Synthesis and structural analysis of nonstoichiometric ternary fulleride $\text{K}_{1.5}\text{Ba}_{0.25}\text{CsC}_{60}$

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Abstract: The existence of cation-vacancy sites in fullerides might lead to long-range ordering and generate a new vacancy-ordered superstructure. The purpose of this work is to search whether or not long-range ordering of vacant tetrahedral sites, namely superstructure emerges in nonstoichiometric $\text{K}_{1.5}\text{Ba}_{0.25}\text{CsC}_{60}$ fulleride. Therefore, $\text{K}_{1.5}\text{Ba}_{0.25}\text{CsC}_{60}$ with cation-vacancy sites is synthesized using a precursor method to avoid inadequate stoichiometry control and formation of impurity phases within the target composition. For this purpose, first, phase-pure $\text{K}_{1.5}\text{Ba}_{0.25}\text{CsC}_{60}$ and Cs$^{+}$ precursors are synthesized. Stoichiometric quantities of these precursors are used for further reaction with Cs, to afford $\text{K}_{1.5}\text{Ba}_{0.25}\text{CsC}_{60}$. Rietveld analysis of the high-resolution synchrotron X-ray powder diffraction data of the precursors and $\text{K}_{1.5}\text{Ba}_{0.25}\text{CsC}_{60}$ confirms that K, Ba, and Cs precursors are single-phase and they crystallize in a body-centered-cubic structure (I\(\text{m}\bar{3}\)) as reported in the literature. The analysis also shows that $\text{K}_{1.5}\text{Ba}_{0.25}\text{CsC}_{60}$ phase can be perfectly modeled using a face-centered cubic structure. No new peaks appear which could have implied the appearance of a superstructure. This suggests that there is no long-range ordered arrangement of vacant tetrahedral sites in $\text{K}_{1.5}\text{Ba}_{0.25}\text{CsC}_{60}$.

Key words: Cation-vacancy, solid-state synthesis, A$_x$C$_{60}$, nonstoichiometric fullerides

1. Introduction

The intercalated products of fullerides display unique structural, magnetic, and electronic properties which depend on the amount, size, and nature of the intercalated species, and the synthetic route employed for the intercalation of dopant into solid C$_{60}$, i.e. exohedral doping [1]. Synthetic efforts have been essentially focused on the synthesis of alkali fullerides with stoichiometries A$\text{C}_{60}$ (A = alkali metal, 1 ≤\(x\) ≤ 12, e.g. RbC$_{60}$, Li$_{1.5}$C$_{60}$), due to their novel electronic properties. For instance, the observation of metallic behavior in alkali metal intercalated C$_{60}$ films at 300 K [2] was followed by the discovery of superconductivity for the first time in an alkali fulleride K$_{1.5}$C$_{60}$ with a transition temperature, $T_s$, of 18 K [3], where superconducting phase is a face-centered-cubic (fcc) structure [4,5]. This led to the discovery of new A$_x$C$_{60}$ superconductors through varying the interfullerene separation (e.g. RbC$_{60}$ with a $T_s$ of 28 K [6] and 30 K [4], Rb$_{1.5}$Cs$_{60}$ and RbCs$_{1.5}$C$_{60}$ with a $T_s$ of 31 K and 33 K, respectively [7], fcc Cs$_{1.5}$C$_{60}$ with a maximum $T_s$ of 35 K at ~7 kbar [8] and fcc Rb$_{1.5}$C$_{60}$, C$_{60}$ (0.35 ≤\(x\) ≤ 2) with $T_s$ varying between 25.9 K and 32.9 K at ambient pressure [9]). Since then, extensive research has been carried out on fcc A$_x$C$_{60}$ and A$_{0.75}$C$_{60}$ fullerides to discover superconductors with higher $T_s$ and understand their molecular electronic structure [8–12]. Current understanding proves that the A$_x$C$_{60}$ superconducting fullerides belong to the family of unconventional superconductivity where electron correlations play an important role for the pairing mechanism [8–11, and 13–18]. Besides that, molecular electronic structure [9,19,20] and cation specific effects [12] are crucially important in producing the unconventional superconductivity in the A$_x$C$_{60}$ family.

Upon exohedral doping of solid C$_{60}$, the dopant occupies interstitial lattice positions of the solid C$_{60}$ and provides electrons to the host C$_{60}$ molecules, creating C$_{60}^{-}$ anions [1]. The charge transfer alters the properties of C$_{60}$ (e.g. inducing metallicity and superconductivity) and has thus received the most attention. In the A$_x$C$_{60}$ family, intercalation of three alkali leads to a half-filled $t_{2g}$ band and hence a metallic behavior, excluding fcc Cs$_{3}$C$_{60}$ [8]. The superconducting phase of the A$_x$C$_{60}$ fullerides adopts the fcc structure where all tetrahedral ($T_d$) and octahedral ($O_h$) holes are entirely occupied by the alkali cations [21]. In fcc A$_x$C$_{60}$ structure, there are two $T_d$ cavities (\(r = 1.12\) Å) and one $O_h$ (\(r = 2.06\) Å) per C$_{60}$ unit. As the $T_d$ cavity is smaller than the $O_h$ one, the size of the alkali cation occupying the $T_d$ site instead of the $O_h$ one will determine the degree of lattice expansion; therefore, the volume of the A$_x$C$_{60}$ fullerides can be changed systematically through substituting the alkali metals with larger ones.

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Various synthetic routes have been developed to prepare A$_2$C$_{60}$ fullerides. The most common and effective one is the ‘solid-state direct reaction method’ where solid C$_{60}$ is exposed to vapor of the alkali metal which then disperses into the C$_{60}$ acceptor molecules at temperatures of ~100–410 °C. All the A$_2$C$_{60}$ and A$_2$A’C$_{60}$ compounds, except Cs$_2$C$_{60}$ [8,10], can be synthesized with this method [1]. The A$_2$C$_{60}$ fullerides can be synthesized using the direct reaction method and used later as precursors for further reaction with C$_{60}$ to obtain target A$_2$Cs$_3$A’C$_{60}$ compounds. The precursor method offers a significant benefit compared to the direct synthesis method because fine A$_2$C$_{60}$ powders enable better stoichiometry control of the desired compound. The saturated A$_2$C$_{60}$ compounds can also be prepared by a vapor-transport method [22]. In this study, direct reaction and vapor-transport methods were used to synthesize the K$_{x}$C$_{60}$/Ba$_{y}$C$_{60}$ and Cs$_{x}$C$_{60}$ precursors, respectively, which were later reacted with C$_{60}$ to afford the target composition.

Besides the exploration of cation related effects on the structural and electronic properties of fullerides, the effects of cation-vacancy can be investigated as well. For example, tetrahedral rare-earth metal vacancies in Sm$_{2.57}$C$_{60}$ and Yb$_{2.75}$C$_{60}$ exhibit long-range ordering of tetrahedral vacancies, generating a superstructure [23,24]. Such structural response to tetrahedral vacancy could be established in fcc A$_2$Cs$_3$A’C$_{60}$ fullerides, resulting in a different structure to the fcc. For such an exploration, in this work, [1.025K$_{0.5}$Ba$_{1.5}$CsC$_{60}$]—where [ ] represents vacant tetrahedral sites of the fcc structure — was synthesized using stoichiometric quantities of single phase, fine, black colored K$_{x}$C$_{60}$-Ba$_{y}$C$_{60}$ and Cs$_x$C$_{60}$ powders together with C$_{60}$ as starting materials. Here, an easy method for the synthesis of nonstoichiometric K$_{x}$Ba$_{y}$CsC$_{60}$ is presented together with the results of Rietveld analysis of high-resolution synchrotron X-ray powder diffraction data collected at ambient conditions for the structural investigation.

2. Materials and methods

2.1. Synthetic route

All sample operations were performed in an argon-filled glove box (MBraun MB 200B, H$_2$O and O$_2$ < 0.1 ppm) due to the extreme air- and moisture-sensitivity of reactants. As purchased pristine C$_{60}$ (MER corporation, 99.9%) was sublimed prior to synthesis. Solid C$_{60}$ (~500–600 mg) were first ground and then loaded in a quartz ampoule with a separating zone. Before the product was cooled down to ambient temperature, the temperature gradient was reversed to get rid of C$_{60}$ and Cs sublimate. Once the cooling was complete, the product was removed from the glove box and evacuated for 30 min before sealing under ~400 mbar of He gas pressure. The sealed sample within the glove box. Each cycle of annealing of the intermediate and final products was ended through allowing the furnace to cool down to room temperature with a rate of 5 °C/min. Once each annealing cycle was complete, these products were ground using a pestle and mortar to improve crystallinity.

Synthesis of K$_{x}$C$_{60}$

Stoichiometric amount of K metal was placed in a 5 mm diameter Ta cell and then stoichiometric amount of sublimed C$_{60}$ was introduced onto K in the cell. The cell was then located in a glass tube enclosed with a Swagelok fitting, removed from the glove box, evacuated for 30 min before sealing under 350 mbar of He gas pressure. The sealed sample within the glass tube was placed vertically in a box furnace and heated to 250 °C with a rate of 5 °C/min, followed by another 20 h annealing and cooling to ambient temperature with the same rate as heating. After the initial annealing was completed, the product was transferred to the glove box, removed from the reaction vessel, and ground. The ground product was then pressed into a pellet, introduced into a Ta holder for further period of 2 days annealing at 300 °C to increase the crystallinity.

Synthesis of Cs$_x$C$_{60}$

Phase-pure Cs$_x$C$_{60}$ was synthesized by a vapor transport method using a ~2.3× excess amount of Cs. The solid C$_{60}$ was first placed into a glass tube with a striction. The cesium metal was inserted in a small glass capsule (~7 mm diameter) which was lowered in the glass tube down to where the striction was. The tube enclosed with a Swagelok fitting was removed from the glove box and evacuated for 30 min before sealing under ~400 mbar of He gas pressure. A 3-zone horizontal tube furnace was used in order to create a temperature gradient between Cs and C$_{60}$ for vapor transport. The zone where Cs locates was ramped to 350 °C from room temperature with a rate of 2 °C/min and held there for 3 days. Simultaneously, the zone where C$_{60}$ locates was ramped to 330 °C (2 °C/min) for transportation of vapor from the Cs to C$_{60}$ zone. Before the product was cooled down to ambient temperature, the temperature gradient was reversed to get rid of any undoped Cs from the freshly formed Cs$_x$C$_{60}$. Once the cooling was complete, the product was removed from the glass tube, ground thoroughly, pelleted, and located in a Ta cell with tightened screw ends which was then sealed under He, after evacuation under dynamic vacuum, and annealed at 350 °C for another 3 days to increase the crystallinity.
Synthesis of Ba$_6$C$_{60}$

Prior to synthesis, in order to obtain oxide-free barium powder, the oxidized surface of a barium rod was first removed by filing. These initial filings were discarded, and a new diamond file was used to exfoliate the required mass of clean fine powder. Once the clean fine powder was obtained, stoichiometric amount of barium powder and C$_{60}$ were mixed and ground using a mortar and pestle, and then pressed into a pellet. The reaction mixture was loaded into a Ta holder which was placed a 15 mm diameter quartz tube then evacuated for 30 min before sealing under 500 mbar of He gas pressure. The sealed mixture was heated inside a muffle furnace using the following thermal protocol: from ambient temperature to 550 °C; held for 1 h; to 650 °C; held for 13 h; to 700 °C; held for 4 h; to 720 °C; held for 18 h. The ramping rate between each step of heating was 5 °C/min. After cooling to room temperature, the product was removed from the reaction vessel, ground, and finally pressed into a pellet and inserted into the same Ta holder for reannealing at 740 °C for 16 h.

Synthesis of the target compound K$_{1.5}$Ba$_{0.25}$Cs$_{0.25}$C$_{60}$

K$_{1.5}$Ba$_{0.25}$Cs$_{0.25}$C$_{60}$ was prepared by a solid-state synthetic route according to the following stoichiometric equation describing the ideal reaction: 6K$_6$C$_{60}$ + 4Cs$_6$C$_{60}$ + Ba$_6$C$_{60}$ + 13C$_6$ → 24K$_{1.5}$Ba$_{0.25}$Cs$_{0.25}$C$_{60}$. Stoichiometric amounts of K$_6$C$_{60}$, Ba$_6$C$_{60}$, Cs$_6$C$_{60}$, and sublimed C$_6$ precursors were mixed and ground thoroughly. The ground mixture was pelletized, introduced into a Ta cell with tightened screw ends which was then placed in a quartz tube, and evacuated for 30 min before sealing under 450 mbar of He gas pressure. The sealed pellet was then positioned in a muffle furnace at room temperature and heated at 600 °C for 16 h with an initial ramp rate of 5 °C / min, finally, the furnace was switched off to cool down to room temperature. The intermediate product was removed from the tube in the glove box, ground, and then pressed into a pellet which was introduced into the same Ta holder for further period of annealing at 300 °C for 1 h and 600 °C for 16 h with the same heating rate with 2 intermediate grindings and pelletizations to increase crystallinity.

2.2. Instrumentation

Ambient temperature high-resolution synchrotron x-ray powder diffraction (SXRPD) data of the precursors were collected with the diffractometer on beamline ID31 (λ = 0.40006 Å for K$_6$C$_{60}$ and Cs$_6$C$_{60}$ and λ = 0.399838 Å for Ba$_6$C$_{60}$) at the ESRF, Grenoble, France. SXRPD data of the target compound K$_{1.5}$Ba$_{0.25}$Cs$_{0.25}$C$_{60}$ were collected on beamline BL44B2 (λ = 0.500127 Å) at the SPring-8, Japan. The samples were loaded into 0.5 mm diameter glass capillaries and sealed under ~350 mbar He pressure for the SXRPD measurements.

SXRPD data were analyzed using the Rietveld refinement technique with the GSAS suite of the Rietveld programs [25]. The following procedure was applied for the Rietveld analysis: a complex peak shape function known as the pseudo-Voigt, which is a combination by addition of Gaussian and Lorentzian functions [26] was used to model the peak shape, and peak shape coefficients $GU$, $GV$, $GW$, $LX$, $LY$ and $Lij$ (i, j = 1–3) were refined. Low-angle peak asymmetry rising from axial divergence was modeled with coefficients $S/L = 0.001$, $H/L = 0.0005$ where $L$ is the diffractometer radius, and $H$ and $S$ are the sample and detectors heights, respectively [25]; a Chebyshev polynomial function (~20 terms) was applied to fit the background; the anomalous contributions to the X-ray form factors of all atoms, $f'$ and $f''$ corrections to $f$, were calculated (in e/atom) using the program DISPANO [27] and implemented into GSAS as follows: for $κ = 0.4$ Å$^{-1}$ $f' = 0.054$, $f'' = 0.079$ for K, $f' = -1.771$, $f'' = 0.819$ for Ba and $f' = -1.921$, $f'' = 0.758$ for Cs and for $κ = 0.5$ Å$^{-1}$ $f' = 0.094$, $f'' = 0.125$ for K, $f' = -1.190$, $f'' = 1.228$ for Ba and $f' = -1.247$, $f'' = 1.138$ for Cs. Intermediate refinements of lattice parameters, occupancies of the tetrahedral sites, thermal parameters, peak shape coefficients, zero correction, and background function were applied during the Rietveld analysis.

3. Results

3.1. Structural characterization of the K$_6$C$_{60}$, Cs$_6$C$_{60}$ and Ba$_6$C$_{60}$ precursors

Rietveld refinements of the SXRPD data (Figure 1) collected for K$_6$C$_{60}$, Cs$_6$C$_{60}$, and Ba$_6$C$_{60}$ confirm that samples are high quality, phase-pure, and crystallize with a body-centered-cubic structure with a space group of Im3 and lattice parameters $a_{K6C60} = 11.3775(2)$ Å, $a_{CsC60} = 11.7887(2)$ Å, and $a_{BaC60} = 11.1879(2)$ Å respectively. These values are in agreement with the previously-reported lattice parameters: 11.39 Å [28], 11.79 Å [29], and 11.1850(7) Å[30], respectively. This confirms that the synthesized A$_6$C$_{60}$ fullerenes can be used effectively as precursors. Fractional atomic coordinates of K$_6$C$_{60}$, Cs$_6$C$_{60}$, and Ba$_6$C$_{60}$ were taken from [28], [29], and [31], respectively and were not refined. Only lattice constants and thermal displacement parameters, which were modeled isotopically, were refined together with instrumental (e.g. zero shift) and profile shape coefficients. As seen in Figure 1, a good agreement between the calculated and observed profile is obtained from the Rietveld analysis with χ$^2$ ~ 1.

3.2. Structural characterization of the target compound K$_{1.5}$Ba$_{0.25}$Cs$_{0.25}$C$_{60}$

Rietveld analysis of the X-ray diffraction data of K$_{1.5}$Ba$_{0.25}$Cs$_{0.25}$C$_{60}$ readily reveals that the sample is single phase and adopts the cubic structure with fcc symmetry (Figure 2). All diffraction peaks can be indexed with the cubic structure, with no
sign of additional reflections that could have indicated the existence of a vacancy-ordered superstructure. A merohedrally disordered fcc model with the space group of $Fm\bar{3}m$ was employed to model the fcc phase. A cation disordered model was applied as follows. As the $O_h$ interstitial site of the fcc $C_{60}$ structure ($r = 2.06$ Å) is significantly larger than the $T_d$ one ($r = 1.12$ Å), larger Cs$^+$ ions preferentially reside in the $O_h$ site. As a result, the $O_h$ cavity is only occupied by Cs$^+$ while the smaller K$^+$ and Ba$^{2+}$ ions ($r_{K^+} = 1.38$ Å, $r_{Ba^{2+}} = 1.35$ Å, $r_{Cs^+} = 1.67$ Å) preferentially occupy the $T_d$ site. Hence, the latter is filled by a disordered mixture of K$^+$ and Ba$^{2+}$. The applicability of this method has been previously confirmed by $^{133}$Cs, $^{39}$K, and $^{87}$Rb NMR measurements [9,32].

The fractional atomic coordinates of the fcc phase were not allowed to refine, instead they were rescaled from fcc $Rb_{6}C_{60}$ (with $C_{60}$ C-C bond distances of 1.42 Å [28]). Thermal displacement parameters of the atoms ($U$) were modeled isotropically and allowed to refine but under the condition that $U_{iso}$ of the C atoms and $U_{iso}$ of the K$^+$ and Ba$^{2+}$ ions introduced into the tetrahedral site were forced to be equivalent to each other, respectively. The K$^+$ and Ba$^{2+}$ occupancy in the $T_d$ site of the fcc structure was allowed to refine but total site occupancy was fixed at 1.75, and the remaining is the vacant tetrahedral site occupancy which is 0.25. The refined occupancy ratio converged to K$^+$: Ba$^{2+} = 0.712(10):0.163(10)$ leading to a refined composition of $K_{1.42(1)}Ba_{0.33(1)}CsC_{60}$. The structural parameters of the fcc phase obtained from the Rietveld refinement are summarized in Table.

Indeed, substitution of smaller Ba$^{2+}$ for the K$^+$ cation, and the presence of the $T_d$ vacancy in fcc $K_{x}Cs_{3−x}C_{60}$ led to a significant lattice contraction. The fcc lattice parameter of refined composition $K_{1.42(1)}Ba_{0.33(1)}CsC_{60}$, is obtained as 14.2616(1) Å, which is smaller than those of any $K_{x}Cs_{3−x}C_{60}$ ternary compositions (Figure 3), covering the compositional
range $0.22(1) \leq x \leq 2$ and lattice constants $14.28571(7) \text{ Å} \leq a \leq 14.7011(2) \text{ Å}$ [32]. This reflects the fact that the average ionic radii of the cations residing in the $T_d$ and $O_h$ cavities, $\langle r_A \rangle$ in $K_{1.42(1)}Ba_{0.33(1)}CsC_{60}$ is smaller, $\langle r_A \rangle = 1.36(1) \text{ Å}$, than that of any $K_xCs_{3-x}C_{60}$ compositions ($1.38 \text{ Å} \leq \langle r_A \rangle \leq 1.64(1) \text{ Å}$). Refined isotropic thermal displacement parameters of the cations occupying the $T_d$ and $O_h$ cavities, and also of the C atoms are found to be in good agreement with those known from the literature[12]. Because of the smaller size of the $T_d$ site compared with the $O_h$ one, thermal displacements of the atoms residing in the former one is expected to be relatively smaller than the ones in the latter.

4. Discussion
The molecular, alkali doped $A_xC_{60}$ fulleride family possesses remarkable physical properties (e.g. unconventional superconductivity, and strong electron correlations) originating from their molecular electronic structure which can
be easily tuned via physical/chemical pressure and temperature without altering their high fcc symmetry. The donor intercalants in molecular fulleride family possessing unique properties are not only limited to alkali and alkaline earth metals, for example, rare-earth doped Yb$_{2.75}$C$_{60}$ fulleride becomes superconducting below 6 K and shows an exceptional crystal structure contrary to the literature [24]. In a hypothetical Yb$_3$C$_{60}$, Yb cations reside at the centers of the O$_h$ and T$_d$ sites of the fcc C$_{60}$ lattice. However, in Yb$_{2.75}$C$_{60}$, Yb cations occupy off-centered interstitial sites and leave one out of every eight T$_d$ sites vacant. These vacancy sites display long-range ordering, generating a new cation-vacancy-ordered superstructure, which leads to a unit cell with dimensions twice as large as those of the common fcc fulleride structures [24]. A similar situation is also encountered in Sm$_{2.75}$C$_{60}$ [23]. In both cases, their complex structure arises from the long-range ordering of tetrahedral rare-earth metal vacancies. In this study, we also aimed to induce such structural response to the presence of vacancy site in K$_{1.42(1)}$Ba$_{0.33(1)}$CsC$_{60}$, however, this could not be achieved. Inspection of the diffraction profile did not reveal any superlattice peaks at low angles that could be indexed to an enlarged unit cell, which may possibly signify the generation of a superstructure as in Sm$_{2.75}$C$_{60}$ and Yb$_{2.75}$C$_{60}$. The underlying physical origin of this type of vacancy-ordering was attributed to a strong directional interaction between electron-poor, charge-deficient five-membered rings of C$_{60}$ and divalent ytterbium cations but not to the cation size difference [24]. However, this suggestion might not be valid in the case of using larger cations as in the present study, i.e. K$^+$ (1.38 Å), and Ba$^{2+}$ (1.35 Å), than that of the tetrahedral hole (1.12 Å) but the ionic radius of Yb$^{3+}$ and Sm$^{2+}$ are 1.02 and 1.14 Å, respectively, comparable to that of the tetrahedral hole. As it is well known, the size and amount of the dopant species has a primary effect on the crystal structure of fullerides, for instance, contrary to the literature, at low temperatures, the structure of Na$_2$CsC$_{60}$ ($r_{Na} = 1.02$ Å) is primitive cubic (Pm$ar{3}$) being isostuctural with pristine C$_{60}$ and undergoes a phase transition on heating to an fcc phase with a space group of Fm$ar{3}$m [33], and the structure of Yb$_{2.75}$C$_{60}$ is orthorhombic with space group Pcab [24]. Therefore, it could be tentatively suggested that the size of the cations residing in the tetrahedral site should be taken into account if one aims to generate a long-range arrangement of vacant sites, namely a superstructure.

5. Conclusion

In conclusion, the preparation of the nominal K$_{1.5}$Ba$_{0.25}$CsC$_{60}$ fulleride using stoichiometric quantities of K$_6$C$_{60}$, Cs$_6$C$_{60}$, and Ba$_6$C$_{60}$ precursors, which overcomes inadequate stoichiometry control, via solid-state synthetic route is presented. Structural characterization of the precursors and the target compound was performed with Rietveld analysis of the high-resolution synchrotron X-ray powder diffraction data. The analysis confirmed that the structure of the precursors is body-centered-cubic (Im$ar{3}$) as reported in the literature and free from impurity phases such as oxides of the metals which can be easily formed during the synthetic protocol applied.

The X-ray diffraction pattern of the target compound K$_{1.5}$Ba$_{0.25}$CsC$_{60}$ (refined composition: K$_{1.42(1)}$Ba$_{0.33(1)}$CsC$_{60}$) has shown no evidence for the emergence of superstructure peaks which could have resulted from the long-range ordering of the vacant tetrahedral sites. All the Bragg reflections existing in the diffraction pattern originate from the cubic structure (Fm$ar{3}$m) without any violation. This suggests that there is no long-range ordered arrangement of tetrahedral alkaline-earth
metal vacancies in $K_{1.42(1)}Ba_{0.33(1)}CsC_{60}$. The reason for this could be the use of highly symmetric $CsC_{60}$ fulleride as a parent phase and of moderately large dopant species, i.e. $K^+$, $Ba^{2+}$. This issue merits more detailed investigation through the synthesis and characterization of vacancy-doped fullerenes with lower symmetry, for instance, primitive cubic $Na-CsC_{60}$ could be gradually substituted nonstoichiometrically by a smaller divalent cation which might generate ordering of cation-vacancy and also noninteger valence of $C_{60}$.

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