Doping and two distinct phases in strong-coupling kagome superconductors

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The vanadium-based kagome superconductor CsV$_3$Sb$_5$ has attracted tremendous attention due to its unconventional anomalous Hall effect (AHE), its charge density waves (CDWs), and a pseudogap pair density wave coexisting with unconventional strong-coupling superconductivity (SC). The origins of time-reversal symmetry breaking (TRSB), unconventional SC, and their correlation with different orders in this kagome system is of great significance, but, so far, is still under debate. Doping by the chemical substitution of V atoms in the kagome layer provides the most direct way to reveal the intrinsic physics that originates from the kagome lattice, but remains unexplored. Here, we report, for the first time, the synthesis of Ti-doped CsV$_3$Sb$_5$ single crystals with controllable carrier doping concentration. The Ti atoms directly substitute for V in the vanadium kagome layers. Remarkably, the Ti-doped CsV$_3$Sb$_5$ SC phase diagram shows two distinct SC phases. The lightly-doped SC phase has a V-shaped gap pairing, coexisting with CDWs, indicating a strong-coupling unconventional SC nature. The other SC phase has a U-shaped gap pairing without CDWs, displaying a conventional SC feature. This is the first observation of the two distinct phases in superconductors, revealed through Ti doping of CsV$_3$Sb$_5$. These findings pave a new way to synthesise doped CsV$_3$Sb$_5$ and represents a new platform for tuning the superconducting pairing and multiple orders in kagome superconductors.
The newly discovered kagome metals AV$_3$Sb$_5$ (A=K, Rb, Cs) have attracted tremendous research interest as a novel platform to study the interplay between nontrivial band topology, superconductivity (SC), and multiple density waves.$^{1-6}$ The AV$_3$Sb$_5$ carries no magnetic order at low temperature but exhibits an unconventional anomalous Hall effect (AHE) that is usually observed in ferromagnetic materials$^{6-8}$. Most recently, correlated electronic state and roton pair density wave (PDW) have been observed in the strong-coupling kagome superconductor CsV$_3$Sb$_5$$^{9,10}$. Time-reversal symmetry breaking (TRSB) was proposed to originate from the unconventional charge density waves (CDW)$^{1,11,12}$, but this is still under debate$^{13-25}$. Therefore, the nature of the superconducting state remains elusive. Theoretically, CsV$_3$Sb$_5$ has a Z$_2$ nontrivial topological band structure with topological surface states, indicating an unconventional superconductor$^{4,26}$, while some theoretical works propose the conventional s-wave SC in CsV$_3$Sb$_5$. Experimentally, transport evidence for gap nodes$^{27}$ and gapless core states in magnetic-field induced vortices$^2$ have been reported, while tunneling diode oscillator$^{28}$ and nuclear quadrupole resonance$^{29}$ experiments showed the nodeless superconductivity nature of CsV$_3$Sb$_5$. Therefore, full understanding of the pairing of the superconducting state and its correlation with the kagome geometry, TRSB and unconventional density waves remains an important issue to be urgently resolved.

Tuning different orders via mechanisms like carrier doping or external pressure provides an effective way to study the nature of the superconducting state and its correlation with the other orders$^{30-33}$. In experiments, selective oxidation of exfoliated thin flakes is reported to have a notable effect on both SC and CDW orders in the Cs variant. A superconducting dome was obtained as a function of doping content$^{34}$. Furthermore, the pressure effects have recently been studied, showing that superconducting domes arise upon applied pressure with enhanced SC transition temperature and no sign of a structural phase transition$^{5,35-40}$. Although tuning of $T_c$ has been achieved in these works, the microscopic origin of SC pairing and its correlation with the charge orders are still elusive. As the unusual properties are believed to come from the proximity of the V 3d orbitals close to the van Hove singularity (vHs), chemical substitution of the transition metal V in the kagome layer should be an effective way to directly tune the vHs and unveil the origin of intrinsic electronic structures of AV$_3$Sb$_5$, but remains so far unexplored.

In this Letter, we report the synthesis of titanium-doped CsV$_{3-x}$Ti$_x$Sb$_5$ crystals with controlled carrier doping concentration for the first time. We confirm that the Ti atoms mainly substitute the V sites in the VSb kagome layer through high-resolution scanning transmission electron microscopy (STEM) chemical imaging. Low temperature scanning tunneling microscopy/spectroscopy (STM/S) reveals that the 2$a_0 \times$
2\(a_0\) and 4\(a_0\) CDWs evolve from long-range to short-range modulations, and gradually disappear as the titanium content, \(x\), increases. The d\(I/dV\) spectra show that the SC transitions from V-shaped pairing at \(x=0.03\) to U-shape pairing at \(x=0.15\). The magnetic susceptibility and transport measurements indicate that, as \(x\) increases, both the onset temperatures of CDW gradually decrease and are absent at around \(x=0.15\). In addition, as the doping content increases, \(T_c\) drops to a minimum around \(x=0.04\), then increases to 3.5 K at around \(x=0.15\), showing a double-dome shape in the phase diagram. The two dome regions show very different superconducting transition behavior in the transport measurement. These results demonstrate that the CsV\(_{3-x}\)Ti\(_x\)Sb\(_5\) exhibits two distinct SC phases. The lightly doped region shows an unconventional SC phase with a V-shape gap pairing, coexisting with CDWs, while the other phase displays a conventional SC phase with a fully-gapped pairing.

**Synthesis of the Ti-doped CsV\(_{3-x}\)Ti\(_x\)Sb\(_5\) single crystals**

We have successfully grown Ti-doped CsV\(_{3-x}\)Ti\(_x\)Sb\(_5\) crystals with different doping ratios ranging from \(x=0\) to 0.15. The as-grown Ti-doped CsV\(_{3-x}\)Ti\(_x\)Sb\(_5\) single crystals (Methods) exhibit a stacking sequence of Cs-Sb2-VSb1-Sb2-Cs layers with hexagonal symmetry (space group P 6/mmm). In the VSb1 layer, the kagome sub-lattice of vanadium is interwoven with a simple hexagonal sub-lattice formed by the Sb1 atoms. The similar ionic radii of Ti\(^{4+}\) (60.5 pm) and V\(^{3+}\) (61.5 pm) ions suggest the possibility of Ti substitution at the V sites in the kagome lattice (Fig. 1a). A typical CsV\(_{3-x}\)Ti\(_x\)Sb\(_5\) crystal with a lateral size of over 1 cm and regular shape is shown in Fig. 1b. The representative x-ray diffraction (XRD) pattern of the CsV\(_{3-x}\)Ti\(_x\)Sb\(_5\) single crystal only shows the (00l) diffraction peaks and confirms the pure phase of the as-grown single crystal, with a preferred [001] orientation (Fig. 1c). The lattice parameters \(a\), \(b\), and \(c\) are measured to be 5.521, 5.521 and 9.336 Å, respectively, by single crystal diffraction, which are slightly smaller than those of pristine CsV\(_3\)Sb\(_5\) (5.548, 5.548, and 9.349 Å, respectively) due to the smaller ionic radius of Ti\(^{4+}\). The Ti-doped CsV\(_{3-x}\)Ti\(_x\)Sb\(_5\) single crystal is thin and can show some regular hexagonal morphology with a natural tendency to exfoliate (Fig.1 d). The doping contents of CsV\(_{3-x}\)Ti\(_x\)Sb\(_5\) are determined by both EDS and the inductively coupled plasma (ICP), for which the measurement results are well consistent. The doping contents of a typical Ti-doped CsV\(_{3-x}\)Ti\(_x\)Sb\(_5\) single crystal determined by energy-dispersive x-ray spectroscopy (EDS) is \(x=0.15\) as shown in Fig. 1e, corresponding to the 5 % substitution ratio of V.
Determination of the Ti substitution position

To confirm the successful doping of Ti into the CsV₃Sb₅ lattice, we carried out atomic-scale structural and chemical analysis on cross-sectional samples using aberration corrected STEM. Figures 2a and b show the simultaneously acquired STEM annular bright-field (ABF) image and high-angle annular dark-field (HAADF) Z-contrast image of the Ti-doped Cs₃₋ₓTiₓSb₅ (x=0.15) sample along the [100] projection, with the structural models overlaid. Both images clearly reveal the perfect crystalline structure of the Ti-doped sample without noticeable structural defects, suggesting that Ti doping does not degrade the crystal quality. The distinct sequential layers of Cs-Sb₂-VSb₁-Sb₂-Cs were further confirmed by the elemental mapping shown in Figure S1. Chemical analysis via electron energy-loss spectroscopy (EELS) unambiguously confirms the presence of Ti dopants (Fig. 2c), with the overall Ti substitution of V measured to be ~5 %, which is consistent with the EDS and ICP measurements. The spatial distribution of the Ti dopants is revealed by the atomic-resolution chemical mapping shown in Figs. 2d-f. By comparing the simultaneously acquired V map (Fig. 2d) and Ti map (Fig. 2e), it is clear that most of the Ti dopants are located in the V-Sb₁ layer, coinciding with the V atomic columns. Imaging and chemical analysis of the cross-sectional sample along the [210] projection (Figure S2) reveal similar information. These results, thus, suggest that the majority of the Ti dopants is substituting the V sites in the CsV₃Sb₅ lattice, with a tiny amount forming interstitial dopants in the Cs and Sb layers.

STM/S investigation of the Ti-doped CsV₃Sb₅ samples

We then studied the evolution of CDW on the surface of the Cs₃₋ₓTiₓSb₅ samples with various Ti doping contents at the atomic scale by low temperature STM/S (Fig. 3a-j). In the STM measurements, almost all the surface regions show large-scale Cs surface topography. Large-scale Sb surface topography was rarely observed. Thus, we applied the STM manipulation method to sweep the top Cs atoms away to expose large-scale Sb surfaces. In both STM topography (T(r,V)) and dI/dV maps (dI/dV(r,V)) of the large-scale Sb surface, we found that, as compared to the undoped CsV₃Sb₅ sample many small dark spots appear and randomly distribute in the STM images. Atomically resolved STM images demonstrate that the Sb lattice remains continuous across the dark spots (inset in Fig. 3a), which indicates that the dark spots originate from electron scattering near the Ti dopants in the underlying VSb₁ layer. Furthermore, we analyzed the height histogram of the STM images of the Sb surface and found that the area density of the dark spots shows a positive correlation with the dopant contents (Fig. 3k and Fig. S3), which further
demonstrates that the dark spots in the STM images originate from Ti dopants in the underlying VSB1 kagome layer.

In addition to the emergence of dark spots, there are significant changes of the CDW in both STM images and dI/dV mapping of the Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$ samples as compared with the undoped sample. We find that the bi-directional $2a_0 \times 2a_0$ (green circles in Fig. 3c) and unidirectional $4a_0$ CDWs (red squares in Fig. 3c) at all energies (details in Fig. S4) are preserved for the lightly doped CsV$_{3-x}$Ti$_x$Sb$_5$ samples ($x=0.03$ and $x=0.04$) (Figs. 3a-f). In addition, the single-domain 1Q-$4a_0$ CDW in the 60 nm $\times$ 60 nm area in the $x=0.03$ sample (Fig. 3a) split into two or three domains (highlighted by the blue and green dotted lines in Fig. 3d) in the $x=0.04$ sample, indicating that the 1Q-$4a_0$ CDW evolves from long-range to short-range order. Eventually, both $2a_0 \times 2a_0$ and $4a_0$ CDWs almost disappear in the Fourier transform of the topography and dI/dV mapping of the $x=0.15$ sample (Figs. 3g-i). Just small patches of local $4a_0$ CDW domains can be observed in the STM images (Fig. 3j).

The simultaneous suppression and disappearance of long-range $2a_0 \times 2a_0$ and $4a_0$ charge orders strongly indicates that these two CDWs are intertwined with each other. It should be noticed that, the bidirectional $4/3a_0$ PDW peaks$^9$ (labeled by pink circles in Fig. S4a,b) in the Fourier transform of dI/dV maps at low energy ($< 5$ meV) are suppressed at $x=0.03$ and 0.04 sample but invisible at the $x=0.15$ sample (Fig. S4c), which suggests that the PDW is intertwined with $2a_0 \times 2a_0$ and $4a_0$ CDWs. In addition, accompanying the disappearance of $2a_0 \times 2a_0$ and $4a_0$ CDWs in the $x=0.15$ doped sample, the 1D stripe-like quasiparticle interference (QPI) patterns, labelled as $q_2$ in previous reports of undoped CsV$_3$Sb$_5$,$^{10}$ are also absent, indicating that the intrinsic rotation symmetry breaking has been restored (Fig. S4).

To study the microscopic evolution of superconductivity in the doped CsV$_{3-x}$Ti$_x$Sb$_5$ samples, we lowered the sample temperature to 400 mK and collected a series of dI/dV spectra. We find that the $x=0.03$ doped sample shows a V-shaped SC paring (blue curve in Fig. 3l) while the $x=0.15$ doped sample shows a fully gapped U-shaped paring (red curve in Fig. 3l). The V-shaped SC gap in the $x=0.03$ doped sample is slightly smaller than that of the undoped sample (black curve), and the zero-bias conductance is much higher than that in the undoped sample, indicating the decrease of $T_c$. For the $x=0.15$ doped sample, the SC paring is totally different from the undoped and lightly doped samples, demonstrating the transition into a new SC phase. The new SC phase may emerge from a normal state without CDW due to the change of the carrier concentration and the electronic states.
Susceptibility and transport properties of the Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$

Finally, we investigated the responses of CDW and superconducting transitions to the doping of Ti in CsV$_{3-x}$Ti$_x$Sb$_5$ single crystals via the combination of magnetization, specific heat capacity, and electrical transport measurements. The CDW transition temperature shows an obvious decrease from ~94 K to ~60 K with increasing doping contents, as evidenced by kinks in the temperature-dependent resistivity curves of the Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$ (x=0, 0.03, and 0.04) crystals (Fig. 4a). Then the kink fades out in the Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$ (x=0.09 and 0.15) indicating the absence of CDWs. The temperature-dependent magnetization and specific heat-capacity measurements (Fig. S5a and b) also provide strong evidence for the undetectability of CDWs in the Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$ (x=0.09 and 0.15).

To further investigate the doping effect on the normal state properties of this kagome superconductor system, systematic electrical transport measurements were conducted. Firstly, we measured the in-plane angular-dependent magnetoresistance (AMR) of the CsV$_{3-x}$Ti$_x$Sb$_5$ (x=0.15) crystal under a field of 5 T at different temperatures above $T_c$. The ratios of $\Delta R/R_{\text{min}} = [R(\theta,T)-R_{\text{min}}(T)]/R_{\text{min}}(T)\times 100\%$ are summarized in Fig. S5c by polar-coordinate plots, showing an isotropic nature, in contrast to that of undoped CsV$_3$Sb$_5$. This indicates clearly the absence of the two-fold rotational symmetry, consistent with the absence of the 1Q-$4\delta_0$ CDW and anisotropic QPI patterns in the STM/S measurements of x=0.15 doped sample. Secondly, we performed field-dependent Hall measurements of CsV$_{3-x}$Ti$_x$Sb$_5$ crystals with different doping contents at various temperatures (Fig. S6a,b,c,d).

Moreover, the doping effects on the superconductivity in CsV$_{3-x}$Ti$_x$Sb$_5$ single crystals with $x$ between 0 and 0.15 were examined by diamagnetism measurements. Bulk superconductivity with onset temperature $T_c^M$ is evidenced by the magnetic susceptibilities corrected for demagnetization factor under zero-field cooling (ZFC) and field cooling (FC, 1 Oe along the c axis), as shown in Fig. 4b. It clearly shows that $T_c^M$ decreases to about 2.0 K at $x=0.04$ doping and then increase to 3.0 K and 3.5 K at $x=0.09$ and $x=0.15$ doping, respectively. The onset superconducting transition temperature ($T_c^R$) derived from the temperature-dependent normalized resistivity of the undoped CsV$_3$Sb$_5$ occurs above 4.0 K, about 1.0 K higher than that of the CsV$_{3-x}$Ti$_x$Sb$_5$ (x=0.15) crystal (Fig. S5d). However, after applying different magnetic fields from 0.02 to 1T, the $T_c^R$ of the undoped CsV$_3$Sb$_5$ shifts to lower temperatures with a relatively small $\Delta T$, resembling the features of broad SC transitions observed in copper-oxide and iron-based high temperature superconductors, while the $T_c^R$ of the Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$ (x=0.15)
decreases rapidly with applied fields showing a conventional superconductivity behavior similar with that of MgB$_2$\textsuperscript{50}.

Shown in Fig. 4c is the phase diagram of CsV$_{3-x}$Ti$_x$Sb$_5$ single crystals, where the onset temperatures of CDW and superconductivity, together with their amplitude, are summarized as a function of doping content. $T_{\text{CDW}}$ is depressed with increasing Ti doping and become absent around $x=0.09$, accompanied by the strongly correlated evolution of the signal amplitude (Fig. 4c upper panel). In addition, the CsV$_{3-x}$Ti$_x$Sb$_5$ system shows two superconducting domes. The $T_c$ decreases from $\sim 3.5$ K of the undoped sample to $\sim 2.0$ K of the $x=0.04$ doped sample in the first dome. In this dome (the SC-I phase), the superconducting phase exhibits a V-shape pairing gap (Fig. 3I) and broadening transition behavior under magnetic field (Fig. S5d, dashed lines), indicating a nodal superconducting phase. In the second dome, the $T_c$ increases from $\sim 2.0$ K ($x=0.04$) to $\sim 3.5$ K ($x=0.15$). The superconducting phase in the second dome (the SC-II phase) exhibits a U-shape pairing gap (Fig. 3I) and sharp SC transition at the expense of $T_c$ under magnetic field (Fig. S5d, solid lines), indicating a nodeless superconducting phase.

In summary, we have studied the evolution of CDW and SC in Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$ samples where the Ti atoms directly substitute the V sites in the VSb1 kagome layer. $2a_0 \times 2a_0$ and $4a_0$ CDWs are both suppressed with the increasing doping content of Ti. Furthermore, the phase diagram shows two distinct SC domes where the first dome is characteristic of a V-shape nodal pairing while the second dome features a U-shape nodeless pairing. To our knowledge, the Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$ is the first superconductor reported so far that two distinct SC phases emerge upon chemical doping at ambient pressure, correlating with CDW. Based on this pathway, with other dopants into the AV$_3$Sb$_5$ (A=K, Rb, Cs) kagome superconductors, it is expected that new kinds of superconductors with novel physical properties can be created. The present work provides a new platform to study the fundamental mechanism of SC and CDW in the kagome superconductors.
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Main Figures

Fig. 1. Crystalline structure, structure characterization, and stoichiometric ratio of the Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$. a, Schematic of atomic structure of Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$ crystal with Cs atoms in light purple, Sb atoms in light blue, V atoms in red and Ti atoms in green. The Ti atoms replace the V atoms in Kagome lattice. b, A photo of a single crystal of the as-prepared Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$ (x=0.15) crystal. c, Typical XRD pattern of the Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$ (x=0.15) crystal. d, The SEM image of the Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$ (x=0.15) crystal showing the uniform structure at the surface. e, EDS of the crystal showing the stoichiometric ratio of Cs:V:Ti:Sb = 0.96:2.85:0.15:4.95.
Fig. 2. Atomic-scale structural and chemical analysis of Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$. a, b Simultaneously acquired atomic resolution STEM-ABF image (a) and STEM-HAADF Z-contrast image (b) of Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$ crystal viewed along the [100] projection, with the atomic structural models overlaid. The Cs, V, Sb atoms are shown in purple, red, and light blue, respectively. c, Background-subtracted EELS spectrum showing clear Ti, V, Sb, and Cs signals. Quantification of the Ti and V signals shows an atomic ratio of Ti:V $\sim$ 5.3:94.7. Note that this analysis is only semi-quantitative due to errors in calculating the inelastic scattering cross-sections for the different element edges. d,e, Atomic-resolution chemical mapping acquired via STEM-EELS spectrum imaging, with the simultaneously acquired V mapping shown in red (d) and Ti mapping shown in green (e). f, Overlay of the V (red) and Ti (green) signals. Ti is mostly doped into the V sites.
Fig. 3. STM images, dI/dV spectra and dI/dV mapping for the comparison of CDW states and superconducting gap of Ti-doped CsV$_{3-x}$Ti$_x$Sb$_5$ between $x=0.03$ and $x=0.15$. a-c, STM topography (a),
\( \frac{dI}{dV(r,-5mV)} \) (b) and the corresponding drift-corrected Fourier transform (FT) (c) at the large-scale Sb surface of CsV\(_{3-x}\)Ti\(_x\)Sb\(_5\) (\(x=0.03\)) obtained at 4 K, showing the 3Q-2\(a\) and 1Q-4\(a\) CDWs. Many dark spots appear correlated to the Ti dopants in the STM image of (a). The Insert in (a): Zoom-in STM image showing the continuous lattice around the dark spots. d-f, STM topography (d), \( \frac{dI}{dV(r,-5mV)} \) (e) and the corresponding drift-corrected FT (f) at the large-scale Sb surface of CsV\(_{3-x}\)Ti\(_x\)Sb\(_5\) (\(x=0.04\)), showing the presence of short-ranged 1Q-4\(a\) CDW multiple domains. Two 4\(a\) CDW domains can be clearly observed (highlighted by the blue and light blue dotted lines). h-j, STM topography (h), \( \frac{dI}{dV(r,-5mV)} \) (i) and the corresponding drift-corrected FT (j) at the large-sized Sb surface of CsV\(_{3-x}\)Ti\(_x\)Sb\(_5\) (\(x=0.15\)), showing the absence of 3Q-2\(a\), 1Q-4\(a\) CDW states in the FT. k, Typical small-scale STM image of the CsV\(_{3-x}\)Ti\(_x\)Sb\(_5\) (\(x=0.15\)) sample. Small patches of local 4\(a\) modulations can be observed (guided by the white dotted lines). l, Relationship between the doping content and the area ratio of the dark spots in the STM images, indicating that the dark spots in the STM images origin from Ti dopant in the underlying VSb layer. m, Spatially-averaged \( dI/dV \) spectra obtained on the Sb surface of the undoped (black curve), CsV\(_{3-x}\)Ti\(_x\)Sb\(_5\) (\(x=0.03\)) (blue curve) and CsV\(_{3-x}\)Ti\(_x\)Sb\(_5\) (\(x=0.15\)) samples, showing a transition from V-shape to U-shape symmetry through Ti doping. Setting parameter: tunneling current setpoint \( I_s = 1.0 \) nA. Bias modulations in (l): \( V_{mod} = 0.05 \) mV.
Fig. 4. Electrical transport, magnetic properties and phase diagram of CsV$_{3-x}$Ti$_x$Sb$_5$ crystals. a, The electrical resistivity of CsV$_{3-x}$Ti$_x$Sb$_5$ crystals with x from 0 to 0.15. The CDW is suppressed upon increasing x and undetectable when x exceeds 0.09. b, The temperature-dependent magnetic susceptibilities corrected for demagnetization factor under zero-field cooling (ZFC) and field cooling (FC, 1 Oe along the c axis). Bulk superconductivity is confirmed by the diamagnetism. c, Phase diagram of the CsV$_{3-x}$Ti$_x$Sb$_5$ crystals. In the SC-I regime, $T_{CDW}$ and $T_c^M$ are significantly reduced with increasing x. In the SC-II regime, the superconductivity tends to gradually increase: $T_c^M$ rises from $\sim 3$ K at x = 0.09 to $\sim 3.5$ K at x=0.15.
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Competing Interests: The authors declare that they have no competing interests.

Data availability

Data measured or analyzed during this study are available from the corresponding author on reasonable request.