

# Effect of Cation Substitution on the Lattice Vibration and Crystal Structure of Magnetic $\text{RuSr}_{1.9}\text{A}_{0.1}\text{GdCu}_2\text{O}_8$ ( $\text{A} = \text{Ca}, \text{Sr}, \text{and Ba}$ ) Superconductors

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The lattice vibration and crystal structure of alkaline earth metal-substituted  $\text{RuSr}_{1.9}\text{A}_{0.1}\text{GdCu}_2\text{O}_8$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{and Ba}$ ) have been investigated with micro-Raman spectroscopy. The present  $\text{RuSr}_{1.9}\text{A}_{0.1}\text{GdCu}_2\text{O}_8$  materials show not only several weak Raman peaks corresponding to the vibrations of  $\text{O}_{\text{Cu}}$  and  $\text{O}_{\text{Ru}}$ , but also strong characteristic phonon lines related to  $\text{O}_{\text{Sr}}$  vibration mode. A comparison between the frequency of  $\text{O}_{\text{Sr}}$  vibration and the bond distances of ( $\text{Ru}-\text{O}_{\text{Sr}}$ ) and ( $\text{Cu}-\text{O}_{\text{Sr}}$ ) in the present ruthenocuprates reveals that the vibration energy of  $\text{O}_{\text{Sr}}$  is mainly dependent on the bond distance of ( $\text{Ru}-\text{O}_{\text{Sr}}$ ). The peak splitting of the  $\text{O}_{\text{Sr}}$  phonon lines was observed for the unsubstituted  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ , suggesting the existence of two different ( $\text{Ru}-\text{O}_{\text{Sr}}$ ) bond distances. Such a peak splitting caused by the appearance of low-energy shoulder reflects the presence of internal charge transfer pathway from the  $\text{RuO}_2$  plane to the superconductive  $\text{CuO}_2$  one. After the substitution of Sr with Ca or Ba, the low-energy shoulder peak of  $\text{O}_{\text{Sr}}$  vibration becomes suppressed, underscoring the depression of internal charge transfer between the  $\text{RuO}_2$  and  $\text{CuO}_2$  planes. The weakened role of  $\text{RuO}_2$  layer as charge reservoir in the  $\text{RuSr}_{1.9}\text{A}_{0.1}\text{GdCu}_2\text{O}_8$  ( $\text{A} = \text{Ca}, \text{Ba}$ ) would be responsible for the depression of  $T_c$  upon the Ca/Ba substitution.

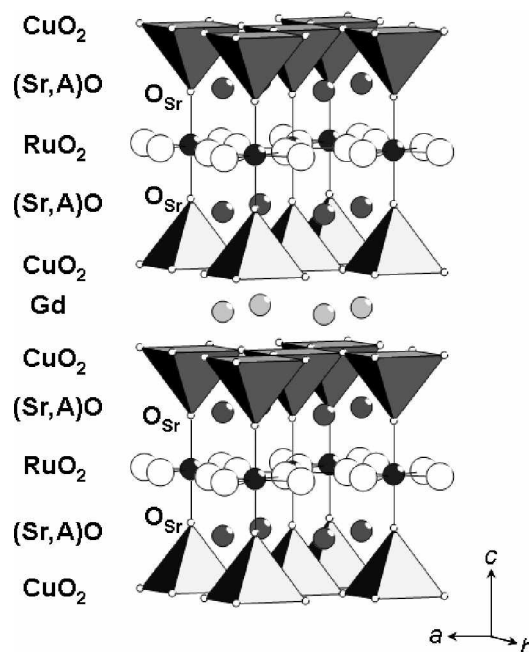
**Key Words:** Micro-Raman spectroscopy,  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ , Alkaline earth metal substitution, Internal charge transfer,  $T_c$  evolution

## Introduction

During the past decade, ruthenocuprates  $\text{RuSr}_2\text{LnCu}_2\text{O}_8$  ( $\text{Ln} = \text{Gd}, \text{Eu}$ ) have received special attention because of the coexistence of magnetic  $\text{RuO}_2$  layers and superconductive  $\text{CuO}_2$  ones in the unit cell.<sup>1-3</sup> As illustrated in Figure 1, both the layers are directly linked by a bridging oxygen ion (denoted as  $\text{O}_{\text{Sr}}$ ). Hence an internal magnetic field in the  $\text{RuO}_2$  layer is believed to significantly affect the superconductivity of the  $\text{CuO}_2$  layers. These magnetic superconductors are of special importance as model compound for studying the interplay between internal magnetic field and superconductivity. There have been several reports claiming that the magnetic coupling of Ru moments induces a pair breaking effect on superconductive  $\text{CuO}_2$  layer.<sup>3-6</sup> In the line of these researches, we have tried to probe the interplay between magnetic coupling and superconductivity in  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  by controlling the inter-layer distance between the  $\text{RuO}_2$  and  $\text{CuO}_2$  layers via the Ca/Ba substitution.<sup>7</sup> We have found that the superconducting transition temperature ( $T_c$ ) of the  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  phase is commonly decreased by the replacement of Sr with Ca or Ba. The  $T_c$  depression upon the Ca/Ba substitution could not be fully understood in term of a change of hole density in the  $\text{CuO}_2$  plane and/or a variation of interlayer distance. In term of oxygen content, the  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  phase is quite different from other copper oxide-based superconductors with excess oxygen, since this compound does not have any excess oxygen. Instead of oxygen nonstoichiometry, the internal charge transfer between the charge reservoir  $\text{Ru}^{4+5+}$ - $\text{O}_2$  layer and the superconductive  $\text{Cu}^{2+3+}$ - $\text{O}_2$  layer is responsible for the hole doping and superconductivity of this ruthenocuprate material.<sup>4,8-10</sup> In the light of this, we have speculated that local structural

frustrations affecting the internal charge transfer would be responsible for the  $T_c$  evolution upon the alkaline earth metal substitution. To verify this speculation, micro-Raman spectroscopy would be one of the most suitable tools because of its sensitivity to local structural distortion as well as to variation of chemical bond strength.<sup>11-15</sup>

In this work, we have carried out micro-Raman spectroscopic



**Figure 1.** Crystal structure of the alkaline earth metal-substituted  $\text{RuSr}_{1.9}\text{A}_{0.1}\text{GdCu}_2\text{O}_8$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{and Ba}$ ).

analysis for the alkaline earth metal-substituted  $\text{RuSr}_{1.9}\text{A}_{0.1}\text{GdCu}_2\text{O}_8$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{and Ba}$ ) to probe the effects of the cation substitution on the lattice vibration and crystal structure of the ruthenocuprate. The origin of  $T_c$  evolution upon the Ca/Ba substitution was discussed on the basis of the obtained information on the accompanying local structural modification.

### Experimental Section

The polycrystalline  $\text{RuSr}_{1.9}\text{A}_{0.1}\text{GdCu}_2\text{O}_8$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{and Ba}$ ) were prepared by heat-treatment for stoichiometric mixture of  $\text{RuO}_2$ ,  $\text{SrCO}_3$ ,  $\text{Gd}_2\text{O}_3$ , and  $\text{CuO}$  at elevated temperature and controlled atmosphere.<sup>7</sup> The single phase nature of the obtained ruthenocuprates was confirmed by XRD measurements using Ni-filtered  $\text{Cu K}\alpha$  radiation with a graphite diffracted beam monochromator. The present micro-Raman spectra were measured with a Dilor-Omars microspectrometer coupled with an optical microscope (spatial resolution of  $1 \mu\text{m}^2$ ) and an intensified 1024-channel photodiode array detector. The samples were excited with the 514.5 nm line of an  $\text{Ar}^+$  laser. All the present spectra were obtained by backscattering from the freshly cleaved surfaces of polycrystalline sample. The resolution of the present spectra was  $3 - 4 \text{ cm}^{-1}$ . In order to prevent possible thermal damage of the sample, the power of the incident laser light was maintained at lower than 5 mW. After each measurement, the sample surface was thoroughly checked to remove the possibility of spectral modification caused by the surface degradation.

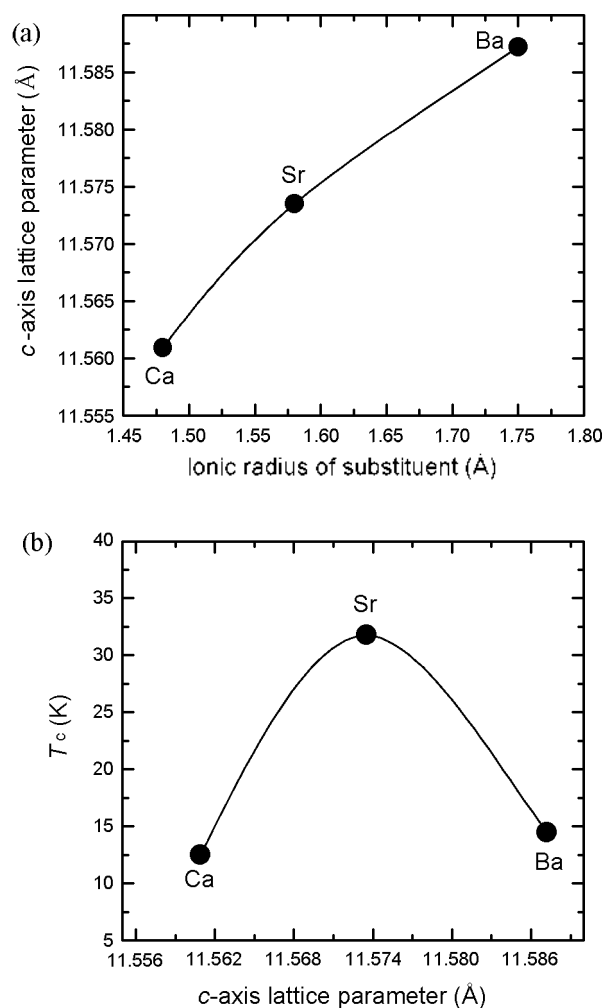
### Results and Discussion

We have examined the relationship between crystal structure and superconductivity in the alkaline earth metal-substituted  $\text{RuSr}_{1.9}\text{A}_{0.1}\text{GdCu}_2\text{O}_8$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{and Ba}$ ). In Figure 2, the  $c$ -axis lattice parameter and  $T_c$  are plotted as a function of the ionic size of substituted alkaline earth metals. There is a pseudo-linear relationship between  $c$ -axis lattice parameter and ionic size. Since the interlayer distance between the adjacent  $\text{CuO}_2$  layers remains nearly unchanged upon the substitution, the observed linear relationship suggests that the interlayer distance between  $\text{CuO}_2$  and  $\text{RuO}_2$  layers can be controlled by the substitution of Ca or Ba for Sr sites. In fact, the Cu K-edge EXAFS analyses clearly demonstrated that the Ca/Ba substitution induces a significant change in the bond distance of  $(\text{Cu}-\text{O}_{\text{Sr}})$ .<sup>7</sup> On the other hand, the  $T_c$  of the present ruthenocuprates shows no distinct correlation with the ionic size of substituents. In case that the pair breaking effect plays important role in the superconductivity of the present ruthenocuprate, the replacement of Sr with larger Ba should lead to the increase of  $T_c$ . But this is not the case. Hence the observed depression of  $T_c$  upon Ca/Ba substitution could not be explained on the basis of variation of lattice parameters. This strongly suggests that the magnetic coupling in  $\text{RuO}_2$  layer has little influence on the superconducting property of  $\text{CuO}_2$  layer.

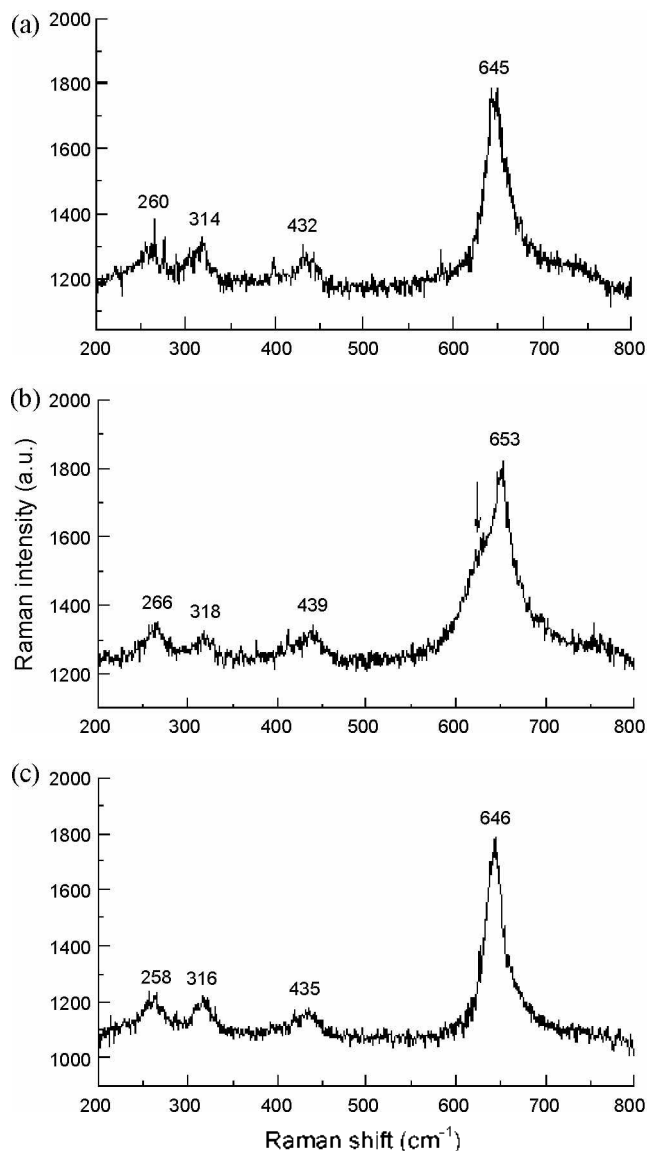
The effect of the alkaline earth metal substitution on the lattice vibration and chemical bonding nature in the magnetic superconductor  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  was investigated with micro-Raman spectroscopy. According to the factor group analysis,<sup>14</sup>

this ruthenocuprate possesses many Raman active modes of  $6A_{1g} + 2B_g + 5B_{2g} + 11E_g$ . As shown in Figure 3, the overall Raman spectral features of the present ruthenocuprates are similar to the previously reported ones.<sup>10,11,14</sup> The strongest peak at  $\sim 640 - 650 \text{ cm}^{-1}$  was interpreted as  $c$ -axis polarized vibration of axial  $\text{O}_{\text{Sr}}$  oxygen while the other phonon lines at  $\sim 318$  and  $\sim 439 \text{ cm}^{-1}$  correspond to the out-of-plane and in-plane vibrations of  $\text{O}_{\text{Cu}}$  ions, respectively.<sup>10,11</sup> In addition, the peak at  $266 \text{ cm}^{-1}$  can be assigned as the  $A_{1g}$  vibration of  $\text{O}_{\text{Ru}}$ .<sup>10,11</sup> As illustrated in Figure 3, the unsubstituted  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  shows a distinct shoulder peak on the low energy side of the strong  $\text{O}_{\text{Sr}}$  phonon line, indicating two different vibration energies of  $\text{O}_{\text{Sr}}$ . Upon the replacement of Sr with Ca or Ba, this shoulder peak of the  $\text{O}_{\text{Sr}}$  vibration becomes suppressed, leading to the merging of the separated  $\text{O}_{\text{Sr}}$  phonon lines into a single peak. Both the Ca/Ba-substituted ruthenocuprates exhibit nearly identical position for the  $\text{O}_{\text{Sr}}$  phonon line, which is similar to the average position of the separated  $\text{O}_{\text{Sr}}$  phonon lines observed for the pristine  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ .

In order to probe main structural factor affecting the vibration frequency of  $\text{O}_{\text{Sr}}$ , we have plotted the bond distances of

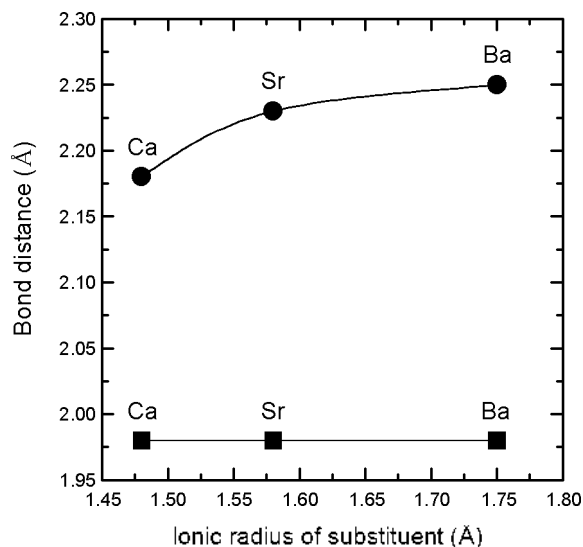


**Figure 2.** Dependences of (a)  $c$ -axis lattice parameter and (b)  $T_c$  on the ionic size of substituted alkali metal ions in  $\text{RuSr}_{1.9}\text{A}_{0.1}\text{GdCu}_2\text{O}_8$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{and Ba}$ ).



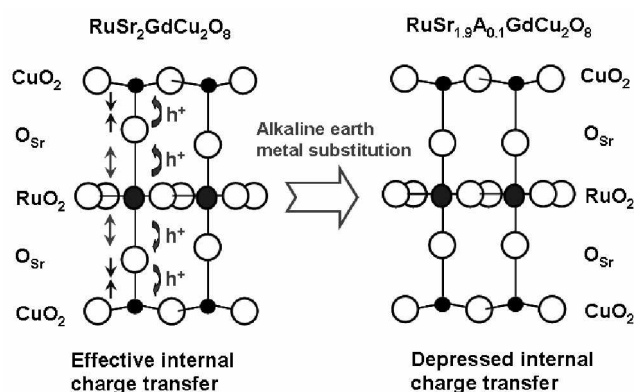
**Figure 3.** Micro-Raman spectra for the alkaline earth metal-substituted  $\text{RuSr}_{1.9}\text{A}_{0.1}\text{GdCu}_2\text{O}_8$  with A = (a) Ca, (b) Sr, and (c) Ba. In (b), the arrow denotes the low energy shoulder peak of  $\text{O}_{\text{Sr}}$  vibration mode.

$(\text{Cu}-\text{O}_{\text{Sr}})$  and  $(\text{Ru}-\text{O}_{\text{Sr}})$  estimated from the previous EXAFS analysis<sup>7</sup> as a function of the ionic radius of substituent alkaline earth metal. As plotted in Figure 4, the replacement of Sr with Ca or Ba gives rise to notable variation of the  $(\text{Cu}-\text{O}_{\text{Sr}})$  bond distance while there is no significant change in the bond length of the  $(\text{Ru}-\text{O}_{\text{Sr}})$  upon the Ca/Ba substitution. Taking into account negligible difference in the vibration frequency of  $\text{O}_{\text{Sr}}$  mode between the Ca- and Ba-substituted ruthenocuprates, the frequency of  $\text{O}_{\text{Sr}}$  vibration is insensitive to the variation of  $(\text{Cu}-\text{O}_{\text{Sr}})$  bond distance but is well correlated with the variation of  $(\text{Ru}-\text{O}_{\text{Sr}})$  bond distance. The latter bond has much shorter distance than the former one,<sup>4,7</sup> implying that bridging  $\text{O}_{\text{Sr}}$  ions are more strongly bound with Ru ions than Cu ones. In this regard, it is reasonable that the  $(\text{Ru}-\text{O}_{\text{Sr}})$  bond has more prominent influence on the vibration frequency of  $\text{O}_{\text{Sr}}$  compared with the  $(\text{Cu}-\text{O}_{\text{Sr}})$  one. In the light of this, the observed



**Figure 4.** Dependences of axial bond distances of  $(\text{Cu}-\text{O}_{\text{Sr}})$  and  $(\text{Ru}-\text{O}_{\text{Sr}})$  on the ionic size of substituent alkali metal ions in  $\text{RuSr}_{1.9}\text{A}_{0.1}\text{GdCu}_2\text{O}_8$  (A = Ca, Sr, and Ba). The circles and squares represent the bond distances of  $(\text{Cu}-\text{O}_{\text{Sr}})$  and  $(\text{Ru}-\text{O}_{\text{Sr}})$ , respectively.

peak splitting of  $\text{O}_{\text{Sr}}$  phonon lines in the pristine  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  material can be regarded as evidence for the presence of two different bond distances of  $(\text{Ru}-\text{O}_{\text{Sr}})$ . Also, this peak splitting of  $\text{O}_{\text{Sr}}$  vibration mode would reflect the flexibility of the  $\text{O}_{\text{Sr}}$  position in the pristine  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  phase, which is advantageous for the internal charge transfer between the  $\text{RuO}_2$  and  $\text{CuO}_2$  layers. Considering the inverse relationship between vibration frequency and bond distance, the shoulder peak at lower energy side should correspond to the  $\text{O}_{\text{Sr}}$  vibration with a longer  $(\text{Ru}-\text{O}_{\text{Sr}})$  bond distance. From the viewpoint of bond competition, the axial  $(\text{Cu}-\text{O}_{\text{Sr}})$  bond linked to the elongated  $(\text{Ru}-\text{O}_{\text{Sr}})$  bond is expected to have a shorter bond distance, as illustrated in Figure 5. In terms of bond valence sum calculation, the shorter  $(\text{Cu}-\text{O}_{\text{Sr}})$  bond distance implies a higher oxidation state of copper ions. That is, the observation of this low energy shoulder peak reflecting the presence of elongated  $(\text{Ru}-\text{O}_{\text{Sr}})$  bond can be interpreted as evidence for internal charge transfer providing the  $\text{CuO}_2$  planes with holes. As plotted in Figure 4, the substitution of Ca or Ba suppresses the low-energy shoulder of  $\text{O}_{\text{Sr}}$  phonon lines, suggestive of the weakened internal charge transfer between the  $\text{RuO}_2$  and  $\text{CuO}_2$  layers. Since the  $T_c$  of the  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  phase is proportional to the hole concentration of  $\text{CuO}_2$  layer,<sup>8,16,17</sup> the depressed role of the  $\text{RuO}_2$  layer as charge reservoir would be responsible for the observed lowering of  $T_c$  upon the Ca/Ba substitution (Figure 1). The observed merging of  $\text{O}_{\text{Sr}}$  vibration mode in the Raman spectra of the Ca/Ba substituted derivatives suggests that the partial replacement of Sr ions with different sized alkaline earth metal ions would decrease the flexibility of  $\text{O}_{\text{Sr}}$  position. This would be due to the change in electrostatic potential field around the  $\text{SrO}$  plane favoring two different  $\text{O}_{\text{Sr}}$  positions. It is worthwhile to mention that the splitting of  $(\text{Ru}-\text{O}_{\text{Sr}})$  bond distances in the unsubstituted  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  was not evident in the previous Ru K-edge EXAFS results.<sup>7</sup> This is because the elongated bonds of axial  $(\text{Ru}-\text{O}_{\text{Sr}})$  in the  $\text{RuSr}_2$



**Figure 5.** Evolution of crystal structure of  $\text{RuSr}_{1.9}\text{A}_{0.1}\text{GdCu}_2\text{O}_8$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{and Ba}$ ) upon the substitution of alkaline earth metal.

$\text{GdCu}_2\text{O}_8$  might be overlapped with in-plane ( $\text{Ru}-\text{O}_{\text{eq}}$ ) bonds with similarly elongated bond distance. Like dynamic Jahn-Teller distortion, the splitting of ( $\text{Ru}-\text{O}_{\text{Sr}}$ ) bond distances is thought to be dynamic at room temperature and hence it is hard to detect this structural variation by powder XRD technique reflecting average crystal structure.

### Conclusion

In this study, we have studied the lattice vibration and crystal structure of the alkaline earth metal-substituted ruthenocuprates  $\text{RuSr}_{1.9}\text{A}_{0.1}\text{GdCu}_2\text{O}_8$  ( $\text{A} = \text{Ca}, \text{Sr}, \text{and Ba}$ ) using micro-Raman spectroscopy. The pristine  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  shows the splitting of  $\text{O}_{\text{Sr}}$  phonon lines, indicative of the presence of two different ( $\text{Ru}-\text{O}_{\text{Sr}}$ ) bond distances and the flexibility of  $\text{O}_{\text{Sr}}$  position. This provides strong evidence for the internal charge transfer between the  $\text{RuO}_2$  and  $\text{CuO}_2$  planes, providing the latter plane with holes. The substitution of Ca or Ba makes the peak splitting of  $\text{O}_{\text{Sr}}$  phonon lines suppressed, implying the weakening of internal charge transfer. Taking into account the fact that the hole density in the  $\text{CuO}_2$  plane is provided by the charge transfer from the hole-reservoir  $\text{RuO}_2$  plane, we can

attribute the  $T_c$  depression upon the Ca/Ba substitution to the depression of the internal charge transfer in the ruthenocuprate.

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