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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: $\text{Sr}_2\text{SrCu}_2\text{O}_4(\text{X},\text{O})_2$ ($\text{X} = \text{F}$, Cl , and Br) and $M(\text{Sr},\text{Ba})_2\text{SrCu}_2\text{O}_y$ ($M = \text{Hg}/\text{Re}$, Tl , and B/C), where strontium exists between the CuO_2 planes. Oxyfluoride 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 $\text{Sr}_2\text{SrCu}_2\text{O}_4\text{F}_2$ and $(\text{B},\text{C})\text{Sr}_2\text{SrCu}_2\text{O}_y$ 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.

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Driven by the first report of 30 K superconductivity in a La–Ba–Cu–O system¹, many structural variations have been achieved in cuprate superconductors^{2–6}, leading to the drastic enhancement of T_c up to 134 K⁷ 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 $MAe_2Ae'_{n-1}\text{Cu}_n\text{O}_{2n+2}$, $M_2Ae_2Ae'_{n-1}\text{Cu}_n\text{O}_{2n+4}$ (M : metals such as Hg, Tl, and Bi, Ae and Ae' : alkaline-earth metals), and $Ae_2Ae'_{n-1}\text{Cu}_n\text{O}_{2n}X_2$ (X : halogen). These are simply referred to as M -12($n-1$) n , M -22($n-1$) n , and 02($n-1$) n - X , respectively. Their crystal structure is characterized by the alternate stacking of CuO_2 and blocking layers along the tetragonal c -axis⁸. The Ae and O atoms form a rock-salt or fluorite structure as the blocking layer. The Ae' metal separates the CuO_2 planes, forming infinite-layered $Ae'\text{CuO}_2$ 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 atoms⁹. On the other hand, for oxyhalide cuprates, the apical O site is occupied by a halogen atom¹⁰. 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 $Ae'\text{CuO}_2$ 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 cations⁹. Because $n \geq 2$ phases are generally required for T_c exceeding 100 K¹¹, 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' correspond to the same metal, the number of constituent elements is lowered, which possibly simplifies the synthesis process. To the best of our knowledge, $\text{La}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6+y}$ (0212 phase)¹² 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' site by the mixing of Sr and La¹³.

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 ($X = \text{F}$, Cl , and Br), M -12($n-1$) n ($M = \text{Hg/Re}$, Tl , and B/C), and M' -22($n-1$) n ($M' = \text{Tl}$ 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 $Ae' = \text{Ca}$ 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 $Ae' = \text{Sr}$ were systematically 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 $Ae' = \text{Ca}$ case¹⁴. Note that neither $M'-22(n-1)n$ nor $n = 3$ phases have been obtained under the temperature and pressure conditions adopted in the present study. Figure 1a–d show the results of powder X-ray diffraction (XRD) measurements for the Ca-free double-layered cuprates exhibiting superconductivity. 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 ($z \sim 0.2$). In this

Table 1 Phase availability of various multilayered cuprates with the chemical formulas of $Ae_2Ae'_{n-1}\text{Cu}_n\text{O}_{2n}X_2$, $MAe_2Ae'_{n-1}\text{Cu}_n\text{O}_{2n+2}$, and $M_2Ae_2Ae'_{n-1}\text{Cu}_n\text{O}_{2n+4}$.									
$n = 2$									
Ae	Ae'	0212-F	0212-Cl	0212-Br	(Hg,Re)-1212	Tl-1212	(B,C)-1212	Tl-2212	Bi-2212
Ca	Ca	×	49 K ¹⁰	NS ¹⁰	×	×	×	×	×
Sr		99 K ¹⁰	83 K ³⁷	×	90 K ³⁴	75 K ³⁸	105 K ³⁹	78 K ⁴⁰	85 K ⁴¹
Ba		90 K ⁴²	×	×	108 K ²⁴	93 K ³⁰	×	110 K ⁴³	×
Sr	Sr	107 K	NS	NS	110 K	75 K	78 K	×	×
Ba		×	×	×	85 K	36 K	×	×	×
$n = 3$									
Ae	Ae'	0223-F	0223-Cl	0223-Br	(Hg,Re)-1223	Tl-1223	(B,C)-1223	Tl-2223	Bi-2223
Ca	Ca	×	×	×	×	×	×	×	×
Sr		111 K ¹⁰	35 K ¹⁴	×	120 K ³⁴	107 K ⁴⁴	115 K ³⁹	70 K ⁴⁰	110 K ⁴¹
Ba		120 K ⁴²	×	×	132 K ²⁴	133.5 K ⁴⁵	×	125 K ⁴³	×
Sr	Sr	×	×	×	×	×	×	×	×
Ba		×	×	×	×	×	×	×	×
The cross mark (×) 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.

Fig. 1 Phase formation of Ca-free double-layered cuprates. **a–d** Powder X-ray diffraction (XRD) patterns of as-synthesized **a** 0212-F, **b** (Hg,Re)-1212, **c** TI-1212, and **d** (B,C)-1212 samples with $\text{Ae} = \text{Ae}' = \text{Sr}$. For 0212-F, the sample was synthesized with the addition of a small amount of $\text{Sr}(\text{OH})_2$ as a hydrogen source. The indexed peaks are derived from the tetragonal double-layered phase. The black circle, triangle, and diamond markers represent XRD peaks originating from the impurities $\text{Sr}_2\text{CuO}_2\text{F}_2$, Sr_2CuO_3 , and $\text{TiSr}_2\text{CuO}_5$, respectively. For TI-1212, the peak originating from Ag is due to the reduction of the oxidizer AgO . **e** The XRD pattern of an as-synthesized sample with the starting composition of $\text{Sr}_2\text{SrCu}_2\text{O}_{4.4}\text{F}_{1.6}$ without adding hydrogen. The peaks coming from 0201-F ($\text{Sr}_2\text{CuO}_2\text{F}_2$) are indexed, and those indicated by the black asterisk originate from the 0212-F phase. **f** Relationship between the oxygen (x) and hydrogen (y) concentrations in the nominal composition of $\text{Sr}_2\text{SrCu}_2\text{O}_x\text{F}_{1.6}\text{H}_z$. The contour plot indicates the XRD intensity ratio between the (105) and (103) peaks of the 0212-F and 0201-F phases, respectively. The warmer the color, the more predominant the formation of the 0212-F phase within the bulk sample. The verified composition point is represented by an open circle. **g** Rietveld analysis results for the tetragonal $I4/mmm$ phase of 0212-F with the starting composition of $\text{Sr}_2\text{SrCu}_2\text{O}_{4.4}\text{F}_{1.6}\text{H}_{0.2}$. The observed and calculated XRD patterns are represented by I_{obs} and I_{cal} , respectively. A difference curve ($I_{\text{obs}} - I_{\text{cal}}$) and Bragg positions (λ) are shifted appropriately along the y-axis to improve visibility. The partial lack of I_{cal} and the difference data is due to the elimination of impurity-derived peaks, as we performed single-phase analysis. The chemical composition, $\text{Sr}_2\text{SrCu}_2\text{O}_4\text{F}_2$, was estimated by the present fitting. The inset illustrates the refined structure of 0212-F, visualized using VESTA software⁴⁶.

regard, we performed the optimization of the starting contents of x and y in $\text{Sr}_2\text{SrCu}_2\text{O}_x\text{F}_{1.6}\text{H}_z$. From the results shown in Fig. 1f, the optimal values of x and z were in the range of $x = 4.55\text{--}4.70$ and $z = 0.15\text{--}0.25$, respectively. Even though the effect of the slight addition of $\text{Sr}(\text{OH})_2$ 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 $\text{Cu}^{2+\delta}$ 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

Table 2 Lattice constants of the as-synthesized samples of Ca-free 0212-F, (Hg,Re)-1212, Tl-1212, and (B,C)-1212 cuprate superconductors.

System	Ae = Ae' = Sr		Ae = Ba, Ae' = Sr	
	<i>a</i> (Å)	<i>c</i> (Å)	<i>a</i> (Å)	<i>c</i> (Å)
0212-F	3.883	20.29	–	–
(Hg,Re)-1212	3.848	12.46	3.881	12.66
Tl-1212	3.821	12.25	3.880	13.06
(B,C)-1212	3.898	10.87	–	–

For (Hg,Re)-1212 and Tl-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: $\text{Sr}_2\text{SrCu}_2\text{O}_4\text{F}_2$, space group: $I4/mmm$

$Z = 2$, $a = b = 3.8815(1)$ Å, $c = 20.2842(6)$ Å, $V = 305.6$ Å³

Site	Wyckoff	<i>x</i>	<i>y</i>	<i>z</i>	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	0.4116(1)	1
F1	4e	0	0	0.2936	1

The atomic displacement parameter, U_{iso} , was commonly set for all atoms and converged to 0.029(1) Å². The site occupancies, Occ., were fixed for all crystallographic sites. The best fit provided a weighted-profile reliability factor (R_{wp}) and expected reliability one (R_e) as $R_{\text{wp}} = 0.1590$ and $R_e = 0.1265$, respectively, ensuring the validity of our analysis.

pattern is well fitted by an identical structure model to that of the conventional $\text{Ba}_2\text{CaCu}_2\text{O}_4\text{F}_2$ 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 $\text{Sr}_2\text{SrCu}_2\text{O}_4\text{F}_2$. 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, Tl-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 (ρ), as shown in the inset of Fig. 2d. After the ρ –*T* curve displayed a metallic behavior down to T_c (~ 78 K), the zero resistivity was achieved, indicating the emergence of superconductivity. The absolute ρ -value at 300 K is the same order of magnitude as that of the Ca-containing (B,C)-based cuprates¹⁹. 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 $\text{Sr}_2\text{SrCu}_2\text{O}_{4+x}\text{F}_{2-x}\text{H}_x$ ($z = 0.2$), 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

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, $\text{Sr}_2\text{CuO}_{3+\delta}$ crystallizing in the K_2NiF_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 structure²¹; 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 ρ –*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 Tl-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 $<1\%$ 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_c s of (Hg,Re)-1212 and Tl-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.

To further increase the variation in Ae, we attempt to replace the Ae atoms with Ba. As a result, the (Hg,Re)-1212 and Tl-1212 phases were found to be stabilized, although no double-layered phases were obtained in the apical halogen and (B,C)-based compounds. Because the isovalent substitution of Ba for Sr leads to lattice expansion reflecting the difference in their ionic radii, we could not obtain the Tl-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 Tl-1212, respectively; moreover, their T_c 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 Tl-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 ~ 40 – 60% , implying a relatively poor crystalline

Fig. 2 Superconductivity in Ca-free double-layered cuprates. **a–d** Temperature (T) dependence of the magnetic susceptibility (M/H) of **a** 0212-F, **b** (Hg,Re)-1212, **c** TI-1212, and **d** (B,C)-1212 samples with $Ae = Ae' = Sr$, measured under $H = 10$ Oe. For (B,C)-1212, the zero-field electrical resistivity (ρ) as a function of temperature is presented in the inset of **d**. **e, f** M/H vs. T data for **e** (Hg,Re)-1212 and **f** TI-1212 with $Ae = Ba$ and $Ae' = Sr$. The open (closed) circle indicates the data for the as-synthesized (fluorinated or annealed) sample. For all the susceptibility curves, the lower and upper parts of the data branching to lower T corresponds to zero-field cooling (ZFC) and field cooling (FC), respectively. **g, h** Enlarged view near the highest peak in the XRD patterns of the Ca-free **g** (Hg,Re)-1212 and **h** TI-1212 for $Ae = Sr$ (dashed line) and Ba (solid line). Each datum is normalized to the (103) peak intensity. The double arrow indicates the FWHM of the (103) peak.

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, TI-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 $Sr_2SrCu_2O_4F_2$, 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–l** The change in the **a–d** in-plane Cu–Cu distance ($d_{\text{Cu-Cu}}^{\parallel}$), **e–h** out-of-plane Cu–Cu distance ($d_{\text{Cu-Cu}}^{\perp}$), 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 $d_{\text{Cu-Cu}}^{\parallel}$ ($d_{\text{Cu-Cu}}^{\perp}$) 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** $n = 2$ and **n** $n = 3$. 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 $d_{\text{Cu-Cu}}^{\parallel}$ and $d_{\text{Cu-Cu}}^{\perp}$, respectively.

Fig. 3a–l compare these parameters for each type of cuprate. The former distance, $d_{\text{Cu-Cu}}^{\parallel}$, 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, $d_{\text{Cu-Cu}}^{\perp}$ (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 $d_{\text{Cu-Cu}}^{\perp}$ 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 $(\text{Hg,Re})\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ ²⁴, the genuine $d_{\text{Cu-Cu}}^{\perp}$ 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 $d_{\text{Cu-Cu}}^{\perp}$, 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 $d_{\text{Cu-Cu}}^{\parallel}$ value approaches that of the corresponding infinite-layered compound $\text{Ae}'\text{CuO}_2$ ^{25,26} with increasing n .
2. In terms of the interlayer Cu–Cu distance, $d_{\text{Cu-Cu}}^{\perp}$ with $\text{Ae}' = \text{Ca}$ almost remains unchanged with respect to n , and all $d_{\text{Cu-Cu}}^{\perp}$ values are comparable with that of CaCuO_2 .
3. When Ca at the Ae' site is replaced by Sr, $d_{\text{Cu-Cu}}^{\perp}$ extends to a distance closer to that of SrCuO_2 .
4. The Ca-free double-layered cuprates have a T_c comparable with those of Ca-containing systems.

Item 1 suggests that if $n \geq 3$ phases with $\text{Ae}' = \text{Sr}$ are stabilized, the a value is closer to that of SrCuO_2 . As can be seen from Fig. 3a–c, for 0212-F, (Hg,Re)-1212, and Tl-1212, the a -axis length in the $\text{Ae} = \text{Ae}' = \text{Sr}$ case agrees well with those of the $\text{Ae} = \text{Ba}$ and $\text{Ae}' = \text{Ca}$ cases, where even the $n \geq 3$ phases have been stably obtained^{7,27,28}. This implies that the $n = 2$ phase with $\text{Ae} = \text{Ae}' = \text{Sr}$ exhibits good in-plane lattice matching. Further elongating a , i.e., replacing $\text{Ae} = \text{Sr}$ 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 $\text{Ae} = \text{Sr}$ case were observed in the susceptibility and XRD data, respectively. However, the a -value needs to be increased artificially to obtain $n \geq 3$ members, and which would be difficult via HP synthesis. As mentioned in the previous section, in the $\text{Ae} = \text{Ba}$ case, the Tl-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 $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ (also known as the T' -phase)⁵. In this study, the as-synthesized Ca-free 0212-F, (Hg,Re)-1212, and Tl-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 $d_{\text{Cu-Cu}}^{\perp}$ mentioned in item 3 is understandable. According to the results of the structure refinement of the as-synthesized 0212-F, though the analyzed $d_{\text{Cu-Cu}}^{\perp}$ length (3.59 Å) are ~5% longer than that of the infinite-layered SrCuO_2 , the $d_{\text{Cu-Cu}}^{\perp}$ value are significantly expanded compared to that of CaCuO_2 (3.18 Å). Note that the $d_{\text{Cu-Cu}}^{\perp}$ of (Hg,Re)-1212 with $\text{Ae} = \text{Ba}$ and $\text{Ae}' = \text{Sr}$ 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 $\text{Ae} = \text{Ba}$ 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 $\text{HgBa}_2\text{CaCu}_2\text{O}_y$ ²⁹ and $\text{TlBa}_2\text{CaCu}_2\text{O}_y$ ³⁰. This result suggests the existence of cation disorder near the apical site and/or between CuO_2 planes, as reported in the literature³¹. Furthermore, as mentioned above, the replacement of Ca by Sr resulted in a significant increase in the $d_{\text{Cu-Cu}}^\perp$ distance, which may correspond to the application of negative chemical pressure. Since it has been reported that T_c of many cuprate superconductors increases by applying the external pressure^{32,33}, we speculate that the chemical pressure effect is also responsible for the slightly lower T_c in the Ca-free cuprates. On the other hand, with a few exceptions, Fig. 3i–l indicate that the enhancement in T_c with an increase in n . This is a widely accepted rule for various multilayered cuprates¹¹; however, as depicted in Fig. 3j, a slight decrease in T_c was confirmed in the Ca-free (Hg,Re)-12($n-1$) n system with $Ae = \text{Ba}$, 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 CuO_2 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 $\text{Sr}_2\text{SrCu}_2\text{O}_4\text{F}_2$ and $(\text{B,C})\text{Sr}_2\text{SrCu}_2\text{O}_y$. These advantages make the material synthesis process simpler and safer. From the lattice parameters and the results of the susceptibility measurements, the in-plane/out-of-plane Cu–Cu distances and T_c were classified in terms of n . We found that, to multiply n in both, $Ae' = \text{Ca}$ and Sr cases, the length of the a -axis needs to approach that of the infinite-layered compound $Ae'\text{CuO}_2$; furthermore, the Ca-free cuprate has 100 K-class T_c , as is the case with conventional Ca-containing multilayered systems. Since the present study provides the double-layered cuprates with the significantly expanded $d_{\text{Cu-Cu}}^\perp$ distance, an investigation of such local chemical pressure effects on the electronic structure may play a role in understanding the physics of high- T_c superconductivity. Meanwhile, a possible Ca-free triple-layered cuprate potentially exhibiting a higher T_c could be structurally unstable or metastable due to the in-plane lattice mismatch, because SrCuO_2 has a long a -axis (~ 3.93 Å). Our findings reveal that the combination of Ae and Ae' in the homologous series of cuprates is still underdeveloped, providing new directions in the materials search for cuprate superconductors.

Methods

Sample preparation. HP synthesis was conducted to prepare polycrystalline samples of 0212-F, (Hg,Re)-1212, Tl-1212, and (B,C)-1212. As a precursor, we prepared Sr_2CuO_3 via the conventional solid-state reaction. Powders of SrCO_3 and CuO weighed in a molar ratio of 2:1 were ground using an agate mortar, and then sintered at 900 °C for 24 h under oxygen flow. The 0212-F samples were synthesized from a mixture of Sr_2CuO_3 , SrF_2 , CuO , the oxidizer AgO , and $\text{Sr}(\text{OH})_2$ with a nominal composition of $\text{Sr}_2\text{SrCu}_2\text{O}_{4+z+y}\text{F}_{2-y}\text{H}_z$. For (Hg,Re)-1212, HgO , ReO_3 , Sr_2CuO_3 , BaO , CuO , and, as necessary, AgO , were weighed in a molar ratio of $\text{Hg} + \text{Re} : \text{Sr} : \text{Ba} : \text{Sr} : \text{Cu} : \text{O} = 1 : 2 : 1 : 2 : 6 : 5$. A typical ratio of Hg to Re is 0.75:0.25. Re was partially substituted for Hg for attaining structural stability by attracting the additional oxygen around the Hg/Re site^{24,34}. For the synthesis of Tl-1212, the starting composition of $\text{TlSr}_2\text{SrCu}_2\text{O}_7$ was prepared using Tl_2O_3 as a source of Tl. In the case of Tl-1212 with $Ae = \text{Ba}$, an evacuated quartz ampoule enclosing the precursors prepared with the same starting composition as for HP synthesis was heated at 800 °C for 10 h. On the other hand, for (B,C)-1212, a stoichiometric composition of $(\text{C}_{0.6}\text{B}_{0.4})\text{Sr}_2\text{SrCu}_2\text{O}_7$ was prepared using SrCO_3 , B_2O_3 , Sr_2CuO_3 , and CuO . The starting materials for each sample (total ~ 150 mg) were mixed well in an agate mortar, and then pelletized ($\Phi 4.7$ and ~ 2 mm thickness) and sealed into a gold capsule ($\Phi 5.4$) to prevent external contamination. Considering the hygroscopicity of the precursors, the entire procedure was performed in a dry-nitrogen-filled glovebox. An HP cell with the sample was rapidly heated to 900 °C under a pressure of 3.4 GPa, and maintained at this condition for 1 h, and finally quenched

to room temperature (~ 25 °C) before releasing the pressure. All the obtained samples were black in color.

To perform the topochemical fluorination for the 0212-F system, first, the as-synthesized sample was ground into a powder and pressed into a pellet. Next, the pellet was sealed in an evacuated quartz tube with CuF_2 powders ($\text{Sr}_2\text{SrCu}_2\text{O}_{4.4}\text{F}_{1.6}\text{H}_{0.2} : \text{CuF}_2 = 1:1$ molar ratio), after which it was heated at 180 °C for 12 h in a box furnace and cooled to room temperature (~ 25 °C). The (Hg,Re)-based and Tl-based samples were post-annealed for 12 h at 450 °C in an evacuated quartz tube at several pascals.

Phase identification and structure refinements. The phases of the obtained samples were identified by powder XRD with $\text{Cu-K}\alpha$ radiation at ~ 293 K. The bulk sample was mechanically crushed and then flatly spread on a glass plate. The diffraction intensity data were collected in a 2θ range from 3° to 80° in 0.01° steps using a commercial diffractometer (Ultima-IV, Rigaku) employing a high-speed 1D X-ray detector (D/teX Ultra, Rigaku). The lattice parameters were calculated by the least-square method³⁵. For the as-synthesized 0212-F, we performed the structure refinements based on the Rietveld method using BIOVIA Materials Studio (MS) Reflex software (version 2018 R2)³⁶.

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 fixed 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 ($\Phi 0.03$) 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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