Calcium-free double-layered cuprate superconductors with critical temperature above 100 K

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Calcium is a vital constituent in multilayered cuprate superconductors with critical temperatures ($T_c$) above 100 K, because it plays a key role in separating CuO$_2$ planes. Here, we demonstrate the synthesis of calcium-free double-layered cuprates: Sr$_2$SrCu$_2$O$_4$(X,O)$_2$ ($X = F, Cl,$ and $Br$) and M(Sr,Ba)$_2$SrCu$_2$O$_y$ ($M = Hg/Re, Tl,$ and $B/C$), where strontium exists between the CuO$_2$ planes. Oxylfluoride and mercury-based materials show a $T_c$ of 107 K and 110 K, respectively, which are high compared to existing calcium-free cuprates. These findings indicate $T_c$ greater than 100 K can be realized by replacing both barium and calcium, which have been indispensable in conventional multilayered cuprates, with strontium. Furthermore, the non-toxicity of Sr$_2$SrCu$_2$O$_4$F$_2$ and (B,C)Sr$_2$SrCu$_2$O$_y$ simplifies the synthesis process and ensures their safety in potential applications. We also perform a comparison of the characteristic structural parameters between the calcium-free and calcium-containing cuprates considering the number of CuO$_2$ planes.
Driven by the first report of 30 K superconductivity in a La-Ba-Cu-O system, many structural variations have been achieved in cuprate superconductors, leading to the drastic enhancement of $T_c$ up to 134 K by multilayering CuO$_2$ planes. Using a number of CuO$_2$ planes per formula unit cell, $n$, a typical homologous series can be expressed as $M_{1-n-1}Ae_nCu_{O_2n+2}$, $M_2Ae_nAe\_1Cu_{O_2n+4}$ ($M$: metals such as Hg, Tl, and Bi, and $Ae\_1$: alkaline-earth metals), and $Ae_nAe\_1Cu_{O_2n+2}X_2$ (X: halogen). These are simply referred to as $M_{1-n}Cu_{O_2n}X_2$ ($n$: metal separates the CuO$_2$ planes, forming in finite-layered $Ae\_2CuO_2$ units. In the case of hole-doped single-layered systems ($n = 1$), the O atoms in octahedral coordination surround the Cu atom, whereas in the double-layered systems ($n = 2$), Cu is located at the base of the pyramidal coordination formed by O atoms. On the other hand, for oxyhalide cuprates, the apical O site is occupied by a halogen atom. As can be seen from the chemical formula, the composition and cation framework in the blocking layer are almost unaffected by an increase in $n$. Consequently, with increasing $n$, the structure of the single-layered phase (0201-X or M-1201) pulls in infinite-layered $Ae\_2CuO_2$ units one by one between the blocking layers.

In most such multilayered cuprates, either Ba, Sr, or Ca are employed as the $Ae$ metal; nevertheless, the choice of $Ae$ tends to be limited to metals with relatively small ionic radii, such as divalent Ca and/or trivalent rare-earth cations. Because $n \geq 2$ phases are generally required for $T_c$ exceeding 100 K, Ca must be present between the CuO$_2$ planes in their structure. Therefore, pioneering other metals that can separate the CuO$_2$ planes will result in a significant increase in the variety of available cuprate superconductors. Furthermore, if both, $Ae$ and $Ae\_1$ correspond to the same metal, the number of constituent elements is lowered, which possibly simplifies the synthesis process. To the best of our knowledge, La$_2$Sr$_{1-n}$Cu$_{O_2n+1}$ (0212 phase) is the only double-layered cuprate in which Sr separates the CuO$_2$ planes; however, it is known to exhibit no superconductivity due to the lattice disorder associated with the random occupation at the $Ae\_1$ site by the mixing of Sr and La.

Motivated by the considerations presented above, in the present study, we aim to comprehensively develop Ca-free cuprates for various homologous series of $02(n-1)\_n-X(F = F, Cl, and Br), M_{1-2(n-1)n}(M = Hg/Re, Tl, and B/C), and M'_{2-2(n-1)n}(M' = Tl and Bi)$. Specifically, this work focuses on obtaining the multilayered cuprates containing Sr-separated CuO$_2$ planes, via high-temperature pressure synthesis. We consequently provide double-layered phases with $T_c$ above 100 K. Moreover, the relationship between the structural parameters and number of CuO$_2$ planes ($n$) in various cuprate systems is clarified, distinguishing between the $Ae\_1 = Ca$ and Sr cases. We discuss the possibility of further expanding the available range of Ca-free cuprates.

### Results

**Phase formation and structural characterization.** Various multilayered cuprates with $Ae\_1 = Sr$ were synthetically synthesized, and the results are summarized in Table 1. We obtained six types of the Ca-free double-layered phases: 0212-F, -Cl, and -Br, and (Hg,Re)-, Tl-, and (B,C)-1212 systems. Moreover, we confirmed that grain growth of the oxyhalide compounds appears to be stimulated compared to those of (Hg,Re)-, Tl-, and (B,C)-Based samples. Although the 0212-Cl and -Br compounds exhibited no superconductivity down to a temperature of $T = 5$ K, it may be possible to obtain single crystals of the Ca-free cuprates with apical halogens. The absence of superconductivity suggests that the samples are severely underdoped. The difficulty with introducing the hole carriers arising from the size mismatch of ionic radii between Cl$^-$ and O$^2$ has been reported for the $Ae\_1 = Ca$ case. Note that neither $M'_{2-2(n-1)n}$ nor $n = 3$ phases have been obtained under the temperature and pressure conditions adopted in the present study. Figure 1 shows the results of powder X-ray diffraction (XRD) measurement for the Ca-free double-layered cuprates containing Sr.

The main XRD peaks of each pattern were found to be indexed by a tetragonal structure with double CuO$_2$ layers. Although a small amount of impurities was observed, none were superconductors. The lattice parameters calculated based on the least-square method are summarized on the left side of Table 2.

For the 0212-F phase, we found (by accident, and later, intentionally used) that the introduction of a small amount of Sr (OH)$_2$ significantly promotes the formation of this phase, relative to that of the single-layered 0201-F. As illustrated in Fig. 1a and e, the 0212-F phase is clearly more predominant in the sample containing a small amount of added hydrogen ($z = 0.2$). In this

### Table 1 Phase availability of various multilayered cuprates with the chemical formulas of $Ae_nAe\_1Cu_{O_2n+2}X_2$, $M_{1-n}Ae_nAe\_1Cu_{O_2n+4}$, and $M_2Ae_nAe\_1Cu_{O_2n+2}$.

| $n$ = 2 | $Ae$ | $Ae\_1$ | 0212-F | 0212-Cl | 0212-Br | (Hg,Re)-1212 | Tl-1212 | (B,C)-1212 | Tl-2212 | Bi-2212 |
|---|---|---|---|---|---|---|---|---|---|---|
| Ca | x | x | x | x | x | x | x | x | x | x |
| Sr | x | x | x | x | x | x | x | x | x | x |

Table 1 Phase availability of various multilayered cuprates with the chemical formulas of $Ae_nAe\_1Cu_{O_2n+2}X_2$, $M_{1-n}Ae_nAe\_1Cu_{O_2n+4}$, and $M_2Ae_nAe\_1Cu_{O_2n+2}$.

| $n$ = 3 | $Ae$ | $Ae\_1$ | 0223-F | 0223-Cl | 0223-Br | (Hg,Re)-1223 | Tl-1223 | (B,C)-1223 | Tl-2223 | Bi-2223 |
|---|---|---|---|---|---|---|---|---|---|---|
| Ca | x | x | x | x | x | x | x | x | x | x |
| Sr | x | x | x | x | x | x | x | x | x | x |

The cross mark (x) implies that there are no reports of phase formation. NS indicates that the structure exists although it is non-superconducting. The temperature in the table represents the reported $T_c$, the Ca-free cuprates synthesized in this work are shown in bold.
regard, we performed the optimization of the starting contents of $x$ and $y$ in Sr$_2$SrCu$_2$O$_{x+F_{1.6}H_z}$. From the results shown in Fig. 1f, the optimal values of $x$ and $z$ were in the range of $x = 4.55 - 4.70$ and $z = 0.15 - 0.25$, respectively. Even though the effect of the slight addition of Sr(OH)$_2$ on phase formation remains unclear, it is likely that OH$^-$ ions do not act as constituents but as a chemical agent, promoting the possible hydrothermal reaction. This is because negatively charged hydride ions (H$^-$) are known to exist only under extremely reduced conditions in several transition metal oxides$^{15-17}$, and therefore cannot coexist with Cu$^{2+}$ ions which are stable under ambient/oxidizing atmospheres. Moreover, for the sample synthesized with the optimized nominal composition, we refined its XRD data based on the Rietveld method. As shown in Fig. 1g and Table 3, the XRD
dependence of magnetic susceptibility ($T_c$) the as-synthesized sample shows a large diamagnetic signal below an increase in for the other Ca-free cuprate systems.

Resistivity was achieved, indicating the emergence of super-magnitude as that of the Ca-containing (B,C)-based cuprates\(^19\).

Sr\(_2\)SrCu\(_2\)O\(_4\)F\(_2\). The lattice parameters re and Ca are replaced by a pure Sr, with the chemical formula of Sr\(_2\)SrCu\(_2\)O\(_4\)F\(_2\). As a preliminary data of the 0212-F system, we con

post-annealing, we measured the $T_c$ curve displayed a metallic behavior down to $T_c = 121$ K, which corresponds to an underdoped region promoted the phase formation of Hg- or Tl-1201 and other impurities relative to that of the target phase. Moreover, to change the doping state from overdoped to underdoped, we also performed the post-annealing under the stronger reducing conditions. The reduction annealing at 500°C and above tended to result in the decomposition of the 1212 phase with the evaporation of Hg or Tl, which suggests the difficulty in controlling the doping states in the underdoped region.

To further increase the variation in $T_c$, we attempt to replace the $Ae$ atoms with Ba. As a result, the (Hg,Re)-1212 and Ti-1212 phases were found to be stabilized, although no double-layered phases were obtained in the apical halogen and (B,C)-based cuprates. Because the isovalent substitution of Ba for Sr leads to lattice expansion reflecting the difference in their ionic radii, we could not obtain the Ti-1212 phase via HP synthesis. Figure 2e and f show the magnetic susceptibility data for the Ca-free cuprates with $Ae = Ba$. The as-synthesized sample displayed superconductivities below $T_c = 80$ and 20 K for (Hg,Re)-1212 and Ti-1212, respectively; moreover, their $T_s$ were enhanced via post-annealing, as is the case with $Ae = Sr$. The magnified XRD patterns around the main peak of (Hg,Re)- and Ti-1212 are plotted in Fig. 2g and h, respectively. Compared to the case with $Ae = Sr$, the full-width at half-maximum (FWHM) with $Ae = Ba$ was widened by $\approx 40$–60 K, implying a relatively poor crystalline

but in a nearly optimal or overdoped state. Additionally, after several trials, we also found that the extra O\(^{2-}\) ions at the apical site are exchanged with F\(^-\) by a topochemical reaction with CuF\(_2\), which resulted in a decrease in the excess hole carriers. This soft chemical method has been effectively adopted in the 0201-F system and plays a major role in improving its $T_c$\(^20\). As illustrated in Fig. 2a, the fluorinated sample exhibited $T_c = 107$ K, which is significantly higher than that of the sample before fluorination. The structure of the fluorinated 0212-F might possess lower symmetry, such as orthorhombic, than that of the as-synthesized sample, because several XRD peaks appear to have split. However, Sr\(_2\)CuO\(_3\)\(_{1.6}\) crystallizing in the K\(_2\)NiF\(_4\)-type structure, has been reported to display the remarkable enhancement of $T_c$ by the rearrangement of the apical oxygen with the orthorhombically modulated structure\(^21\); therefore, the symmetry lowering of 0212-F could originate from the similar effect. Further studies on the detailed effects of the topochemical reaction on the 0212-F structure will provide an important key to unraveling this issue. Since materials obtained by the soft-chemical reduction technique, such as the topochemical fluorination, are known to have a relatively low crystallinity, as represented by broad XRD peaks with the weak intensity.\(^22\)\(^23\) Indeed, the fluorinated 0212-F sample did not exhibit the metallic $\rho-T$ behavior in the normal state, nor did it show the zero resistivity below $T_c$. This result could be attributed to the poor grain connectivity arising from the low-temperature topochemical reaction.

For the (Hg,Re)- and Ti-1212 compounds, we carried out the reduction annealing under vacuum conditions without using CuF\(_2\), based on the speculation that doping states of the as-synthesized samples are overdoped due to high-pressure (HP) synthesis in an oxidizing atmosphere. From XRD measurements on the post-annealed samples, we confirmed an increase of $\approx 1$% in the $a$-axis, empirically indicating a decrease in the oxygen concentration in the sample. Through post-annealing, as depicted in Fig. 2b and c, the $T_s$ of (Hg,Re)-1212 and Ti-1212 drastically increased to 110 and 75 K, respectively. The zero resistivity was also not observed for the annealed (Hg,Re)-1212 sample, implying the introduction of the grain-boundary disorder through the post-annealing process. Further optimization of the annealing conditions will improve this situation. On the other hand, the sample synthesis with a starting composition that corresponds to an underdoped region promoted the phase formation of Hg- or Tl-1201 and other impurities relative to that of the target phase. Moreover, to change the doping state from overdoped to underdoped, we also performed the post-annealing under the stronger reducing conditions. The reduction annealing at 500°C and above tended to result in the decomposition of the 1212 phase with the evaporation of Hg or Tl, which suggests the difficulty in controlling the doping states in the underdoped region.

pattern is well fitted by an identical structure model to that of the conventional Ba\(_2\)CaCu\(_2\)O\(_4\)F\(_2\).\(^18\) The determined crystal structure, as depicted in the inset of Fig. 1g, demonstrates that both the Ba and Ca are replaced by a pure Sr, with the chemical formula of Sr\(_2\)SrCu\(_2\)O\(_4\)F\(_2\). The lattice parameters refined via the Rietveld analysis and those calculated based the least-square method exhibit quite similar $a$- and $c$-axis lengths, as listed in Tables 2 and 3. Therefore, it is reasonable to assume that we have obtained sufficiently reliable values just based on the least-square method for the other Ca-free cuprate systems.

Superconductivity. Figure 2a–d depict the temperature ($T$) dependence of magnetic susceptibility ($M/H$), which revealed that the as-synthesized sample shows a large diamagnetic signal below $T_c = 60, 66, 22,$ and 78 K for 0212-F, (Hg,Re)-1212, Ti-1212, and (B,C)-1212, respectively. Because the as-synthesized (B,C)-1212 sample exhibited the highest $T_c$ without performing the post-annealing, we measured the $T$ dependence of electrical resistivity ($\rho$), as shown in the inset of Fig. 2d. After the $\rho-T$ curve displayed a metallic behavior down to $T_c$ (~78 K), the zero resistivity was achieved, indicating the emergence of superconductivity. The absolute $\rho$-value at 300 K is the same order of magnitude as that of the Ca-containing (B,C)-based cuprates\(^19\). Compared to the optimal $T_c$ of conventional cuprate superconductors, the as-synthesized sample of the other Ca-free cuprates exhibited a relatively low $T_c$, which suggests that these sample are not in an optimally doped state.

As a preliminary data of the 0212-F system, we confirmed that an increase in $x$ in Sr\(_2\)SrCu\(_2\)O\(_4\)F\(_2\)-$x$H\(_x\) ($x = 0.2$), namely, the excess hole doping, demonstrates a systematic decrease in its $T_c$ down to 30 K for $x = 0.6$. These findings imply that the as-synthesized 0212-F sample is at least not in an underdoped state

| System       | $Ae = Ae' = Sr$ | $Ae = Ba, Ae' = Sr$ |
|--------------|-----------------|---------------------|
|              | $a (\lambda)$   | $c (\lambda)$      |
|              | $a (\lambda)$   | $c (\lambda)$      |
| 0212-F       | 3.883           | 20.29               |
| (Hg,Re)-1212 | 3.848           | 12.46               |
| Ti-1212      | 3.821           | 12.25               |
| (B,C)-1212   | 3.893           | 10.87               |

For (Hg,Re)-1212 and Ti-1212, the case where $Ae = Ba$ is also listed.

Table 3 Atomic coordinates of the as-synthesized sample of Ca-free 0212-F.

| Chemical formula: Sr\(_2\)SrCu\(_2\)O\(_4\)F\(_2\), space group: I4/mmm |
|---|---|---|---|---|---|
| Z = 2, $a = b = 3.8815(1)$ Å, $c = 20.8244(6)$ Å, $V = 305.6$ Å\(^3\) |
| Site | Wyckoff | $x$ | $y$ | $z$ | Occ. |
| Sr1  | 2a      | 0  | 0  | 0  | 1    |
| Sr2  | 4e      | 0  | 0  | 0.1721(1) | 1 |
| Cu1  | 4e      | 0  | 0  | 0.4116(1) | 1 |
| O1   | 8g      | 0.5| 0  | 0  | 1    |
| F1   | 4e      | 0  | 0  | 0.2936 | 1 |

The atomic displacement parameter, $U_{eq}$, was commonly set for all atoms and converged to 0.029(1) Å\(^2\). The site occupancies, Occ., were fixed for all crystallographic sites. The best fit provided a weighted-proliferity reliability factor ($R_p$) and expected reliability one ($R_e$) as $R_p = 0.1590$ and $R_e = 0.1265$, respectively, ensuring the validity of our analysis.

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quality. This was supported by the lower $T_c$ and the broader superconducting transition than with $Ae = Sr$ case, which is probably due to the $Ae$ site mixing between Ba and Sr. The lattice parameters determined from the XRD pattern are listed in the right side of Table 2. Both, the $a$- and $c$-axis lengths, increased upon replacing Sr by the larger-sized Ba. The obtained Ca-free cuprate superconductors are essentially stable in air and maintain their bulk superconducting nature for at least one month. Only for the as-synthesized 0212-F sample, the long-term exposure to the air is likely to deteriorate its superconducting volume fraction; however, the fluorinated sample with $T_c = 107$ K is stable.

**Discussion**

Without using Ca, cuprates like 0212-F, (Hg,Re)-1212, Tl-1212, and (B,C)-1212, in which the Sr atom exists between the CuO$_2$ planes, were obtained, and superconductivity was observed at above 100 K, particularly in the 0212-F and (Hg,Re)-1212 systems. Since both the $Ae$ and $Ae'$ sites are occupied by the Sr atom, as represented by the composition of Sr$_2$SrCu$_2$O$_4$F$_2$, we have achieved 100 K-class superconductivity with a minimal number of elements in cuprates. Additionally, the 0212-F and (B,C)-1212 systems contain no toxic elements, such as Hg, Tl, and Pb, which could be a great advantage from a practical application point of view. However, a series of Ca-free cuprates was difficult to obtain particularly in the case of $Ae = Ba$; furthermore, as described in Table 1, the synthesis of $n \geq 3$ members has not been achieved. To discuss these reasons, we considered the relationship among the number of CuO$_2$ planes ($n$), characteristic structural parameters, and their $T_c$, in comparison with typical multilayered cuprates possessing $Ae' = Ca$. Here, we focused on the in-plane and out-of-plane Cu–Cu distances together with their $T_c$ and
Fig. 3 Comparison of the characteristic structural parameters and their $T_c$ for $n$ in the typical homologous series of cuprates with the tetragonal structure. a–d The change in the $d_{\text{Cu}-\text{Cu}}$ in-plane Cu–Cu distance ($d_{\text{Cu}-\text{Cu}}^1$), e–h out-of-plane Cu–Cu distance ($d_{\text{Cu}-\text{Cu}}^2$), and i–l $T_c$, in the optimally doped region of the apical F, (Hg,Re)-, Tl-, and (B,C)-based cuprates, with respect to $n$. The thick solid line and curves are a visual guide. The upper and lower horizontal dotted lines represent the values of $d_{\text{Cu}-\text{Cu}}^1$ ($d_{\text{Cu}-\text{Cu}}^2$) for the infinite-layered SrCuO$_2$ and CaCuO$_2$, respectively. For the Ca-free 0212-F compound, $T_c$ of the fluorinated sample is plotted. Part of data were acquired from the literature.$^{10,18,24,34,39,42,44,45}$ The closed circle and diamond markers represent the data for Ca-free cuprates in the $Ae$ = Sr and Ba cases, respectively. m, n Magnified views near the CuO$_2$ layers in the crystal structure of cuprates with $m = 2$ and $n = 3$ each atom corresponds to $Ae$, $Ae'$, Cu, and O or O/X in order from the largest ball. The horizontal and vertical double arrows represent lengths for $d_{\text{Cu}-\text{Cu}}^1$ and $d_{\text{Cu}-\text{Cu}}^2$, respectively.

Fig. 3a–l compare these parameters for each type of cuprate. The former distance, $d_{\text{Cu}-\text{Cu}}^1$, corresponds to the a-axis length (see Fig. 3m and n). Since the structure of the multilayered cuprate is considered as a hybrid of the infinite-layered and single-layered ($n = 1$) phases, the latter distance, $d_{\text{Cu}-\text{Cu}}^2$ (indicated by the vertical double arrows in Fig. 3m and n), was defined by dividing the obtained c-axis length subtracted from that of the 0201 phase, by the corresponding $n$. Note that the $d_{\text{Cu}-\text{Cu}}^2$ value calculated based on this method may contain a certain amount of uncertainty. However, according to a previously reported data of the crystallographic parameters of (Hg,Re)Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2+x-2}$,$^{24}$ the genuine $d_{\text{Cu}-\text{Cu}}^2$ lengths are 3.156 and 3.153 Å for $n = 2$ and $n = 3$ phases, respectively. These values are <1% longer than those calculated by our definition of $d_{\text{Cu}-\text{Cu}}^2$. The discrepancies of which are significantly smaller than the difference between the ionic radii of Ca$^{2+}$ and Sr$^{2+}$. From Fig. 3a–l, we can identify the following features.

1. For all $Ae'$, the $d_{\text{Cu}-\text{Cu}}^1$ value approaches that of the corresponding infinite-layered compound $Ae'$CuO$_2$. As can be seen from Fig. 3a–c, for 0212-F, (Hg,Re)-1212, and Ti-1212, the a-axis length in the $Ae$ = Sr case agrees well with those of the $Ae$ = Ba and $Ae'$ = Sr cases, where even the $n = 2$ phases have been stably obtained.$^{27,28}$ This implies that the $n = 2$ phase with $Ae$ = $Ae'$ = Sr exhibits good in-plane lattice matching. Further elongating $a$, i.e., replacing $Ae$ = Sr with Ba, could make the structure more unstable. Indeed, as depicted in Fig. 2e–h, a broader superconducting transition and wider FWHM than those in the $Ae$ = Sr case were observed in the susceptibility and XRD data, respectively. However, the $a$-value needs to be increased artificially to obtain $n = 3$ members, and which would be difficult via HP synthesis. As mentioned in the previous section, in the $Ae$ = Ba case, the Ti-1212 phase was indeed obtained by synthesis at the ambient pressure. Generally, a relatively long a-axis above 3.9 Å suggests the formation of an electron-doped cuprate possessing no apical oxygen sites, such as Nd$_2$-Ce$_x$CuO$_4$ (also known as the T' phase)$^{38}$. In this study, the as-synthesized Ca-free 0212-F, (Hg,Re)-1212, and Ti-1212 cuprates are isostructural to the conventional Ca-containing systems with the apical oxygen or halogen; moreover, the reduction annealing and fluorination processes, reducing the oxygen concentration, resulted in an increase in their $T_c$. These experimental results are sufficient to be concluded as the appearance of p-type superconductivity, which suggests that a hole-doped multilayered cuprate with an extremely long a-axis is structurally unstable.

Item 2 indicates that CaCuO$_2$ units are inserted one by one between the blocking layers with increasing n. Considering the difference in the ionic radii between Ca and Sr, the increasing trend of $d_{\text{Cu}-\text{Cu}}^1$ mentioned in item 3 is understandable. According to the results of the structure refinement of the as-synthesized 0212-F, though the analyzed $d_{\text{Cu}-\text{Cu}}^1$ length (3.59 Å) are ~5% longer than that of the infinite-layered SrCuO$_2$, the $d_{\text{Cu}-\text{Cu}}^1$ value are significantly expanded compared to that of CaCuO$_2$(3.18 Å). Note that the $d_{\text{Cu}-\text{Cu}}^3$ of (Hg,Re)-1212 with $Ae$ = Ba and $Ae'$ = Sr exhibits a tendency to deviate from this trend, as depicted in Fig. 3f. Because the change in $T_c$ of this compound through post-annealing was small, as shown in Fig. 2e, the as-synthesized sample was considered to be in the nearly optimally doped state, and consequently, might have a shorter c-axis. Another possibility is that the $Ae$ = Ba site is partially replaced by the smaller-sized Sr, which suppresses the expansion of c. Item 4 suggests that the Ca-free cuprate shows promise as a functional material comparable to a Ca-containing multilayered system. However, the confirmed $T_c$s are slightly
lower than those of the previously reported n = 2 cuprates such as HgBa2CaCu2O8+δ and TlBa2CaCu2O8. This result suggests the existence of cation disorder near the apical site and/or between CuO2 planes, as reported in the literature. Furthermore, as mentioned above, the replacement of Ca by Sr resulted in a significant increase in the dCu–O distance, which may correspond to the application of negative chemical pressure. Since it has been reported that Tc of many cuprate superconductors increases by applying the external pressure, we speculate that the chemical pressure effect is also responsible for the slightly lower Tc in the Ca-free cuprates. On the other hand, with a few exceptions, Fig. 3i–l indicate that the enhancement in Tc with an increase in n. This is a widely accepted rule for various multilayered cuprates; however, as depicted in Fig. 3j, a slight decrease in Tc was confirmed in the Ca-free (Hg-Re)-12(n–1)n system with Ae = Ba, which might be due to the crystallinity in the sample. Reconsidering the synthesis conditions such as the starting materials and compositions, as well as the reaction temperature and pressure, will aid in improving such microstructures.

In summary, we obtained a variety of Ca-free double-layered cuprates for the first time as far as we know, primarily via HP synthesis, and demonstrated that Sr metal can be employed to partition two CuO2 planes. The obtained materials, where Sr occupies both of Ae and Ae' sites, not only can significantly reduce the intermixing of the different atoms at these sites, but also possess no toxic ingredients in the chemical composition, particularly for Sr2SrCu2O4F2 and (B,C)Sr2SrCu2O5. These advantages make the material synthesis process simpler and safer.

The chemical pressure effects on the electronic structure may play a role in the application of negative chemical pressure. Since it has been reported that the electronic properties of the precursors, the entire procedure was performed in a dry-nitrogen-flow. The 0212-F samples were synthesized from a mixture of Sr2CuO3, SrF2, CuO, the oxidizer AgO, and Sr(OH)2 with a CuO weighed in a molar ratio of 2:1 were ground using an agate mortar, and then pelletized (Ø4.7 and ~2 mm thickness) and sealed into an agate mortar, and then pelletized (Ø4.7 and ~2 mm thickness) and sealed into a glass plate. The 0212-F sample with silver paste. Data were collected using the 1D X-ray detector (D/teX Ultra, Rigaku). The lattice parameters were calculated by the least-square method. For the as-synthesized 0212-F, we performed the phase identification and structure refinements based on the Rietveld method using BIOVIA Materials Studio (MS) Reflex software (version 2018 R2). Physical-property measurements. The emergence of superconductivity was evaluated by measuring the temperature (T) dependence of magnetic susceptibility, which was defined as the magnetization (M) divided by the field (H). The sample was first placed inside a plastic straw. Data were collected both, in the zero-field cooling (ZFC) and field cooling (FC) modes, using a SQUID magnetometer (MPMS-XL, Quantum Design), in a temperature range from 5 to 120 K, under a field of H = 10 Oe. We also measured the electrical resistivity (ρ) using the standard four-probe method under the electric current of 1 mA. The sample was shaped into a rectangle with a typical volume of 1 mm3, after which the gold wire (00.03) was attached to the prepared sample with silver paste. Data were collected using the Physical Property Measurement System (PPMS, Quantum Design) while scanning the temperature from 300 to 5 K.

Data availability
The data that support the findings in the current study are available from the corresponding author on reasonable request.

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Author contributions
H.N., K.K., A.I., and H.E. prepared the sample and evaluated their superconducting properties. H.F. and Y.G. performed the structure refinements. H.N., K.K., A.I., S.I., H.O., Y.Y., and H.E. wrote the manuscript. H.N., K.K., A.I., H.F., Y.G., and H.E. discussed the crystal structure and classifications of various cuprates. All authors reviewed the manuscript and provided further suggestions.

Competing interests
The authors declare no competing interests.

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