Emergence of double-dome superconductivity in ammoniated metal-doped FeSe

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Various metal-intercalated FeSe superconductors have recently been prepared using the liquid NH₃ technique, and high superconducting transition temperatures, Tₙ₁’s, have been reported for NH₃/intercalated FeSe materials, (NH₃)ₙ,M,FeSe (M: alkali, alkaline-earth and lanthanide atoms)¹⁻³. Furthermore, we found new superconducting phases in (NH₃)ₙ,M₆FeSe₉₅Te₀₅₆, and their Tₙ₁’s were lower than those of the corresponding (NH₃)ₙ,M₆FeSe materials. The highest reported Tₙ₁ in these materials is now 46 K for (NH₃)₉Na₉₀FeSe⁸. Therefore, the NH₃/M₆FeSe materials are attractive research targets in the hunt for high-Tₙ₁ superconductors. The Tₙ₁ increases markedly with the intercalation of ions with smaller ionic radius. Furthermore, a correlation between Tₙ₁ and the lattice constant c was observed in (NH₃)ₙ,M₆FeSe materials, suggesting that an increase in two-dimensionality (2D) is a key for raising the Tₙ₁ of the materials. This would be similar to HINCl, in which NH₃ or tetrahydrofuran (THF) is inserted into the space between HINCl layers. If the dimensionality is the key factor for raising the Tₙ₁ metal doped FeSe, it is important to investigate the Tₙ₁ systematically as a function of c in (NH₃)ₙ,M₆FeSe, i.e., the effect of both physical and chemical pressures on Tₙ₁ should be comprehensively studied to clarify the correlation between Tₙ₁ and plane spacing.

Very recently, we investigated the pressure dependence of Tₙ₁ in (NH₃)₉Cs₉FeSe up to 3.2 GPa and plotted the Tₙ₁ as a function of pressure p, which showed a negative pressure effect for Tₙ₁. From our previous data, the Tₙ₁ vs. p plot was found to show a brief upward deviation from its straight-line approximation. However, the Tₙ₁ has not previously been plotted as a function of c or FeSe plane spacing because the pressure dependence of lattice constants has not been available. In the present study we examined the crystal structure of (NH₃)₉Cs₉FeSe over the wide pressure range of 0 to 41 GPa using synchrotron X-ray diffraction, and the lattice constants a and c were

The pressure dependence of the superconducting transition temperature (Tₙ₁) and unit cell metrics of tetragonal (NH₃)₉Cs₉₀FeSe were investigated in high pressures up to 41 GPa. The Tₙ₁ decreases with increasing pressure up to 13 GPa, which can be clearly correlated with the pressure dependence of c (or FeSe layer spacing). The Tₙ₁ vs. c plot is compared with those of various (NH₃)ₙ,M₆FeSe (M: metal atoms) materials exhibiting different Tₙ₁ and c, showing that the Tₙ₁ is universally related to c. This behaviour means that a decrease in two-dimensionality lowers the Tₙ₁. No superconductivity was observed down to 4.3 K in (NH₃)₉Cs₉₀FeSe at 11 and 13 GPa. Surprisingly, superconductivity reappeared rapidly above 13 GPa, with the Tₙ₁ reaching 49 K at 21 GPa. The appearance of a new superconducting phase is not accompanied by a structural transition, as evidenced by pressure-dependent XRD. Furthermore, Tₙ₁ slowly decreased with increasing pressure above 21 GPa, and at 41 GPa superconductivity disappeared entirely at temperatures above 4.9 K. The observation of a double-dome superconducting phase may provide a hint for pursuing the superconducting coupling-mechanism of ammoniated/non-ammoniated metal-doped FeSe.
doped FeSe\(_{1.5}\). The drop was assigned to the superconducting transition. The zero-resistance has been reported so far in ammoniated metal oxide samples. No observation was made because of polycrystalline powder samples. The XRD patterns were recorded at the synchrotron X-ray radiation facility of the Institute of High Energy Physics, Beijing, China, from 1.9 to 13 GPa, and the \(T_c\) value was determined from the \(M/H\) vs. \(T\) plot at each pressure. The DC/AC magnetic susceptibility measurement was not performed above 4 GPa since it is difficult in the higher pressure range than 4 GPa. Namely, the resistance is only a realistic tool for proving superconductivity at high pressures. In this report, the \(T_c\) values are plotted as a function of \(p\) from 0 to 41 GPa, and the pressure range is extended in comparison with that (0–3.2 GPa) in the previous report. It has been found from the \(T_c\) vs. \(c\) plot obtained that the change in \(T_c\) is related to the change in the FeSe plane spacing up to 11 GPa, where the superconductivity vanishes. Surprisingly, the \(T_c\) quickly recovers above 13 GPa and reaches 49 K at 21 GPa, which is one of the highest reported for bulk superconductors of FeSe-derived materials. The \(T_c\) slowly decreases above 21 GPa and at 41 GPa no superconductivity is observed at temperatures above 4.9 K.

Results

Pressure dependence of \(T_c\). Figure 1(a) shows the \(M/H\) vs. \(T\) plots of a typical \((\text{NH}_3)\text{Cs}_0.4\text{FeSe}\) sample measured under ambient pressure in zero-field cooling (ZFC) and field-cooling (FC) modes; \(M\) and \(H\) refer to magnetization and applied magnetic field, respectively. A clear superconducting transition was observed in both modes, with \(T_c^{\text{onset}}\) and \(T_c\) of 33 and 31 K, respectively, in ZFC mode, compared with 33 and 32 K, respectively, in FC mode; the \(T_c\) was determined from the intersection of two lines (see inset of Figure 1(a)). No antiferromagnetic-like phase was observed in the \(M/H\) vs. \(T\) plot; it shows the superconductivity with \(T_c = 8\) K. The shielding fraction at 2.5 K is 30%. These values are the same as those in the previous report. The \(M/H\) vs. \(T\) plots of the \((\text{NH}_3)\text{Cs}_0.4\text{FeSe}\) sample measured at different pressures (0–0.84 GPa) are shown in Figure 1(b). The plots gradually shift to the left in higher pressures, as seen from Figure 1(b).

We determined the \(T_c\)’s in the pressure range from 1.9 to 13 GPa from the resistance (\(R\)) vs. \(T\) plots. All \(T_c\)’s determined from the temperature dependences of \(M/H\), \(\chi’\) and \(R\) are plotted as a function of \(p\) in Figure 1(c); \(\chi’\) is the real part of AC magnetic susceptibility. In the case of \(M/H\) and \(\chi’\) measurements, the \(T_c\) was determined from the intersection point, as shown in the inset of Figure 1(a). The \(R\)-\(T\) curves below 13 GPa (Figure S1 in Supplementary information) showed the clear drop of \(R\), but the zero-resistance could not be observed because of polycrystalline powder sample. No observation of zero-resistance has been reported so far in ammoniated metal doped FeSe\(_{1.5}\). The drop was assigned to the superconducting transition. For resistance measurement, the \(T\) corresponding to the midpoint of the \(R\) vs. \(T\) plot in normal and superconducting states was defined as \(T_c\) in the pressure range from 1.9 to 13 GPa, while above 13 GPa the \(T_c\) was determined from the intersection point; the \(T_c\) determination from the midpoint in the pressure range below 13 GPa is the most reasonable way because of existence of background of semiconducting behaviour as seen from Figure S1. As described later, the \(T_c\) determined from the midpoint follows the \(T_c \sim 0.49\) GPa. The plots are shown in Figure 1(c)). At 11 and 13 GPa, no superconductivity was observed down to 4.3 K.

Pressure dependence of lattice constants. The XRD patterns measured in the pressure range from 0 to 41 GPa are shown in Figure 2(a); the XRD patterns were recorded at the synchrotron X-ray radiation facility of the Institute of High Energy Physics, Beijing, China, and at Spring-8, Japan. All Bragg reflections gradually shifted to higher angles, implying that the lattice shrinks with increasing pressure. The XRD pattern did not change substantially as pressure was applied to the \((\text{NH}_3)\text{Cs}_0.4\text{FeSe}\) sample, indicating no structural transition even across this wide pressure range. The crystal structure of \((\text{NH}_3)\text{Cs}_0.4\text{FeSe}\) is body-centred tetragonal (space group: \(I4/mmm\)) at ambient pressure, and the space group is maintained up to 41 GPa.

Figure 1 | (a) \(M/H\) vs. \(T\) plots for \((\text{NH}_3)\text{Cs}_0.4\text{FeSe}\) (ZFC and FC modes) at ambient pressure and (b) \(M/H\) vs. \(T\) plots in ZFC mode under pressure. The inset in (a) shows how the \(T_c\) was determined. (c) \(T_c\) vs. \(p\) plot for \((\text{NH}_3)\text{Cs}_0.4\text{FeSe}\) (\(p = 0–13\) GPa), determined from the temperature dependence of \(M/H\), \(\chi’\) and \(R\) under pressure. In (c), the \(T_c\)’s (blue \((\text{NH}_3)\text{Cs}_0.4\text{FeSe}\) in increasing \(p\)), green \((\text{NH}_3)\text{Cs}_0.4\text{FeSe}\) in lowering \(p\)) and red \((\text{NH}_3)\text{Cs}_0.4\text{FeSe}\) in increasing \(p\) are determined from \(M/H\) vs. \(T\) and \(\chi’\) vs. \(T\) plots. The plots are shown in Figure 3(b) of our previous paper. The \(T_c\)’s (orange) determined from \(R\) vs. \(T\) plots are newly plotted in (c). In (c), the arrows indicate \(T_c\)’s lower than the temperatures denoted by bars.
The pressure dependence of $a$, $c$, and unit cell volume $V$ is shown in Figures 2(b)–(d). The $a$ and $c$ values were determined by applying LeBail fitting to the XRD patterns. The values determined from XRD patterns recorded at both facilities were substantially consistent. The $a$ value decreased dramatically up to 10 GPa and decreased slowly from 10 to 41 GPa, showing an exponential decay of $a$. As seen from Figure 2(c), $c$ also decreased monotonically up to 41 GPa. The difference, $\Delta a$, between the maximum $a$ (= 3.8331(1) Å) at 0 GPa and the minimum $a$ (= 3.604(2) Å) at 41 GPa was 0.23 Å, and the $\Delta a/a$ (0 GPa) = 0.06. In contrast, the difference, $\Delta c$, between the maximum $c$ (=16.217(1) Å) at 0 GPa and the minimum $c$ (=12.59(1) Å) at 41 GPa was 3.63 Å, and $\Delta c/c$ (0 GPa) = 0.22. These results suggest that the FeSe layer spacing $(=c/2)$ shrinks easily, which is reasonable considering that the interaction between FeSe layers is due to van der Waals force. Moreover, the compressibility of $c$ in (NH$_3$)$_y$Cs$_{0.4}$FeSe is much higher than that in parent anti-PbO type FeSe. Here, it may be reasonable that the compressibility is smaller in the metal intercalated FeSe than that in pure FeSe because there is additional ionic bonding with metal atoms. Nevertheless, the compressibility is opposite for the expected one. This may be due to the large space maintained by van der Waals force, which is produced by the insertion of ammoniated metal coordinate or NH$_3$. Namely, the insertion of molecules leads to the large compressibility. In addition, the anisotropy of compressibility is larger presumably because of the large space between FeSe layers.

The $V$ monotonically decreases without any significant change in rate as the pressure increases to 41 GPa, i.e., the $V$ – $p$ plot can be fitted with semi-empirical third-order Birch-Murnaghan equation$^{10}$ (see Figure 2(d)), showing no structural phase transition; the bulk modulus, $K_0$, derivative of bulk modulus with respect to $p$, $K'_0$, and the reference volume ($V$ at 0 GPa), $V_0$, of (NH$_3$)$_y$Cs$_{0.4}$FeSe are 39.6(1) GPa, 4.7(1) and 232.3(1) Å$^3$, respectively. The $K_0$ is larger than that ($K_0 = 30.7(1.1)$ GPa)$^9$ in anti-PbO type FeSe, showing the larger compressibility in (NH$_3$)$_y$Cs$_{0.4}$FeSe even in volume.

**A correlation between $T_c$ and structural parameters.** Figure 3(a) shows a $T_c$ vs. $c$ plot constructed based on the plots of $T_c$ vs. $p$ (Figure 1(c)) and $c$ vs. $p$ (Figure 2(c)). The $T_c$ decreases monotonically and reaches 11 K at $c = 14.665(5)$ Å (9 GPa) and <4.3 K at $c = 14.45(5)$ Å (11 GPa); the $c$ values at 9 and 11 GPa are evaluated based on the fitting curve with exponential formula shown in Figure 2(c); the fitting for experimental $c$ – $p$ plot with simple exponential expression was achieved to evaluate the $c$ at any pressure, which was a reasonable way to evaluate the $c$ values at the whole pressure range of 0–41 GPa.

Figure 3(a) suggests a clear correlation between $T_c$ and $c$, i.e. plane spacing, in which the FeSe plane spacing is $c/2$. On the other hand, the $T_c$ (=31 K) of K$_{0.3}$FeSe with a $c$ of 14.0367(7) Å at 0 GPa is higher than the $T_c$ (=11 K) of (NH$_3$)$_y$Cs$_{0.4}$FeSe with a $c$ of 14.665(5) Å (9 GPa), indicating that the variation of $T_c$ with $c$ (or plane spacing) is not universally consistent for all metal-doped FeSe solids (non-ammoniated and ammoniated solids).

Figure 3(b) shows a $T_c$ vs. $c$ plot that includes both the $T_c$ vs. $c$ plots obtained from the pressure effect ((NH$_3$)$_y$Cs$_{0.4}$FeSe) and from the chemical pressure effect (or $T_c$ vs. $c$ in various metal-doped FeSe); $x$ is 0.4 or 0.5 in the (NH$_3$)$_x$M$_y$FeSe used to determine the chemical pressure effect. The graph clearly shows that the $T_c$ is related to $c$ (FeSe plane spacing), over all the $c$ values recorded, based on both chemical and physical pressure effects. In the (NH$_3$)$_y$M$_x$FeSe solids, the smallest $c$ realized at 0 GPa is 14.84(1) Å for (NH$_3$)$_y$FeSe$_2$ ($T_c = 30$ K), which is smaller than that (16.16(5) Å$^9$) for ammoniated...
KFe$_2$Se$_2$ (= (NH$_3$)$_y$K$_{0.5}$FeSe) with $T_c = 30$ K; this result ($T_c = 30$ K for 14.84(1) Å) is not plotted in the graph shown in Figure 3(b) because the $x$ (=0.6/2 = 0.3) is smaller than 0.5. The result does not follow the $T_c$ vs. $c$ scenario shown in Figure 3(b). The reason why an outlier ($T_c = 30$ K for 14.84(1) Å) is obtained in $(NH_3)_xK_yFeSe$ is unclear, but the factor other than $c$ may be necessary to be considered. Except for the result, the $T_c$ - $c$ plots for $(NH_3)_xM_yFeSe$ ($x \approx 0.5$) seem to be meaningful, as seen from Figure 3(b). In addition, a $c$ of 14.4 Å in $(NH_3)_xM_yFeSe$ has never been achieved without applying pressure. Thus, we determined the $T_c$ for an FeSe plane spacing that cannot be achieved without the application of pressure.

Furthermore, we tried to relate $T_c$ to other factors such as $a$, $c/a$, the Se-Fe-Se angle ($\alpha$), and the anion height (height of Se from the Fe plane). As seen from Figure 3(c), the $T_c$ for $(NH_3)_xCs_{0.4}FeSe$ under pressure is related to the lattice constant $a$, i.e. the $T_c$ decreases monotonically with decreasing $a$. However, the $T_c$ values (chemical pressure effect) realized for various $(NH_3)_xM_yFeSe$ at 0 GPa do not follow the $T_c$ vs. $a$ relationship obtained by the application of pressure (physical pressure effect), indicating that the $T_c$ is not simply or always related to $a$. Moreover, the behaviour of $T_c$ - $c/a$ is also different between physical and chemical pressure effects as seen from Figure 3(d).

Since we did not obtain the Rietveld refinements for XRD patterns, but used LeBail fitting, the atomic coordinates of Fe and Se were not obtained. It should be noted that Fe and Se occupy the positions (0.0, 0.5, 0.25) and (0.0, 0.0, $z$), respectively, and the $x$ and anion height cannot be exactly determined. At the present stage, we tried to evaluate $x$ and anion height based on the lattice constants at each $p$ and the atomic coordinates determined at ambient pressure.$^9$

The correlations between $T_c$ and $x$ or anion height were investigated over the pressure range of 0 to 13 GPa. The $T_c$ decreased monotonically when the $x$ and anion heights approached the ideal values, 109.5$^5$ and 1.38 Å (Figures S2 and S3 in Supplementary Information), respectively, showing different $T_c$ behaviour from the FeAs materials, in which the $T_c$ increases when $x$ and anion height are close to the ideal values of 109.5$^5$ and 1.38 Å, respectively (inverse V-shaped behaviour)$^{12,13}$. These results imply that the $T_c$ may not be simply related to $x$ and the anion height, as in FeAs. However, the Rietveld refinement for the XRD pattern at each $p$ is absolutely required to clarify more precisely the relationship between $T_c$ and $x$ or the anion height. The relationship between $T_c$ and anion height is briefly dealt with in the Discussion section, and an interesting scenario is suggested.

The rapid increase in $T_c$ above 13 GPa. We applied more than 13 GPa pressure to the $(NH_3)_yCs_{0.4}FeSe$ sample. Figure 4(a) shows the $R$ vs. $T$ plots from 16 to 41 GPa, which surprisingly show a drop in $R$ above 45 K in the limited pressure range from 16 to 21 GPa. The $R$ vs. $p$ plots at 21 GPa were measured in an $H$ range of 0 to 7 T (Inset of Figure 4(a)), showing that the $T_c$ shifted to the left as $H$ increased. Therefore, the drop in $R$ (Figure 4(a)) can be unequivocally assigned to a superconducting transition. The $T_c$ was plotted as a function of $p$ over the wide range of 0 to 41 GPa (Figure 4(b)). As described in the previous section, the $T_c$ in $(NH_3)_yCs_{0.4}FeSe$ decreased monotonically with increasing pressure up to 13 GPa, where superconductivity vanished, but the superconductivity quickly recovered above 13 GPa, and the $T_c$ became as high as 46 K at 16 GPa. The $T_c$ increased slightly at pressures up to 21 GPa, reaching 49 K at...
21 GPa. The $T_c$ slowly dropped above 21 GPa, and at 41 GPa no superconductivity was observed down to 4.9 K. This behaviour is similar to that reported previously for Tl$_{0.6}$Rb$_{0.4}$Fe$_{1.67}$Se$_2$ and K$_{0.8}$Fe$_{1.7}$Se$_2$, in which the $T_c$’s increased dramatically up to 48 K or 48.7 K from 0 K (10 GPa) under pressures greater than 11 GPa. The first and the second dome-like superconducting phases were named as SC I and SC II, respectively, as seen from Figure 4(b). Figure 4(b) shows the disappearance of SC I and the emergence of SC II at 11–15 GPa.

To confirm the presence of SC II, we measured the pressure dependence of $T_c$ for another batch (second batch) of (NH$_3$)$_y$Cs$_{0.4}$FeSe, which was made using the same technique as the sample whose results appear in the graph shown in Figure 4(b). This sample is referred to as ‘the second sample’ for the convenience of readers. The $T_c$ decreased as increasing pressure was applied to the sample. The behaviour of $T_c$ in the second sample (Figure 4(c)) was the same as the data described above (Figure 4(b)) in the pressure range up to 6 GPa, but the $T_c$ rapidly increased up to 30 K at 8.8 GPa (see Figure S4 of Supplementary Information). The $R$ vs. $T$ plot for the third sample taken from the second batch of material was also measured, and the $T_c$ vs. $p$ plot is shown in Figure 4(c). Figure 4(d) shows the $T_c$ vs. $p$ plots determined from all the (NH$_3$)$_y$Cs$_{0.4}$FeSe samples. Here it should be noticed that for the samples 2 and 3 of Figures 4(c) and (d), the $T_c$’s are plotted for the superconducting transition ascribable to the SC I, while the $T_c$’s are plotted for that ascribable to SC II, so that the plots can be reasonably compared with those of sample 1.

The $T_c$ values for the second and the third samples (second batch) are consistent with each other (Figure 4(c)). As seen from Figures 4(b) and (d), the SC II emerged suddenly above 15 GPa in the first batch. On the other hand, as seen from Figures 4(c) and (d), the SC II slowly appeared above 5 GPa in the second batch. The $T_c$ for the SC II in the second sample reached 47 K at 14 GPa, which is the same as the $T_c$ for the sample 1 providing the graph shown in Figure 4(b). These results strongly support the presence of SC II.

Here, we briefly discuss the difference in physical and chemical properties of the sample batches, 1 and 2, of (NH$_3$)$_y$Cs$_{0.4}$FeSe. The $T_c$ of the second batch was 32.5 K at ambient pressure, and the shielding fraction was 23% at 10 K, showing the same magnetic properties as the other (NH$_3$)$_y$Cs$_{0.4}$FeSe sample prepared in this study. The XRD pattern provided the lattice constants ($a = 3.8232(3)$ Å and $c = 16.247(3)$ Å) which are close to those ($a = 3.8331(1)$ Å and $c = 16.217(1)$ Å) in Ref. 5. Furthermore, the stoichiometry of Cs was determined by the Rietveld refinement, and the chemical composition for the second batch was evaluated to be (NH$_3$)$_y$Cs$_{0.2}$FeSe, which is almost the same as that, (NH$_3$)$_y$Cs$_{0.255(5)}$FeSe, reported

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**Figure 4** | (a) $R$ vs. $T$ plots for (NH$_3$)$_y$Cs$_{0.4}$FeSe at pressures of 16–41 GPa. Inset of (a): $R$ vs. $T$ plots for (NH$_3$)$_y$Cs$_{0.4}$FeSe at 21 GPa at 0, 3 and 7 T. (b) $T_c$ vs. $p$ plot ($p = 0–41$ GPa) determined from the temperature dependence of $M/H$, $\chi'$, and $R$ for (NH$_3$)$_y$Cs$_{0.4}$FeSe (sample 1 (first batch)) under pressure. Colours of plots in the pressure range below 13 GPa correspond to those in Figure 1(c). The star refers to the $T_c$ determined from the $R$ vs. $T$ plot. (c) $T_c$ vs. $p$ plot ($p = 0–14$ GPa) determined from the temperature dependence of $R$ for (NH$_3$)$_y$Cs$_{0.4}$FeSe (sample 2 and 3 (second batch)) under pressure. Colours of plots in blue and purple refer to the samples 2 and 3, respectively. (d) $T_c$ vs. $p$ plot ($p = 0–41$ GPa) constructed by combining the $T_c$ vs. $p$ plots shown in Figures 4(b) and (c). In (b) and (d), the arrows indicate $T_c$’s lower than the temperatures denoted by bars.
previously\(^7\). These results imply that the second batch is a typical \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\) sample used in this study. Thus, the difference in physical and chemical properties between batches 1 and 2 seems to be too small. Nevertheless, unknown physical and chemical difference may be hidden, but it is unclear at the present stage. More detailed work is indispensable for clarifying the difference.

We carefully checked the \(R\) vs. \(T\) plots of the second sample at 8.8 GPa (9.5 GPa) to clarify whether the material with a superconducting transition lower than 30 K (33 K) observed. The \(R\) vs. \(T\) plots at 8.8 and 9.5 GPa showed a very small drop in \(R\) below 10 K together with the rapid drops at 30 and 34 K, respectively (Figure S4 in Supplementary Information), suggesting the multiple superconducting phases of low and high \(T_c\) at around the pressure range of 8.8 to 9.5 GPa; this may be due to the presence of microstructure corresponding to two superconducting phases, but the exact origin why the multiple superconducting phases were observed in another batch remains to be solved. The investigation using the second batch unequivocally evidenced the presence of second-dome superconducting phase.

These results show the presence of a high-\(T_c\) phase in \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\) (\(T_\text{c} > 45\) K) that emerges in the pressure range from 14 to 21 GPa. The \(T_\text{c}\) of 49 K observed at 21 GPa is one of the highest reported in bulk superconductors of FeSe-derived materials. The low-\(T_c\) phase disappears completely at around 11–13 GPa. Therefore, that pressure may be recognized as a 'quantum critical point'. With reducing pressure, the \(T_c\) follows the \(T_c\) vs. \(p\) plot constructed for increasing pressure (not shown), implying that the pressure dependence of \(T_c\) is reversible.

**Discussion**

In this study, it has been found that the \(T_c\) of \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\) is related to the lattice constant \(c\), i.e. the FeSe plane spacing in the pressure range up to 13 GPa. The variation of \(T_c\) due to plane spacing is convincingly shown not only by the pressure dependence of \(T_c\) in \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\), but also from the \(T_c\)'s in various ammoniated metal doped FeSe's, \((\text{NH}_3)_y\text{M}x\text{FeSe}\). Both chemical and physical pressure effects have made clear the dependence of \(T_c\) on FeSe plane spacing. This implies that an increase in 2D nature produces higher \(T_c\)'s in \((\text{NH}_3)_y\text{M}x\text{FeSe}\), meaning that an increase in Fermi nesting can stabilize the superconducting state. We suggested previously\(^8\) that a spin-density wave (SDW) ground state with a weak magnetic moment played an important role in superconductivity, as suggested in \(\text{NaFe}_y\text{−}x\text{Co}_x\text{As}\)\(^9\). Recently, the intercalation of metal atoms into FeSe was achieved using a solvent (ethylenediamine) other than liquid \(\text{NH}_3\), which expands the FeSe plane spacing more than \(\text{NH}_3\)\(^10\). Nevertheless, the \(T_c\) saturates at around 45 K, meaning that \(T_c\) will not rise above 45 K even if the 2D nature increases further.

Furthermore, we applied pressures of more than 13 GPa to \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\). The new superconducting phase exhibiting higher \(T_c\) emerged dramatically after the first superconducting phase vanished. The re-emerged superconducting phase showed almost a constant \(T_c\) (46–49 K) in the pressure range from 14 to 21 GPa. This behaviour of pressure-induced re-appearance of superconductivity is quite similar to that of previously discovered \(\text{Ti}_0.6\text{Rb}_0.4\text{Fe}_{1.67}\text{Se}_2\) and \(\text{K}_0.6\text{Fe}_{1.7}\text{Se}_2\)\(^11\). Our study reveals the presence of a pressure-induced high-\(T_c\) phase in \(\text{M}x\text{FeSe}\). Sun et al. suggested that the re-emergence of superconductivity in pressurised \(\text{Ti}_0.6\text{Rb}_0.4\text{Fe}_{1.67}\text{Se}_2\) and \(\text{K}_0.6\text{Fe}_{1.7}\text{Se}_2\) is closely associated with a quantum critical transition\(^12\), in which both the antiferromagnetic phase and the low-\(T_c\) superconducting phase disappear. On the other hand, we observed the multiple superconducting phases of low-\(T_c\) and high-\(T_c\) in the second sample (second batch) of \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\) (see Figures S4 in Supplementary Information) at pressures below 13 GPa. This implies that there are inhomogeneous parts of low-\(T_c\) and high-\(T_c\) phases even at the same pressure.

The different \(T – p\) phase diagram between two batches of \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\), that the first batch provides the distinguished SC I and SC II while the second batch provides the superposed SC I and SC II, must be discussed. As described in the results section, the chemical and physical characters of both batches were almost the same. Therefore, the difference may not be assigned to the different physical/chemical nature. Under high pressure, SC II exactly appeared in both batches, implying that SC II is stabilized under high pressure, while SC I disappeared with increasing pressure. In the intermediate pressure, SC I and SC II seem to coexist in the samples 2 and 3. If the inhomogeneity of applied pressure is present, the SCI and SC II may coexist in the DAC cell. If it is the case, the sample 1 may provide the exact \(T – p\) phase diagram in \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\), because the complete disappearance of SC I causes the emergence of SC II. The origin is not still clear, but the presence of high-\(T_c\) phase (SC II) was convinced (Figures 4(b)–(d)).

Here, it should be noted that non-ammoniated \(\text{Ti}_0.6\text{Rb}_0.4\text{Fe}_{1.67}\text{Se}_2\) and \(\text{K}_0.6\text{Fe}_{1.7}\text{Se}_2\) may belong to another type of alkali selenide superconductor with antiferromagnetic insulating and superconducting phases at ambient pressure; antiferromagnetic insulating phase is not unambiguously found in \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\). If the antiferromagnetic state is contained in the sample, the deficiency of Fe may be observed. The deficiency of Fe has not been confirmed in ammoniated metal doped FeSe through our study, which was performed by energy dispersive x-ray spectrometry. Thus, the chemical composition of \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\) is different from the above single crystals \((\text{Ti}_0.6\text{Rb}_0.4\text{Fe}_{1.67}\text{Se}_2\) and \(\text{K}_0.6\text{Fe}_{1.7}\text{Se}_2\) concerning Fe deficiency, implying that the average structure of \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\) is not 245 phase (antiferromagnetic order phase)\(^16\). Since \(\text{Ti}_0.6\text{Rb}_0.4\text{Fe}_{1.67}\text{Se}_2\) and \(\text{K}_0.6\text{Fe}_{1.7}\text{Se}_2\) can be expressed as the 245 phase\(^17\) which was assigned to antiferromagnetic order phase, the volume fraction of the superconducting phase which was assigned to 278\(^18\) may be lower in the above crystals than that of ammoniated metal doped FeSe. Therefore, considering the different microstructures of \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\) and \(\text{Ti}_0.6\text{Rb}_0.4\text{Fe}_{1.67}\text{Se}_2\) and \(\text{K}_0.6\text{Fe}_{1.7}\text{Se}_2\), the mechanism of emergence of a high-\(T_c\) phase in \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\) would be different from that in non-ammoniated alkali selenide superconductors\(^18\).

Namely, in the former, the relationship between the re-emergence of SC II and magnetic properties is still ambiguous, although the latter was closely associated with the magnetic transition (antiferromagnetic to paramagnetic)\(^19\).

The pressure dependence of the XRD pattern showed no clear structural phase transition up to 41 GPa, suggesting that the crystal structure of the high-\(T_c\) phase is the same as that of the low-\(T_c\) phase. Here we must stress that detailed information on atomic coordinates has not yet been obtained under pressure, since we achieved only LeBail fitting for XRD patterns up to 41 GPa. This implies that the possibility of changed atomic coordinates in the high-\(T_c\) phase observed above 13 GPa cannot be ruled out.

We present a scenario for the pressure dependence of \(T_c\) on the anion height. Recently, Lu et al. reported a V-shaped relationship (V-shaped curve) between \(T_c\) and anion height in FeSe-derived superconductors\(^19\). Examination of the plot of \(T_c\) vs. anion height in FeSe-derived superconductors (Figure 4 of Ref. 18), suggests that the \(T_c\) should decrease when the anion height decreases to 1.45 Å from 1.53 Å (the anion height in \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\) at 0 GPa) and it should increase steeply with a decrease in anion height to less than 1.45 Å\(^18\). Furthermore, the \(T_c\) should decrease below 1.38 Å (Figure 45 of Ref. 15) since an inverse V-shaped curve is found in FeAs-derived superconductors\(^12,13\). We plotted the \(T_c\) of \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\) as a function of anion height over the wide pressure range of 0–41 GPa (Figure S5 in Supplementary Information), which shows V-shaped/inverse V-shaped behaviour although the turning points of anion height (1.33 and 1.26 Å) of \((\text{NH}_3)_y\text{Cs}_0.4\text{FeSe}\) deviate from the above values (1.45 and 1.38 Å). Thus, a scenario based on V-shaped and inverse V-shaped curves\(^12,13,19\) describing the dependence
of $T_c$ on the anion height found in FeSe and FeAs based superconductors may provide a physical basis to explain the pressure dependence of $T_c$ observed in this study. To verify this interpretation, more precise analyses of XRD patterns with Rietveld refinement are indispensable.

The possibility that a magnetic transition (variation of magnetic structure) produces the re-emergence of superconductivity (or the appearance of a high-$T_c$ phase) as in $T_{10.6}$Re$_{0.4}$FeSe and $K_{0.8}$Fe$_{1.5}$Se$_2$ cannot be completely ruled out in $(NH_3)_x$Cs$_{0.4}$FeSe at the present. To clarify the correlation between superconductivity and magnetism, measurements of neutron diffraction and magnetism under pressure are indispensable.

Finally, it is important to discuss whether the superconducting coupling mechanism in the high-$T_c$ superconducting phase is the same as that in the low-$T_c$ phase. At the present stage, how the second phase is engendered by pressure is still unclear, although a geometrically based scenario is suggested by the empirical results of this study. The fact that the high-$T_c$ phase appears in $(NH_3)_xM$FeSe as well as $M_x$FeSe at high pressure suggests that a pressure-induced high-$T_c$ phase may be an intrinsic and universal feature in metal doped FeSe superconductors.

**Methods**

**Sample preparation and characterizations.** The samples of $(NH_3)_x$Cs$_{0.4}$FeSe were prepared according to the method described in the previous paper. The XRD pattern of the sample under pressure was measured at 297 K at two synchrotron radiation facilities, the 4W2 beamline at the Beijing Synchrotron Radiation Facility and BL02B2 at SPring-8. A diamond anvil cell (DAC) was used for the high-pressure XRD measurement. The pressure was determined by monitoring ruby fluorescence. The pressure was determined by monitoring ruby fluorescence. The pressure was determined by monitoring ruby fluorescence.

**Temperature dependence of $R$.** The temperature dependence of $R$ was measured in four-terminal measurement mode under pressure. The sample was introduced into the DAC in an Ar-filled glove box so as to apply the pressure to the sample without any exposure to air. The sample was loaded directly onto a plate of cubic BN/epoxy resin/thermoc in the DAC, and the four Pt electrodes for resistance measurement were between the sample and the plate. The experimental details for setting the sample in the DAC and for R-measurement are described elsewhere. The pressure was determined by monitoring ruby fluorescence. A constant electric current, $I (=100 \mu A)$, was supplied by an Advantest R6561 Multimeter, which also measured the voltage. To confirm that a reliable resistance measurement was obtained, the constant current flow in this measurement system and the linear $I$ vs $V$ curve were carefully checked, implying that the data on resistance are reliable and the thermal voltage can be ignored.

1. Ying, T. P. et al. Observation of superconductivity at 30–46 K in $A_x$Fe$_2$Se$_3$ ($A$ = Li, Na, Ba, Sr, Ca, Yb, and Eu). *Sci. Rep.* 2, 426 (2012).
2. Burrard-Lucas, M. et al. Enhancement of the superconducting transition temperature of FeSe by intercalation of a molecular spacer layer. *Nature Mater.* 12, 15–19 (2013).
3. Ying, T. P. et al. Superconducting phases in potassium-intercalated iron selenides. *J. Am. Chem. Soc.* 135, 2951–2954 (2013).
4. Sedimar, S. J. et al. Ammonia-rich high-temperature superconducting intercalates of iron selenide revealed through time-resolved in situ X-ray and neutron diffraction. *J. Am. Chem. Soc.* 136, 630–633 (2014).
5. Zheng, L. et al. Superconductivity in $(NH_3)_x$Cs$_{0.4}$Fe$_{1.5}$Se. *Phys. Rev. B* 88, 094521 (2013).

6. Sukai, Y. et al. Superconducting phases in $(NH_3)_xM_x$Fe$_{1.5}$Se$_2$ ($M$ = Li, Na, and Ca). *Phys. Rev. B* 89, 144509 (2014).
7. Ye, G. I. et al. Superconductivity in $Yb_xM_x$HNCl ($M$ = NH$_3$ and THF). *Phys. Rev. B* 86, 134501 (2012).
8. Hsu, F.-C. et al. Superconductivity in the PBO-type structure a-FeSe. *Proc. Natl. Acad. Sci. USA* 105, 14262 (2008).
9. Margadonna, S. et al. Superconductivity evolution of the low-temperature crystal structure and bonding of the superconductor FeTe ($T_c = 37$ K). *Phys. Rev. B* 80, 085406 (2009).
10. Fan, D., Xu, J., Ma, M., Liu, J. & Xie, H. P.-V. $T_c$ equation of state of molybdenite (MoS$_2$) by a diamond anvil cell and in situ synchrotron angle dispersive X-ray diffraction. *Physica B* 451, 53–57 (2014).
11. Guo, J. G. et al. Superconductivity in the iron selenide K$_x$Fe$_2$Se$_2$ ($0 \leq x \leq 1.0$). *Phys. Rev. B* 82, 100520R (2010).
12. Lee, C.-H. et al. Effect of structural parameters on superconductivity in fluorine-free LiFe$_2$O$_{2.5}$, ($Ln =$ La, Nd). *J. Phys. Soc. Jpn.* 77, 083704 (2008).
13. Mizuguchi, Y. & Takano, Y. Review of Fe chalcogenides as the simplest Fe-based superconductor. *J. Phys. Soc. Jpn.* 79, 102001 (2010).
14. Sun, I. L. et al. Re-emerging superconductivity at 48 kelvin in iron chalcogenides. *Nature* 483, 67–69 (2012).
15. Cai, P. et al. Visualizing the microscopic coexistence of spin density wave and superconductivity in underdoped Na$_x$$_{0.4}$FeSe. *Nature Commun.* 4, 1596 (2013).
16. Hatakeya, T., Noji, T., Kawamata, T., Kato, M. & Koike, Y. New Li-ethylene diamine-intercalated superconductor Li$_x$(C$_2$H$_8$N$_2$)$_2$Fe$_2$Se$_2$ with $T_c = 45$ K. *J. Phys. Soc. Jpn.* 82, 123705 (2013).
17. Ding, X. et al. Influence of microstructure on superconductivity in K$_x$Fe$_2$As$_2$ and evidence for a new parent phase K$_x$Fe$_2$Se$_2$. *Nature Commun.* 4, 1897 (2013).
18. Guo, J. et al. Pressure-driven quantum criticality in iron-selenide superconductors. *Phys. Rev. Lett.* 108, 197001 (2012).
19. Lu, X. et al. Superconductivity in LiFeO$_2$Fe$_2$Se$_2$ with anti-PbO-type spacer layers. *Phys. Rev. B* 89, 020507R (2013).
20. Shimizu, K., Amaya, K. & Suzuki, N. Pressure-induced superconductivity in elemental materials. *J. Phys. Soc. Jpn.* 74, 1345–1357 (2005).

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**Author contributions**

Y.K. designed this research project and supervised experiments. M.I., L.Z. and Y.S. synthesized and characterized $(NH_3)_x$Cs$_{0.4}$FeSe samples. M.S., Y.N. and H.L.T.N. carried out the resistance measurements under pressure. M.I., S.A. and T.C.K. measured DC and AC magnetic susceptibility under pressure. D.G., J.G., J.L., Y.-C.L. and L.S. measured XRD patterns under pressure. Y.S., M.S. and K.P. performed LeBail fitting for XRD data under pressure. Y.K. discussed the experimental results with H.G., M.S., T.K. (Osaka), T.K. (Okayama), K.S., L.S. and K.P. during this study. Y.K. managed (edited) all parts of this paper.

**Additional information**

**Supplementary information** accompanies this paper at http://www.nature.com/scientificreports

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