Preparation and characterization of a new graphite superconductor: Ca\textsubscript{0.5}Sr\textsubscript{0.5}C\textsubscript{6} 

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We have produced a superconducting binary-elements intercalated graphite, Ca\textsubscript{x}Sr\textsubscript{1-x}C\textsubscript{y}, with the intercalation of Sr and Ca in highly-oriented pyrolytic graphite; the superconducting transition temperature, \( T_c \), was ~3 K. The superconducting Ca\textsubscript{x}Sr\textsubscript{1-x}C\textsubscript{y} sample was fabricated with the nominal x value of 0.8, i.e., Ca\textsubscript{0.8}Sr\textsubscript{0.2}C\textsubscript{y}. Energy dispersive X-ray (EDX) spectroscopy provided the stoichiometry of Ca\textsubscript{0.8}Sr\textsubscript{0.2}C\textsubscript{y} for this sample, and the X-ray powder diffraction (XRD) pattern showed that Ca\textsubscript{0.8}Sr\textsubscript{0.2}C\textsubscript{y} took the SrC\textsubscript{2}-type hexagonal-structure rather than CaC\textsubscript{2}-type rhombohedral-structure. Consequently, the chemical formula of Ca\textsubscript{x}Sr\textsubscript{1-x}C\textsubscript{y} sample could be expressed as ‘Ca\textsubscript{0.8}Sr\textsubscript{0.2}C\textsubscript{6}'.

The XRD pattern of Ca\textsubscript{0.5}Sr\textsubscript{0.5}C\textsubscript{6} was measured at 0–31 GPa, showing that the lattice shrank monotonically with increasing pressure up to 8.6 GPa, with the structural phase transition occurring above 8.6 GPa. The pressure dependence of \( T_c \) was determined from the DC magnetic susceptibility and resistance up to 15 GPa, which exhibited a positive pressure dependence of \( T_c \) up to 8.3 GPa as \( \text{Ca}_6 \), SrC\textsubscript{6}, KC\textsubscript{6}, CaC\textsubscript{6} and Ca\textsubscript{0.4}K\textsubscript{0.6}C\textsubscript{6}. The further application of pressure caused the rapid decrease of \( T_c \). In this study, the fabrication and superconducting properties of new binary-elements intercalated graphite, Ca\textsubscript{x}Sr\textsubscript{1-x}C\textsubscript{y}, are fully investigated, and suitable combinations of elements are suggested for binary-elements intercalated graphite.

Some graphite intercalation compounds show superconductivity, and have attracted serious attention because of their high superconducting transition temperatures (\( T_c \)'s). The highest-onset superconducting transition temperature, \( T_{\text{onset}} \), is currently 11.5 K at ambient pressure (0 GPa)\textsuperscript{1–2} and 15.1 K at 7.5 GPa for CaC\textsubscript{6}. However, despite much effort to make new graphite superconductors, no graphite superconductors with higher \( T_{\text{onset}} \) values than 11.5 K have been synthesized. In fact, the \( T_c \) values of graphite superconductors prepared by the intercalation of alkaline metal atoms thus far were 136 mK for KC\textsubscript{8}\textsuperscript{3,4} and 23 mK for RbC\textsubscript{8}\textsuperscript{4}. The graphite superconductors prepared by alkaline earth or lanthanide atoms were SrC\textsubscript{6} (\( T_c = 1.65 \) K), \( \text{BaC}_6 \) (\( T_c = 65 \) mK) and \( \text{YbC}_6 \) (\( T_c = 6.5 \) K).\textsuperscript{1}

Furthermore, binary-elements intercalated graphite was first achieved in KHgC\textsubscript{8}\textsuperscript{5,6} and \( \text{CaC}_6 \). In this study, the fabrication and superconducting properties of new binary-elements intercalated graphite, Ca\textsubscript{x}Sr\textsubscript{1-x}C\textsubscript{y}, are fully investigated, and suitable combinations of elements are suggested for binary-elements intercalated graphite.

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relating to a large softening of the lattice under pressure. Similar behavior under pressure was also observed for binary-elements intercalated graphite Ca$_{0.8}$K$_{0.2}$C$_6$ showing a maximum $T_c$ of 11.6 K at 3.3 GPa.

The mechanism of superconductivity has been extensively discussed based on the theoretical calculation [16, 19]. Calandra and Mauri [14] suggested clearly that the superconductivity in CaC$_6$ is due to an electron-phonon mechanism, and carriers are mostly electrons in the Ca Fermi surface which couples with in-plane Ca-Ca phonon and out-of-plane C-C phonons. They suggested the importance of Ca Fermi surface (not $\pi$ band of graphite) for the superconductivity. On the other hand, Yang et al. experimentally showed the opening of a superconducting gap in the $\pi$ band of graphite [18], suggesting that the superconductivity cannot be assigned to only interlayer band but interaction of $\pi$ and interlayer bands. Thus, the mechanism is still under debate. Furthermore, the superconductivity of metal-doped graphene has recently been pursued from theretical and experimental points of view [20-22]. The study on metal-doped graphene may thus lead to the elucidation of superconductivity in metal-intercalated graphite, since graphene is a thin limit of graphite. The X-ray diffraction (XRD) patterns of Ca$_x$K$_{1-x}$C$_6$ (x = 1) suggested a KGe$_2$-type structure [19] (face-centered orthorhombic, space group No. 70, Fddd) [5], rather than a CaC$_6$-type structure (rhombohedral, space group No. 166, R3m) [14]. The former (KGe$_2$ structure) shows a $\Lambda\alpha\alpha\beta\gamma\delta\gamma\delta$ where $\Lambda$ refers to the graphene sheet, and $\alpha$, $\beta$, $\gamma$, and $\delta$ refer to the four sites occupied by the metal atoms. On the other hand, the latter (CaC$_6$-structure) shows a $\Lambda\alpha\alpha\beta\gamma\delta\gamma\delta\gamma\delta\gamma\delta\gamma\delta\gamma\delta\gamma\delta\gamma\delta\gamma\delta\gamma\delta\gamma\delta\gamma\delta\gamma\delta$ in which metal occupies three different sites. The most interesting point is that in Ca$_{1-x}$K$_x$C$_6$, the $T_c$ is much higher than that of KC$_6$ despite the KC$_6$-type structure.

In this study, we discovered a new binary-elements intercalated graphite superconductor through the intercalation of Ca and Sr. The $T_c$ values of Ca$_x$Sr$_{1-x}$C$_6$ with x = 0.8 or 0.9 were ~3 K in the metal-intercalation to highly-oriented pyrolytic graphite (HOPG). Energy dispersive X-ray (EDX) spectroscopy showed the chemical composition of the prepared Ca$_x$Sr$_{1-x}$C$_6$. The XRD pattern of Ca$_x$Sr$_{1-x}$C$_6$ showed that the crystal structure is SrC$_6$-type (hexagonal, space group R3m). Therefore, the Ca$_x$Sr$_{1-x}$C$_6$ sample was finally expressed 'Ca$_x$Sr$_{1-x}$C$_6$'. The pressure dependence of the XRD pattern of Ca$_x$Sr$_{1-x}$C$_6$ showed monotonic shrinkage of the lattice up to 20 GPa. The pressure dependence of $T_c$ for Ca$_x$Sr$_{1-x}$C$_6$ showed a positive pressure dependence at 0–8.3 GPa, and a sudden drop in $T_c$ was observed with applied pressure above 8.3 GPa. The magnetic characteristics of the $R$ – $T$ plot for Ca$_x$Sr$_{1-x}$C$_6$ were also studied at 0.80, 4.3 and 8.5 GPa.

**Results**

**Preparation and characterization of superconducting Ca$_x$Sr$_{1-x}$C$_6$ sample through metal doping of HOPG.**

The temperature ($T$) dependence of magnetic susceptibility, $M/H$ or $M/H$ – $T$ plot measured in zero-field cooling (ZFC) mode in Ca$_x$Sr$_{1-x}$C$_6$ (x = 0.8) prepared by the intercalation of Sr and Ca to HOPG, which is expressed 'Ca$_{0.8}$Sr$_{0.2}$Cy', is shown in Fig. 1a; $M$ and $H$ refer to magnetization and applied magnetic field, respectively. The optical image of Ca$_{0.8}$Sr$_{0.2}$Cy sample is shown in Fig. 2a, which was bright gold colour.

A rapid drop in $M/H$ is observed below ~3.0 K, and $T_c$ is 3.2 K. how to determine $T_c$ is shown in the inset of Fig. 1a. The $T_c$ onset is 4.0 K from the $M/H$ – $T$ plot in ZFC mode. The $M/H$ – $T$ plot in field-cooling (FC) mode is shown in Fig. 1a, and the $T_c$ was estimated to be also 3.2 K. The shielding fraction was estimated to be 100% at 2 K from the $M/H$ – $T$ plot in ZFC mode. Thus, the Ca$_{0.8}$Sr$_{0.2}$Cy sample is quite simply a bulk superconductor. On the other hand, we prepared the Sr$_{0.1}$C$_6$ sample by the intercalation of Sr in HOPG, which did not show superconductivity down to 2 K, as seen from Fig. 1b. As the $T_c$ onset of Sr$_{0.1}$C$_6$ is 1.65 K, the absence of superconductivity is reasonable, suggesting that the Ca$_{0.9}$Sr$_{0.1}$C$_6$ sample is not SrC$_6$ but Ca/Sr co-doped graphite (Ca$_{0.9}$Sr$_{0.1}$C$_6$).

In this study, we changed nominal x value from 0 to 0.9 in Ca$_x$Sr$_{1-x}$C$_6$. For Ca$_x$Sr$_{1-x}$C$_6$ at x = 0.7, the superconductivity was observed. The Ca$_{0.8}$Sr$_{0.2}$Cy sample with nominal x of 0.9, Ca$_{0.8}$Sr$_{0.2}$Cy, provided both phases of Ca$_x$C$_6$ ($T_c$ ~ 11 K) and Ca$_{0.8}$Sr$_{0.2}$Cy ($T_c$ ~ 4 K), while that with nominal x of 0.7, Ca$_{0.7}$Sr$_{0.3}$Cy, showed smaller fraction of superconductivity ($T_c$ ~ 2.5 K). For the Ca$_{0.8}$Sr$_{0.2}$Cy sample at nominal x of 0.9, we measured the EDX spectra at eight different positions, which showed three different stoichiometry, Ca$_{0.98(1)}$Sr$_{0.02(1)}$Cy (four points), Ca$_{0.58(6)}$Sr$_{0.42(6)}$Cy (three points) and Ca$_{0.35}$Sr$_{0.65}$Cy (only one point), consistent with two superconducting phases ($T_c$ ~ 11 K and $T_c$ ~ 4 K) as described above; the Ca$_{0.35}$Sr$_{0.65}$Cy is probably lower $T_c$ than 4 K. Furthermore, for the Ca$_{0.8}$Sr$_{0.2}$Cy sample at nominal x of 0.7, the EDX spectra were measured at five different positions, showing a single phase, Ca$_{0.2(1)}$Sr$_{0.8(1)}$Cy. This result is consistent with the observation of a single phase exhibiting a small superconducting volume fraction ($T_c$ ~ 2.5 K). Thus, owing to the observation of a very large shielding fraction ($T_c$ = 3.2 K) as shown in Fig. 1a, we investigated the Ca$_{0.8}$Sr$_{0.2}$Cy sample prepared with nominal value of x = 0.8 throughout this study. Finally, we may stress the validity of stoichiometry determined from EDX, based on the consistency between the EDX results and magnetic properties of the Ca$_x$Sr$_{1-x}$C$_6$ samples.

The $M$ – $H$ plot of Ca$_{0.8}$Sr$_{0.2}$Cy at 2 K is shown in Fig. 1c, which shows typical superconducting $M$ – $H$ behaviour. The lower critical field, $H_{c1}$, was determined to be 200 Oe (see inset of Fig. 1c). This $H_{c1}$ is much smaller than 500 Oe (at 6 K) of CaC$_6$. The $M/H$ – $H$ plots at different H’s are shown in Fig. 1d. The $H_{c2}$ – $T$ plot obtained from the $M/H$ – $H$ plots (Fig. 1d) is shown in the inset of Fig. 1d, and the $H_{c2}$ at 0 K, $H_{c2}(0)$, determined to be 200 Oe from the $H_{c2}$ – $T$ plot using the Werthamer–Helfand–Hohenberg (WHH) formula, $H_{c2}(0) = -0.693T_dH_d^2/dT_c$, indicating that the London penetration depth ($\lambda$) and Ginzburg Landau coherent length ($\xi_\perp$) are 215 and 130 nm, respectively. The $H_{c2}$ value is much smaller than 7000 Oe of CaC$_6$. Here, it should be noted that the $H_{c2}$ predicted from the $M$ – $H$ plot at 2 K (Fig. 1c) seems to be higher than 2000 Oe. This is probably due to the contribution from a CaC$_6$ phase, because this sample contains a trace of CaC$_6$ as seen from Fig. 1a. This scenario would be reasonable because the $H_{c2}(0)$ of CaC$_6$ is 7000 Oe.

The EDX of Ca$_{0.8}$Sr$_{0.2}$Cy presented in Fig. 2b, and shows peaks due to Sr, Ca, O and C atoms. The presence of O atoms must be due to the oxidation of Ca$_{0.8}$Sr$_{0.2}$Cy because the sample used for the EDX spectrum was once stored under atmospheric conditions before the EDX measurement, i.e., the contamination of O originates from an extrinsic factor. Therefore, the EDX spectrum suggests that the chemical composition of the Ca$_{0.8}$Sr$_{0.2}$Cy sample can be expressed 'Ca$_{0.8}$Sr$_{0.2}$Cy'; the contamination of Li could not be confirmed by the EDX spectrum because
the energy of the Li Kα peak is too low. The stoichiometry of Ca₀.₈Sr₀.₂Cy was estimated to be Ca₀.₅(2)Sr₀.₅(2)Cy from the area intensity of the peaks in the EDX spectrum. Here we can point out that since each peak is substantially resolved in the EDX spectrum (Fig. 2b), the area intensity is obtained with high accuracy. The estimated standard deviation (e.s.d.) of the chemical composition shown above was somewhat large when a large grain of Ca₀.₈Sr₀.₂Cy was used for the EDX measurement, indicating that the sample was slightly inhomogeneous. From here, we use the chemical formula, Ca₀.₅(2)Sr₀.₅(2)Cy, for the Ca₀.₈Sr₀.₂Cy sample.

Structure of superconducting Ca₀.₅Sr₀.₅Cy.

The XRD pattern of Ca₀.₅Sr₀.₅Cy at around 0 GPa is shown in Fig. 2c, indicating that the main peaks can be assigned to the SrC₆-type structure, which is P₆₃/mmc (No. 194) [24]. Simulation spectra (powder pattern) of LiC₆, CaC₆, SrC₆ and graphite are also shown in Fig. 2c; the simulation was made using the crystal structures of LiC₆ [25], CaC₆ [26], SrC₆ [24], and graphite [26]. Furthermore, as seen from Fig. 2c, the relative intensity of the peaks observed is quite similar to that of SrC₆. Notably, the XRD pattern was measured with synchrotron radiation (wavelength λ = 0.68841 Å), in which the sample is introduced into a diamond anvil cell (DAC). The pressure was determined to be 0 GPa from the fluorescence of ruby, but the exact pressure may be 0–0.2 GPa.

The a and c values were determined to be 4.32 Å from the 100 and 110 peaks, while the lattice constant, c, was determined to be 9.82 Å from the 112 peak using the above a value. Furthermore, the values of a and c were evaluated using iterative approximation. In the iterative approximation, firstly we roughly estimated the a value from 100 and 110 peaks. Secondly, the c value was estimated from all peaks and the a value determined in the first process. Finally the a value was estimated from the all peaks and the c determined in the second process. The a and c were 4.31(1) and 9.85(8) Å, respectively. The Le Bail fitting was also tried for determination of a and c. The Le Bail fitting were 4.3077(3) and 9.883(1) Å, respectively. Actually, because of the impurity peaks, the Le Bail fitting was difficult. Therefore, these values are for reference. The a and c values determined by all ways are consistent each other, implying that the a and c determined were reliable.

It is easy to assume that only 00 l reflections will be measured, if the ab-plane of metal-intercalated HOPG sample is completely aligned to the sample holder. However, all reflections are observed as seen from indices of XRD pattern shown in Fig. 2c, indicating that the metal-intercalated HOPG sample is not completely aligned to the sample holder. Therefore, the XRD pattern observed is powder-like with preferred orientation. Consequently, we could successfully obtained both values of a and c. As seen from Fig. 2c, the XRD pattern of Ca₀.₅Sr₀.₅Cy was simulated using a = 4.31(1) and c = 9.85(8) Å (iterative approximation) and assuming that the 50% of Ca and 50% of Sr randomly occupy the 2c site in the space group (No. 194, P₆₃/mmc) of SrC₆-type crystal.

Figure 1. (a) M/H – T plots in ZFC and FC modes for Ca₀.₈Sr₀.₂Cy. (b) M/H – T plot in ZFC and FC modes for SrC₆. (c) M – H plot at 2 K for Ca₀.₈Sr₀.₂Cy. (d) M/H – T plots at different H’s for Ca₀.₈Sr₀.₂Cy, measured in ZFC mode. Inset of (a) shows how to determine the Tc. The inset of Fig. 1(c) shows the M – H plot in the low-H range. Inset of (d): Hc₂ – T plot for Ca₀.₈Sr₀.₂Cy determined from (d). Stoichiometry of Ca₀.₈Sr₀.₂Cy refers to the experimental nominal value, and all samples were made by the intercalation of Ca and Sr in HOPG.

The lattice constant, a, was determined to be 4.32 Å from the 100 and 110 peaks, while the lattice constant, c, was determined to be 9.82 Å from the 112 peak using the above a value. Furthermore, the values of a and c were evaluated using iterative approximation. In the iterative approximation, firstly we roughly estimated the a value from 100 and 110 peaks. Secondly, the c value was estimated from all peaks and the a value determined in the first process. Finally the a value was estimated from the all peaks and the c determined in the second process.

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It is easy to assume that only 00 l reflections will be measured, if the ab-plane of metal-intercalated HOPG sample is completely aligned to the sample holder. However, all reflections are observed as seen from indices of XRD pattern shown in Fig. 2c, indicating that the metal-intercalated HOPG sample is not completely aligned to the sample holder. Therefore, the XRD pattern observed is powder-like with preferred orientation. Consequently, we could successfully obtained both values of a and c. As seen from Fig. 2c, the XRD pattern of Ca₀.₅Sr₀.₅Cy was simulated using a = 4.31(1) and c = 9.85(8) Å (iterative approximation) and assuming that the 50% of Ca and 50% of Sr randomly occupy the 2c site in the space group (No. 194, P₆₃/mmc) of SrC₆-type crystal. As seen from
the comparison between the experimental XRD pattern and the simulated pattern of Ca$_{0.5}$Sr$_{0.5}$C$_6$ (Fig. 2c), most of peaks in the experimental XRD pattern for Ca$_{0.5}$Sr$_{0.5}$C$_6$ sample were assigned to those of Ca$_{0.5}$Sr$_{0.5}$C$_6$ simulated with SrC$_6$ structure. Thus, the indices for most of peaks were provided at SrC$_6$ structure, but some peaks were assigned to those of CaC$_6$ and graphite. Moreover, some of peaks were not assigned. The difference in relative intensities was found between the experimental XRD pattern and the simulated one of Ca$_{0.5}$Sr$_{0.5}$C$_6$, but the conclusion that the sample takes SrC$_6$ structure is supported. Furthermore, it should be noticed that to completely reproduce the relative intensities observed in the experimental XRD pattern is difficult, because it shows a powder-like pattern affected by strong preferred orientation, as described above.

The $a$ and $c$ values are almost the same as those ($a = 4.316$ Å and $c = 9.88$ Å) of SrC$_6$ and the simulated pattern of Ca$_{0.5}$Sr$_{0.5}$C$_6$ at SrC$_6$ structure is consistent with the experimental XRD pattern. As a result, all XRD results support that the stoichiometry of Ca$_{0.5}$Sr$_{0.5}$C$_6$ can be expressed 'Ca$_{0.5}$Sr$_{0.5}$C$_6$'. The fact that the Ca/Sr binary-elements intercalated graphite takes the SrC$_6$ structure may be reasonable because the ionic radius of Sr$^{2+}$ (1.18 Å for six coordination) is larger than that of Ca$^{2+}$ (1.0 Å for six coordination). Namely, the Ca atoms may be intercalated into the crystal lattice of graphite separated by Sr atoms because of the larger ionic radius of Sr$^{2+}$. In this crystal, the metal atoms occupy two different sites of $\alpha$ and $\beta$, and the graphite layer shows AAA stacking. The stacking form, $\alpha\alpha\beta\alpha\alpha$, of SrC$_6$ is different from that, $\alpha\alpha\beta\alpha\beta\alpha$, of CaC$_6$. The distance, $d_{AA}$, between graphenes in SrC$_6$ is 4.94 Å ($d_{AA} = c/2$), which is larger than the $d_{AA} = 4.524$ Å ($d_{AA} = c/3$) in CaC$_6$, indicating
that the Ca intercalation into SrC₆ (or CaₓSr₁−ₓC₆) may not affect the lattice constant c. In fact, the c value of Ca₀.₅(2)Sr₀.₅(2)C₆ is almost the same as that of SrC₆, as described above. Thus, despite the SrC₆ structure, we could obtain the 3 K superconducting phase in Ca₀.₅(2)Sr₀.₅(2)C₆.

Finally, we must comment upon the peaks that cannot be assigned to Ca₀.₅Sr₀.₅C₆. Some of peaks were assigned to CaC₆ and pure graphite, as seen from Fig. 2c, indicating the presence of small amount of pure graphite in the sample. This may be the origin of the significant diamagnetic background observed in M – H plot (Fig. 1c). As described previously, the presence of CaC₆ in the Ca₀.₅Sr₀.₅C₆ sample was suggested from the M/H — T plot at ZFC mode shown in Fig. 1a. Here, it should be noticed that the M/H — T at FC mode (Fig. 1a) did not show any trace of CaC₆. This may imply that the CaC₆ phase is not bulky but surface (thin layer). As seen from Fig. 2c, some of weak peaks in the XRD pattern were assigned to CaC₆, indicating the presence of CaC₆, which is consistent with the observation of a trace of CaC₆-superconductivity.

**Pressure dependence of superconductivity and structure in Ca₀.₅Sr₀.₅C₆.** Microscope image of Ca₀.₅Sr₀.₅C₆ sample and four electrodes set in DAC is shown in Fig. 2a, in which four electrodes are contacted to the sample. The sample shows bright-gold color. Figure 3a and b show the temperature dependence of resistance (R — T plots) of Ca₀.₅Sr₀.₅C₆ at different pressures. The former shows the R — T plots at 2–300 K, and the latter shows the expanded plots (2–9 K). The pressure dependence of Tc in Ca₀.₅Sr₀.₅C₆ is shown in Fig. 3c; the Tc was determined from the cross point of the R — T plot at normal state and that exhibiting the drop, in the same manner as the inset of Fig. 1a. The Tc increased with increasing pressure up to 8.3 GPa, then suddenly decreased. This behaviour is similar to that of CaC₆ and Ca₀.₆K₀.₄C₈, which is consistent with the observation of a trace of CaC₆-superconductivity.

The R — T plots at H’s of 0 and 500 Oe were measured at 0.80 GPa (Fig. 4a), indicating the suppression of superconductivity at 500 Oe. Furthermore, the R — T plots at different H values were measured at 4.3 and 8.5 GPa.
Figure 4b shows the $R$–$T$ plots at different $H'$ values at 8.5 GPa. The $H_c^2$–$T$ plot determined from the graph shown in Fig. 4b is depicted in the inset of Fig. 4b. The $H_c^2(0)$ at 8.5 GPa was evaluated to be 3100 Oe from the WHH formula. This value is larger than that, 200 Oe, evaluated from $M/H$–$T$ plots at 0 GPa (inset of Fig. 1d). Notably, as seen from Fig. 3a, the behavior of the $R$–$T$ plot in the normal state was metallic up to 12 GPa, i.e., the $R$ decreased with decreasing temperature. But at 14 and 15 GPa, $R$ increased slightly with decreasing temperature below 90 K, suggestive of a change in electric transport in the normal state at around 14 GPa (Fig. 3a). The $M/H$–$T$ plots at different pressures (0–1.3 GPa) for Ca$_{0.9}$Sr$_{0.1}$Cy are shown in Fig. 1S of Supplementary Information, showing the positive pressure dependence. This sample contained three different phases, Ca$_{0.98(1)}$Sr$_{0.02(1)}$Cy, Ca$_{0.58(6)}$Sr$_{0.42(6)}$Cy, and Ca$_{0.35}$Sr$_{0.65}$Cy, as shown previously, but the stoichiometry exhibiting the $T_c$'s determined from the $M/H$–$T$ plots (Figure S1) would be Ca$_{0.58(6)}$Sr$_{0.42(6)}$Cy which is almost the same as Ca$_{0.5}$Sr$_{0.5}$Cy. The $T_c$–$p$ plot obtained from $M/H$–$T$ at 0–1.3 GPa is shown in the inset of Fig. 3c. Figure 3d shows the pressure dependence of $R$ at 280 K for Ca$_{0.5(2)}$Sr$_{0.5(2)}$Cy. The $R$ rapidly increases above 10 GPa, which may be correlated with the change in electric transport above 12 GPa shown in Fig. 3a.

Figure 5a–c show the pressure dependence of three representative peaks of Ca$_{0.5}$Sr$_{0.5}$Cy in the XRD pattern. These peaks shifted to higher 2$\theta$ with an increase in pressure, indicating shrinkage of the unit cell. The 100 peak was observed up to 20 GPa, but suddenly disappeared above 20 GPa, while the 110 peak was clearly observed across the entire range of applied pressure (0–31 GPa). Moreover, the 112 peak quickly disappeared above 8.6 GPa. In Ca$_{0.6}$K$_{0.4}$Cy, the 004 peak completely disappeared at 16 GPa, which was assigned to the structural change from the KC$_6$ structure to a non-graphite type structure. The disappearance of the 112 peak at 10 GPa would be explained by the vanishing of the long-range order of graphite, such as the graphite–non-graphite transition found at around 16 GPa in Ca$_{0.6}$K$_{0.4}$Cy. Furthermore, the change of electric transport (Fig. 3a) and the rapid increase in $R$ (Fig. 3d) may be explained by considering a structural transition at around 10 GPa.

The pressure dependence of lattice constants $a$ and $c$ is plotted in Fig. 5d and e; the $a$ was determined up to 20 GPa, while $c$ determined up to 8.6 GPa because of the rapid disappearance of the 112 peak around 10 GPa. Both plots show a monotonic shrinking of the unit cell with increasing pressure. The pressure dependence of $d_{AA}$ in...
Ca$_{0.6}$K$_{0.4}$C$_6$ and Ca$_{0.5(2)}$Sr$_{0.5(2)}$C$_6$ is shown in Fig. 6; that of Ca$_{0.6}$K$_{0.4}$C$_6$ is taken from ref. 13. The behaviour of $d_{AA}$ is similar in both. Namely, the $d_{AA}$ approaches the $d_{AA}$ ($=4.524$ Å) of CaC$_6$ with increasing pressure, and any Bragg peak disappears when reaching that $d_{AA}$ (above 13.7 GPa for Ca$_{0.6}$K$_{0.4}$C$_6$ and above 8.6 GPa for Ca$_{0.5(2)}$Sr$_{0.5(2)}$C$_6$). To sum up, any structural transition may take place when the $d_{AA}$ reaches the threshold value of $d_{AA}$.

Discussion

In this paper, the most important issue is that a new class of superconducting binary-elements intercalated graphite was prepared by the intercalation of Sr and Ca. These are alkali-earth elements, and their ionic radii differ slightly ($\text{Sr}^{2+}$: 1.18 Å for six coordination and $\text{Ca}^{2+}$: 1.0 Å for six coordination). The ionic radii of some elements which can be intercalated to graphite are shown in Table 1, in which they were taken from ref. 28. On the other hand, the crystal structure is different between CaC$_6$ and SrC$_6$, in which the former takes the rhombohedral structure (space group No. 166, $R\overline{3}m$) and the latter takes the hexagonal structure (space group No. 194, $P\overline{6}_3/mmc$)

Regardless of such a large difference between CaC$_6$ and KC$_8$, Ca$_x$K$_{1-x}$C$_y$ was successfully formed. On the other hand, we tried to fabricate Ca$_x$Yb$_{1-x}$C$_y$, but the M/H – T plot showed a complete phase separation of CaC$_6$ ($T_c = 11.5$ K) and YbC$_6$ ($T_c = 6.7$ K), as seen from Fig. 7. The crystal structure of YbC$_6$ is the same as that of SrC$_6$. The ionic radius of Yb is 1.02 Å for six coordination, which is the same as that of Ca. Nevertheless, the Ca$_x$Yb$_{1-x}$C$_y$ could not be realized thus far. The liquid alloy method has been used for the preparation of binary-elements intercalated graphites, and the YbC$_6$ and CaC$_6$ phases were separately generated in the preparation of Ca$_x$Yb$_{1-x}$C$_y$, suggesting both elements are melted. Therefore, we can rule out the possibility of no melting of either element.

Here, we focus on the fact that the element with the larger ionic radius dominates the crystal structure, i.e., the SrC$_6$ structure in Ca$_x$Sr$_{1-x}$C$_y$ and the KC$_8$ structure in Ca$_x$K$_{1-x}$C$_y$. Furthermore, the $d_{AA}$ in binary-elements intercalated graphite is the same as that of a crystal lattice consisting solely of an element with larger ionic radius; the $d_{AA}$ ($=c/2 = 4.91$ Å ($c = 9.81$ Å) or 4.925 Å ($c = 9.85(8)$ Å) of Ca$_{0.5(2)}$Sr$_{0.5(2)}$C$_6$ is the same as that ($=c/2 = 4.95$ Å) of SrC$_6$ and the $d_{AA}$ ($=c/4 = 5.40$ Å) of Ca$_{0.5(2)}$Sr$_{0.5(2)}$C$_6$ is the same as that ($=c/4 = 5.35$ Å) of KC$_8$, as seen from Fig. 2.
of ref. 23. These facts may point to a scenario in which the crystal lattice formed by the element with larger ionic radius is subsequently doped with the other element with smaller ionic radius. Based on this scenario, we can propose suitable combinations for the superconducting binary-elements or ternary-elements intercalated graphites, i.e., the binary-elements graphites must be realized using Cs and Ca, or Cs and Yb, because of the larger difference

| Element | Coordination number | Ionic radius (Å) |
|---------|---------------------|------------------|
| Li      | 6                   | 0.76             |
| K       | 6                   | 1.38             |
| Cs      | 6                   | 1.67             |
| Ca      | 6                   | 1.0              |
| Sr      | 6                   | 1.18             |
| Yb      | 6                   | 1.02             |

Table 1. Ionic radius of elements (from ref. 28).

Figure 6. Pressure dependence of $d_{AA}$ for $\text{Ca}_{0.6} \text{K}_{0.4} \text{C}_8$ and $\text{Ca}_{0.5(2)} \text{Sr}_{0.5(2)} \text{C}_6$. Dashed lines drawn in red, yellow and blue refer to the $d_{AA}$ values of $\text{KC}_8$, $\text{SrC}_6$ and $\text{CaC}_6$, respectively.

Figure 7. $M/H - T$ plots in ZFC and FC modes for $\text{Ca}_{0.8} \text{Yb}_{0.2} \text{C}_6$. Presence of two phases of $\text{CaC}_6$ and $\text{YbC}_6$ is indicated.
in ionic radii (Cs⁺: 1.67 Å for six coordination), and for the ternary-elements superconductors the combination of Ca (or Yb), Sr (or K) and Ca are probably suitable. The crystal structure of the binary- and ternary-elements intercalated graphites suggested above would be the CsC₆-type structure, because the CsC₆ phase is formed with the CsC₆ structure29.

**Methods**

**Sample preparation and characterization.** The Ca₅Sr₁₋ₓCaₓ samples were prepared using the liquid-alloy method. Ca and Sr metals were mixed in appropriate molar ratios and placed in an iron vessel with Li. The molar ratio of Li was the same as the sum of Ca and Sr. The vessel was then heated to 350 °C, at which temperature the Ca/Sr/Li alloy was completely melted. The HOPG was immersed in the molten Ca/Sr/Li alloy for approximately one week. The whole preparation was performed in an Ar-filled glove box (O₂ and H₂O concentrations were maintained below 0.1 ppm). The M/H – T curves of the Ca₅Sr₁₋ₓCaₓ samples were measured with a SQUID magnetometer (Quantum Design, MPMS2). All XRD patterns at 0–31 GPa were measured at 295 K using synchrotron radiation (λ = 0.68841 Å) at BL12B2 of SPring-8. The simulated XRD patterns for LiCa₁ₓCa₆ and SrCa₆ were made using the VESTA program30 for the analyses of XRD patterns.

The diamond anvil cell was used for the measurements, and the Ca₅Sr₁₋ₓCaₓ sample was placed in the diamond anvil cell without any exposure of the sample to air, as is described below. A 300-µm-thick stainless steel gasket with a 160-µm diameter hole was placed on a diamond with a 400-µm culet, and the sample was introduced into the hole. The sample was covered with daphne oil (Idemitsu Co., Ltd., Daphne 7373) as the pressure medium. Finally the sample was pressed by another diamond. The pressure was monitored by the fluorescence produced into the hole. The sample was covered with daphne oil (Idemitsu Co., Ltd., Daphne 7373) as the pressure medium was the same daphne oil as above. Meanwhile, the pressure dependence of the Tc measurements at high pressure are described elsewhere13. The R was recorded using an AC resistance-bridge (Lakeshore, 370-type Resistance Bridge), limiting the applied current to less than 100 µA. The sample was cooled using liquid He, and the temperature was controlled with a temperature controller (Oxford, ITC503 Temperature Controller).

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**Author Contributions**
Y.K. suggested the idea for this research, and designed this study with S.N., who prepared and characterised all of the CaxSr1−xCy samples with the assistance of X.M. and T.T. The X-ray diffraction of the sample was measured at BL12B2 of SPring-8 by T.T., H.Y., H.I., Y.-F.L. and Y.K; the diamond anvil cell used for pressure-dependent X-ray diffraction was designed by H.Y. The pressure-dependent M/H – T measurement was done by S.N. and T.M. EDX measurement was done by S.N. and X.Y. Pressure-dependent R – T measurement was made by H.F., M.H., K.S., T.K. and S.N.; the experimental setup for R – T measurement was designed by K.S. and T.K. All data were analysed by S.N., T.T. and X.Y. under continuous discussion with Y.K. and H.G. The manuscript was prepared by Y.K. with discussions with all authors.

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