperature dependences of the resistivity of 20 vol.% CuO-mixed CaCu$_3$Ru$_4$O$_{12}$ bulk and thick film are shown in Figure 1b. The thick film showed resistivity as low as the bulk sample. Scanning Electron Microscope (SEM) images of the thick film are shown in Figure 1c–e, where CaCu$_3$Ru$_4$O$_{12}$ grains were firmly bound to adjacent CaCu$_3$Ru$_4$O$_{12}$ grains and to the alumina substrate without cracks and peeling. Recently, we tried to fabricate a SnO$_2$ gas sensor using CuO-mixed CaCu$_3$Ru$_4$O$_{12}$ thick films as electrodes and heater instead of Pt on an alumina substrate [28]. Our trial successfully showed similar sensing performance as the sensor using Pt. In addition, CuO-mixed CaCu$_3$Ru$_4$O$_{12}$ thick film heaters on alumina substrates were robust against thermal shock and rapid thermal cycling.

![Crystal structure of CaCu$_3$Ru$_4$O$_{12}$](image-a)

![Temperature dependence of the resistivity](image-b)

![Cross-sectional SEM image](image-c)

![Magnified images](image-d)

![Magnified images](image-e)

**Figure 1.** (a) Crystal structure of CaCu$_3$Ru$_4$O$_{12}$. (b) Temperature dependence of the resistivity of a CaCu$_3$Ru$_4$O$_{12}$ bulk, a 20 vol.% CuO-mixed CaCu$_3$Ru$_4$O$_{12}$ bulk, and a 20 vol.% CuO-mixed CaCu$_3$Ru$_4$O$_{12}$ thick film. (c) Cross-sectional SEM image of a 20 vol.% CuO-mixed CaCu$_3$Ru$_4$O$_{12}$ thick film on an alumina substrate. (d) and (e) are magnified images of the film and the film–substrate interface, respectively, shown in (c).

We observed that CaCu$_3$Ru$_4$O$_{12}$ and CuO can be easily compounded, and the composite thick film showed excellent sintering on an alumina substrate without any cracks. We further observed that the thick film heater showed excellent durability against rapid heat cycles. All these findings were truly unexpected for a conventional ceramic device. Hence, in this study, we investigated the thermal expansion of CaCu$_3$Ru$_4$O$_{12}$, CuO, and CuO-mixed CaCu$_3$Ru$_4$O$_{12}$ in order to clarify the reason for the excellent properties of our ceramic device. In addition, we compared the thermal expansion of CaCu$_3$Ru$_4$O$_{12}$ with that of other perovskite oxides.

2. Experimental

CaCu$_3$Ru$_4$O$_{12}$ was prepared via a solid-state reaction [22,26,29]. Stoichiometric mixtures of CaCO$_3$, CuO, and RuO$_2$ were pressed into pellets and calcined in air at 1000 °C for 48 h. The pellets
were covered by a mixture of excess CaCO₃, CuO, and RuO₂ powders to prevent Ru sublimation during sintering and subsequent deviations from the desired composition. The CaCu₃Ru₄O₁₂ powder was obtained via mechanical grinding and ball-milling of the calcined pellets.

The CaCu₃Ru₄O₁₂ powder was then mixed with CuO powder (as a sintering additive), then pressed into a pellet and sintered at 1000 °C for 48 h in air. The CuO volume fraction in the bulk was 30 vol.% corresponding to 29.5 wt.%. The volume fraction was calculated using the molecular weights and lattice constants of each material. A CuO bulk sample was obtained by calcining a pressed pellet of CuO powder under the same conditions as the 30 vol.% CuO-mixed CaCu₃Ru₄O₁₂ bulk sample. The relative densities of the 30 vol.% CuO-mixed CaCu₃Ru₄O₁₂ and CuO bulk samples were 73% and 92%, respectively.

X-ray diffraction (XRD) of the CaCu₃Ru₄O₁₂ powder was performed using a standard diffractometer with parallel-beam optics of Cu Ka radiation in the 2θ-θ scan mode (X’Pert Pro MPD, Malvern Panalytical, Malvern, UK) at 25, 100, 200, 300, 400, 500, 600, 700, 800, and 900 °C using a reactor chamber (XRK900, Anton Paar, Graz, Austria) in air [30]. The XRD patterns at all temperatures were analyzed using the Rietveld method [31] and we calculated the lattice constants using the reported space group and crystal structural parameters as the initial value [32]. The CTEs of 30 vol.% CuO-mixed CaCu₃Ru₄O₁₂ and CuO bulk samples were measured in air using a thermomechanical analyzer (TMA; Thermo Plus EVO2, Rigaku, Tokyo, Japan).

3. Results and Discussion

Figure 2 shows the XRD pattern for CaCu₃Ru₄O₁₂ powder measured at 25 °C. All peaks were well-indexed to those of CaCu₃Ru₄O₁₂ [32] and no heterogeneous or impurity phases were identified. Figure 3a shows the lattice constant of CaCu₃Ru₄O₁₂ calculated from powder XRD, plotted as a function of temperature. CaCu₃Ru₄O₁₂ belongs to a large family of ordered perovskites described by the general formula AC₃B₄O₁₂, and can be considered as a fourfold superstructure of the ABO₃ perovskite shown in Figure 1a. The lattice constant increased with increasing temperature, indicating positive thermal expansion, similar to other conventional oxide materials. The plot represents the lattice constant a for the cubic structure, from which the relative thermal expansion and CTE values were evaluated.

![Figure 2](image_url)

**Figure 2.** X-ray diffraction (XRD) (CuKα) pattern of CaCu₃Ru₄O₁₂ powder measured at 25 °C.

Considering the potential applications of the perovskite, the thermal expansion should be evaluated using TMA. However, here the CTE of CaCu₃Ru₄O₁₂ had to be calculated from the lattice constant because CaCu₃Ru₄O₁₂ could not be fully sintered. Figure 3b shows the thermal expansion...
relative to the value at 25 °C (ΔL/L25) for the 30 vol.% CuO-mixed CaCu3Ru4O12 and CuO bulk samples measured using TMA, together with that of CaCu3Ru4O12 calculated from the data shown in Figure 3a. The thermal-expansion curves of CaCu3Ru4O12 and CuO were nearly identical between 25 °C and 900 °C. Hence, we concluded that the addition of 30 vol.% CuO to CaCu3Ru4O12 did not significantly affect thermal-expansion behavior, although a detailed analysis was not performed [33]. This good thermal-expansion match is the reason that no serious cracks or exfoliation at the interface between CaCu3Ru4O12 and CuO were observed in the composite material; this supports the results of our previous study where we successfully used CuO as a sintering additive for CaCu3Ru4O12 [26].

Figure 3c shows the temperature dependence of the CTE of the 30 vol.% CuO-mixed CaCu3Ru4O12 bulk, CuO bulk, and CaCu3Ru4O12 samples. The dotted and broken lines show the CTE at 400 °C of alumina and ZrO2, respectively, for comparison, as they are widely used ceramic substrate materials. Although the ΔL/L25 of the three materials were almost the same at all temperatures, the CTEs, which are generally calculated as the differential value of ΔL/L25, were slightly different, especially around room temperature. The CTE curve of the 30 vol.% CuO-mixed CaCu3Ru4O12 bulk sample was located between those of CuO bulk and CaCu3Ru4O12 at all temperatures, showing an acceptable average value. The 30 vol.% CuO-mixed CaCu3Ru4O12 bulk sample showed almost the same CTE value as alumina. Thus, in our previous study, the CuO-mixed CaCu3Ru4O12 thick film was successfully coated and sintered on alumina substrates without cracking or peering due to this good CTE match.

![Figure 3](image-url)

**Figure 3.** (a) Lattice constant of CaCu3Ru4O12 as a function of temperature. (b) Temperature dependence of ΔL/L25 and (c) temperature dependence of the CTE of the 30 vol.% CuO-mixed CaCu3Ru4O12 bulk, CuO bulk, and CaCu3Ru4O12 samples. Data for the 30 vol.% CuO-mixed CaCu3Ru4O12 bulk and CuO bulk were measured using a thermomechanical analyzer (TMA), while those for CaCu3Ru4O12 were calculated from powder XRD.
Inorganic materials have various favorable properties, including conductivity, dielectricity, and magnetism. The CTE ($\alpha$) depends on such properties, as follows: \[\alpha = \alpha_{\text{vib}} + \alpha_{\text{elec}} + \alpha_{\text{mag}} + \alpha_{\text{fe}} + \alpha_{\text{vac}}\] (1)

where $\alpha_{\text{vib}}$, $\alpha_{\text{elec}}$, $\alpha_{\text{mag}}$, $\alpha_{\text{fe}}$, and $\alpha_{\text{vac}}$ correspond to the CTE due to vibrational, electronic, magnetic, ferroelectric contribution, and vacancy formation, respectively. This formula is derived considering that the CTE is the second derivative of the Gibbs energy, where functional materials have higher energies than materials without these properties. Therefore, $\alpha$ of a simple insulator should be the lowest among ceramic oxide materials, except for ZrW$_2$O$_8$ \cite{35} and LaCu$_3$Fe$_4$O$_{12}$ \cite{36}, which show negative thermal expansion due to peculiar mechanisms, such as lattice bending and valence transitions. Since CaCu$_3$Ru$_4$O$_{12}$ shows particularly high electrical conductivity compared to other perovskite oxides, its $\alpha_{\text{elec}}$ and $\alpha$ values are expected to be larger than those of other materials.

Let us compare CaCu$_3$Ru$_4$O$_{12}$ with other ABO$_3$-type oxides; Table 1 shows the CTE, conducting behavior, B-site cation, electron orbital of the B-site cation, and the number of d-electron of various oxides. Here, we focus on simple ABO$_3$-type oxides in order to simplify the comparison and discussion. The CTE values were taken directly from the references, or calculated from the temperature dependence of the lattice volume. In this paper, the materials are classified as conductor or insulator using 10 $\Omega$cm of resistivity at room temperature as a threshold. As expected, the conductors Sr$_{0.8}$La$_{0.2}$TiO$_3$, SrRuO$_3$, La$_0.6$Sr$_{0.4}$Fe$_{0.2}$Co$_{0.8}$O$_{3-\delta}$, SrCoO$_3$, LaCoO$_3$, and LaCo$_{0.5}$Ni$_{0.5}$O$_3$ show larger CTE values than materials with insulating, ferroelectric, or dielectric properties. However, the CTE of CaCu$_3$Ru$_4$O$_{12}$ is remarkably small compared to other conductors. La$_{0.6}$Sr$_{0.4}$Fe$_{0.2}$Co$_{0.8}$O$_{3-\delta}$, SrCoO$_3$, and LaCoO$_3$ are used as cathode materials in solid oxide fuel cells, and many oxygen vacancies are generated at high temperature; hence, $\alpha_{\text{elec}}$ and $\alpha_{\text{vac}}$ strongly contribute to $\alpha$ in these materials.

| Material       | CTE ($\times 10^{-5}$K) | Conduction Behavior | B-Site Cation | Electron Orbital of B-Site Cation | Number of D-Electron |
|----------------|--------------------------|---------------------|---------------|----------------------------------|----------------------|
| MgTiO$_3$      | [34]                     | 10.1                | Insulator     | Ti$^{4+}$                        | 3d$^0$               | 0                    |
| CaTiO$_3$      | [34]                     | 11.6                | Insulator     | Ti$^{4+}$                        | 3d$^0$               | 0                    |
| BaTiO$_3$      | [34]                     | 12.1                | Insulator     | Ti$^{4+}$                        | 3d$^0$               | 0                    |
| Sr$_2$La$_2$TiO$_3$ | [37]             | 12.5                | Conductor     | Ti$^{4+}$                        | 3d$^0$               | 0                    |
| LaNiO$_3$     | [34]                     | 13.7                | Insulator     | Ni$^{3+}$                        | 3d$^0$               | 0                    |
| CaHfO$_3$     | [34]                     | 9.6                 | Insulator     | Hf$^{4+}$                        | 5d$^0$               | 0                    |
| LiTaO$_3$     | [34]                     | 13.3                | Insulator     | Ta$^{5+}$                        | 5d$^0$               | 0                    |
| KTaO$_3$      | [34]                     | 7.01                | Insulator     | Ta$^{5+}$                        | 5d$^0$               | 0                    |
| YVO$_3$       | [38]                     | 6.4                 | Insulator     | V$^{3+}$                         | 3d$^2$               | 2                    |
| LaCrO$_3$     | [34]                     | 9.2                 | Insulator     | Cr$^{3+}$                        | 3d$^3$               | 3                    |
| YMnO$_3$      | [34]                     | 11.2                | Insulator     | Mn$^{3+}$                        | 3d$^4$               | 4                    |
| LaMnO$_3$     | [34]                     | 10.9                | Insulator     | Mn$^{3+}$                        | 3d$^4$               | 4                    |
| SrRuO$_3$     | [39]                     | 12.7                | Conductor     | Ru$^{3+}$                        | 4d$^4$               | 4                    |
| CaCu$_3$Ru$_4$O$_{12}$ | [34]             | 8.9                 | Conductor     | Ru$^{4+}$                        | 4d$^4$               | 4                    |
| LaFeO$_3$     | [34]                     | 9.7                 | Insulator     | Fe$^{3+}$                        | 3d$^5$               | 5                    |
| La$_{0.4}$Sr$_{0.6}$Fe$_{0.2}$Co$_{0.8}$O$_{3-\delta}$ | [19]           | 21.4                | Conductor     | Fe$^{3+}$, Co$^{3+}$             | 3d$^5$, 3d$^6$       | 5.8                  |
| SrCoO$_3$     | [34]                     | 15.6                | Conductor     | Co$^{4+}$                        | 3d$^5$               | 5                    |
| LaCoO$_3$     | [34]                     | 23.1                | Conductor     | Co$^{4+}$                        | 3d$^6$               | 6                    |
| LaCo$_{0.5}$Ni$_{0.5}$O$_3$ | [40]        | 15.1                | Conductor     | Co$^{3+}$, Ni$^{3+}$             | 3d$^6$, 3d$^7$       | 6.5                  |
| ErNiO$_3$     | [41]                     | 8.1                 | Insulator     | Ni$^{3+}$                        | 3d$^7$               | 7                    |
| CaSnO$_3$     | [34]                     | 9.2                 | Insulator     | Sn$^{4+}$                        | 4d$^{10}$            | 10                   |

The CTE values are quoted at 500 °C; for the datasets where this value was not stated, the data were linearly extrapolated to 500 °C.

The conduction behavior of the perovskite oxides correlates with the number of d-electrons in the B-site cation. Hence, CTE values are plotted as a function of the number of d-electrons in Figure 4, where the conduction behavior of each material is represented by symbols. The CTE values...
of all insulators are located in the lower part of the figure, consistent with the theory expressed by Equation (1). Although the ferroelectric materials, such as BaTiO$_3$, LiTaO$_3$ and LiNbO$_3$, are electrically insulating, they show relatively large CTE values compared to the other insulators because of structural deformations due to polarization. Almost all conductors show CTE values larger than $10 \times 10^{-6}/K$, where that of CaCu$_3$Ru$_4$O$_{12}$ is surprisingly small, despite of its high electrical conductivity. CaCu$_3$Ru$_4$O$_{12}$ and SrRuO$_3$ are closely related materials; they both show high conductivity and have Ru occupying the B-site of perovskite. However, the CTE values of these materials are significantly different, where CaCu$_3$Ru$_4$O$_{12}$ has a smaller value than the simple SrRuO$_3$ perovskite. The structural difference between those materials is that Ca and Cu are ordered at the A-site of the perovskite structure in CaCu$_3$Ru$_4$O$_{12}$. Cu does not usually occupy the A-site because Cu$^{2+}$ normally appears in 6 coordination. However, Cu in CaCu$_3$Ru$_4$O$_{12}$ is stabilized at the A-site owing to the Jahn–Teller effect. CuO octahedra extend in the z-axis direction with separation of the degenerated $e_g$ orbital, while Cu$^{2+}$ acts as a large cation and can occupy the A-site. Cu atoms occupy 75% of the A-site in CaCu$_3$Ru$_4$O$_{12}$, and the Cu-O bond, which is stabilized at lower energy via separation of the degenerated $e_g$ orbital, would be stronger than other simple bonds such as Ca-O and Ru-O. If this Cu-O bond is predominant in the thermal expansion of the CaCu$_3$Ru$_4$O$_{12}$ lattice, the thermal expansion will be similar to that of CuO, as shown in Figure 3b. Such a contribution of the A-site cation to the thermal expansion is a novel feature of ordered perovskite and is a great advantage in material design and applications.

Finally, we show the heater characteristics of a 30 vol.% CuO-mixed CaCu$_3$Ru$_4$O$_{12}$ thick-film heater on an alumina substrate realized by the unusually small thermal expansion of CaCu$_3$Ru$_4$O$_{12}$ and CTE matching between CaCu$_3$Ru$_4$O$_{12}$ and alumina. The thick-film heater was fabricated on an alumina substrate (3.0 × 25 × 0.3 mm) by screen-printing a paste of CuO and CaCu$_3$Ru$_4$O$_{12}$ powders mixed in a suitable vehicle. Figure 5a shows a photograph and a thermal-camera image while 32 V DC voltage was applied to the 30 vol.% CuO-mixed CaCu$_3$Ru$_4$O$_{12}$ thick-film heater. The meandering heater pattern generates heat up to 600 °C due to Joule heating. Figure 5b shows the temperature ($T$), defined as the maximum temperature over the heater pattern in air as a function of the applied voltage. The temperature increased linearly with applied voltage, expressed as $T = 23.4V - 146$ in units of degrees Celsius; this linear $V$-$T$ characteristic indicates good temperature controllability of the heater. The temperature of the heater under 32.0 V pulses, with a width of 10 s and a cycle length of 20 s, is shown in Figure 5c. The temperature increased immediately from room temperature when the voltage was applied, reaching 600 °C within 9 s. The heater temperature followed the cyclic voltage pulses without degradation, and the performance was maintained after many cycles. It is
clear from these results that the 30 vol.% CuO-mixed CaCu$_3$Ru$_4$O$_{12}$ thick-film heater on an alumina substrate is surprisingly robust and is thought to be reliable enough to be used as a substitute for Pt as a conducting material for various electrical devices.

![Image](image_url)

**Figure 5.** (a) Photograph of the 30 vol.% CuO-mixed CaCu$_3$Ru$_4$O$_{12}$ thick-film heater on the alumina substrate and a thermal-camera image with an applied voltage of 32 V DC. (b) Temperature ($T$), defined as the maximum temperature over the meandering heater pattern, as a function of the applied voltage. (c) Temperature of the heater under cyclic 32.0 V pulses with a width of 10 s and cycle time of 20 s. All experiments were performed in air.

4. Conclusions

We measured the CTE of 30 vol.% CuO-mixed CaCu$_3$Ru$_4$O$_{12}$ and CuO bulk samples using TMA and calculated the CTE of CaCu$_3$Ru$_4$O$_{12}$ from the lattice constant determined using high-temperature XRD measurements. The $\Delta L/L_{25}$ of these materials were nearly identical between 25 °C and 900 °C; we measured the values for CaCu$_3$Ru$_4$O$_{12}$, CuO, and 30 vol.% CuO-mixed CaCu$_3$Ru$_4$O$_{12}$ of $8.27 \times 10^{-6}$ K$^{-1}$, $9.59 \times 10^{-6}$ K$^{-1}$, and $8.60 \times 10^{-6}$ K$^{-1}$, respectively, at 500 °C. These values were similar to those of alumina ($8.0 \times 10^{-6}$ K$^{-1}$). The CTE matches between CaCu$_3$Ru$_4$O$_{12}$/CuO and 30 vol.% CuO-mixed CaCu$_3$Ru$_4$O$_{12}$/alumina explain the successful compounding and coating of these material pairs demonstrated in our previous study. The CTE of CaCu$_3$Ru$_4$O$_{12}$ is smaller than that of other conducting perovskite oxides, and close to the values for insulating perovskite oxides. The unusually small CTE of CaCu$_3$Ru$_4$O$_{12}$ is thought to be due to the influence of Cu occupying the A-site of the perovskite via the Jahn–Teller effect. Such a contribution of the A-site cation in the ordered perovskite material to the thermal expansion offers a novel and superior advantage in material design and applications.
Author Contributions: A.T., I.T., and W.S. conceived and designed the experiments; A.T. performed the experiments; K.N. measured and analyzed high-temperature XRD; A.T., I.T., and W.S. analyzed the data; M.M., Y.K., and N.M. helped with the experiments and discussed the results; A.T. wrote the paper.

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