Anomalous Raman shift in the ternary fullerides with $t_{1g}$ states

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Abstract

Raman spectra have been studied on two kinds of highly doped fullerides of $A_xBa_3C_{60}$ (x=0, 3; A=K, Rb) and $K_xSm_{2.75}C_{60}$ (x=0, 3.25). It was found that the Raman spectra are essentially identical to each other for all ternary fullerides. The results show a crossover point at the boundary of $t_{1u}$ and $t_{1g}$ bands for the charge transfer dependence of Raman shift. Particularly, the totally symmetric $A_g(2)$ mode in $t_{1g}$ fullerides cannot be understood by a simple extrapolation from the low doped $t_{1u}$ fullerides, where the $A_g(2)$ mode follows a characteristic shift of $\sim 6.3\text{cm}^{-1}$ per elementary charge. The present result shows that the Raman spectra of $t_{1g}$ states cannot be explained only by charge transfer.

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Raman scattering is a useful technique to study the vibrational properties of the C\(_{60}\) molecule and its doped derivative compounds. Raman scattering is widely used to evaluate the electron-phonon coupling constant \(\lambda\) for the doped C\(_{60}\) superconductors basing on the analysis of the linewidths.\(^1\) In addition, the tangential pinch \(A_g(2)\) mode is of particular interest in the studies of the doped C\(_{60}\) as it yields a strong and narrow line in the Raman spectrum. The different stages of doping can be easily followed by in-situ Raman-scattering experiments. A continuous change of line intensity for the \(A_g(2)\) mode of the stable phase is observed and the doping process leads to a characteristic downshift of this line regarding the number of electrons transferred to the C\(_{60}\) molecule. A down-shift of 6-7 cm\(^{-1}\) per elementary charge on C\(_{60}\) independent of the doping ion is observed.\(^2\)\(^-\)\(^8\) The \(AC_{60}\) phase was discovered by down-shift of the \(A_g\) pinch mode in in-situ Raman-scattering experiments.\(^9\)

\(A_3Ba_3C_{60}\) phases (A=K, Rb, Cs) with a formal C\(_{60}\)\(^{-9}\) charge and half-filling of the \(t_{1g}\) are recently reported.\(^10\) As the intercalation host, \(Ba_3C_{60}\) is a vacancy-ordered derivative of the bcc \(A_6C_{60}\) structure with half of the cation sites empty (A15 structure). Three alkali metal cations are introduced into \(Ba_3C_{60}\) to form a cation-disordered \(A_3Ba_3C_{60}\) phase isostructural with \(A_6C_{60}\). \(K_3Ba_3C_{60}\) with half-filled \(t_{1g}\) band exhibits superconductivity at 5.6 K. However, the insertion of large \(A^+\) cations leads to a decrease in \(T_c\), contrary to the behavior of the \(A_3C_{60}\) phases.\(^11\)

To investigate the vibrational properties of ternary fullerides and comparison of physical properties in between \(t_{1u}\) and \(t_{1g}\) fullerides, we have carried out a Raman scattering study on the fullerides \(A_xBa_3C_{60}\) (x=0, 3; A=K, Rb) and \(K_xSm_{2.75}C_{60}\) (x=0, 3.25). The results show that the Raman spectra are amazingly similar to each other for all ternary fullerides \(A_3Ba_3C_{60}\) and \(K_{3.25}Sm_{2.75}C_{60}\). An anomalous Raman shift of the two \(A_g\) modes is observed when alkali metals are introduced into \(Ba_3C_{60}\) and \(Sm_{2.75}C_{60}\). It does not follow the characteristic relation between charge transfer and Raman shift widely observed for the two \(A_g\) modes in alkali and Ca-doped C\(_{60}\).\(^4\)\(^-\)\(^7\)\(^12\)

Samples of \(Ba_3C_{60}\) and \(Sm_{2.75}C_{60}\) were synthesized by reacting stoichiometric amount of powers of Ba, Sm, and C\(_{60}\). A quartz tube with mixed powder inside was sealed under high
vacuum of about $2 \times 10^{-6}$ torr, and heated at $550 \sim 600 \, ^\circ C$ for three days. Synthesis of $A_3Ba_3C_{60}$ and $K_{3.25}Sm_{2.75}C_{60}$ was carried out in a similar manner to that of alkali doping into pure $C_{60}$. A piece of alkali and $Ba_3C_{60}$ or $Sm_{2.75}C_{60}$ powders were loaded in a Pyrex tube, which was sealed under $2 \times 10^{-6}$ torr and calcined at $250 \, ^\circ C$ for three days. X-ray diffraction analysis was performed by a system equipped with a 4.5 kW rotating molybdenum anode as the x-ray generator and an imaging plate (IP, MAC, Science, DIP320V) as the detector. X-ray diffraction showed that all samples were single phase, which was also confirmed by the single peak feature of the pentagonal pinch $A_g(2)$ mode in the Raman spectra.

Raman scattering experiments were carried out using the 632.8 nm line of a He-Ne laser in the Brewster angle backscattering geometry. The scattering light was detected with a Dilor xy multichannel spectrometer using a spectral resolution of $3 \, cm^{-1}$. In order to obtain good Raman spectra, the samples were ground and pressed into pellets with pressure of about $20 \, kg/cm^2$, which were sealed in Pyrex tubes under a high vacuum of $10^{-6}$ torr.

As reported in reference 10, X-ray diffraction shows that the structure is changed from $A15$ phase to a cation-disordered $A_3Ba_3C_{60}$ phase isostructural with bcc $A_6C_{60}$ (a=K, Ba) when alkali metal is intercalated into $Ba_3C_{60}$. Figure 1 shows the X-ray powder diffraction patterns for the samples $Sm_{2.75}C_{60}$ and $K_{3.25}Sm_{2.75}C_{60}$. For the pattern of $Sm_{2.75}C_{60}$, all peaks can be indexed with an orthorhombic lattice parameters $a=28.158\, \AA$, $b=28.077\, \AA$, and $c=28.270\, \AA$, which is consistent with previous report. It is easily seen in Fig.1 that the diffraction peak is much less in the pattern of $K_{3.25}Sm_{2.75}C_{60}$ than in the pattern of $Sm_{2.75}C_{60}$. In addition, no peak is observed at $2\theta$ below 5 degree. It suggests that the structure of $K_{3.25}Sm_{2.75}C_{60}$ should be simple relative to that of $Sm_{2.75}C_{60}$. We can index all diffraction peaks using a body-centered cubic cell with lattice parameter $a=11.093\, \AA$ except for the two peaks marked by arrows in Fig.1. It is known that the basic structure of $Sm_{2.75}C_{60}$ is fcc, but the cation vacancy ordering in tetrahedral sites leads to a superstructure accompanied with a slight lattice deformation from cubic to orthorhombic. The Sm cations occupying the octahedral and tetrahedral sites experience off-center displacements since one out of every eight tetrahedral sites in the subcell is vacant. X-ray diffraction
suggests that introduction of the alkali cations into $Sm_{2.75}C_{60}$ leads to the disappearance of cation-vacancy ordering and formation of a cation-disordered phase with composition $K_{3.25}Sm_{2.75}C_{60}$, similarly to the case of $A_{3}Ba_{3}C_{60}$. A detailed analysis on the structure of $K_{3.25}Sm_{2.75}C_{60}$ will be reported elsewhere.

Figure 2 shows Raman spectra of $Ba_{3}C_{60}$, $K_{3}Ba_{3}C_{60}$, and $Rb_{3}Ba_{3}C_{60}$. The positions ($\omega$) and halfwidths ($\gamma$) of the Raman modes observed are listed in Table I for all samples. In the $Ba_{3}C_{60}$ spectrum, there are about 13 strong Raman lines observed, some of which are doublets. The low-and high-frequency $A_{g}$ derived modes are located at 506 and 1430.8 cm$^{-1}$, respectively. The position of $A_{g}(2)$ pentagonal pinch mode is identical to that of $K_{6}C_{60}$, suggesting that the charge transfer from Ba to $C_{60}$ is complete, also being consistent with $\sim 6.3$ cm$^{-1}$ redshift per electron relative to neutral $C_{60}$. However, the up-shift of 13 cm$^{-1}$ for the radial $A_{g}(1)$ mode is larger than that for $K_{6}C_{60}$ (9 cm$^{-1}$). It is to be pointed out that the Raman spectrum of $Ba_{3}C_{60}$ is amazingly similar to that of $K_{6}C_{60}$ except for the relative intensities between $A_{g}(2)$ and $H_{g}(2)$ modes.

In the case of $K_{3}Ba_{3}C_{60}$ and $Rb_{3}Ba_{3}C_{60}$, the similar Raman lines to $Ba_{3}C_{60}$ are observed. However, the strongest line is $A_{g}(2)$ mode, similarly to the case of $K_{6}C_{60}$ with bcc structure. It is worth pointing out that the $K_{3}Ba_{3}C_{60}$ and $Rb_{3}Ba_{3}C_{60}$ spectra are essentially identical to each other. These spectra are relatively insensitive to the choice of alkali-metal ion species. This behavior is similar to the case of $A_{3}C_{60}$ and $A_{6}C_{60}$ (A=K, Rb) compounds, where this behavior is explained both by a weak coupling between $C_{60}$ and alkali cations and by a complete charge transfer from the alkali-metals to $C_{60}$ molecules. However, an anomalous Raman shift for the two $A_{g}$-derived modes is observed in $K_{3}Ba_{3}C_{60}$ and $Rb_{3}Ba_{3}C_{60}$. The first thing to be noted is the $A_{g}(2)$ mode observed at 1425.5 (1424.1) cm$^{-1}$ in $K_{3}Ba_{3}C_{60}$ ($Rb_{3}Ba_{3}C_{60}$). The relative down-shift of $A_{g}(2)$ mode measured from that of $Ba_{3}C_{60}$ is only 5.3 and 6.7 cm$^{-1}$ for $K_{3}Ba_{3}C_{60}$ and $Rb_{3}Ba_{3}C_{60}$, respectively. These values are much smaller than that expected basing on the established empirical relation between the formal $C_{60}$ valence and the Raman shift. Another anomaly is found in the radial $A_{g}(1)$ mode, which shows a downshift of 8.6 and 10.5 cm$^{-1}$ relative to $Ba_{3}C_{60}$ for $K_{3}Ba_{3}C_{60}$ ($Rb_{3}Ba_{3}C_{60}$),

\[\text{Figure 2: Raman spectra of } Ba_{3}C_{60}, K_{3}Ba_{3}C_{60}, \text{ and } Rb_{3}Ba_{3}C_{60}. \text{ The positions } (\omega) \text{ and halfwidths } (\gamma) \text{ of the Raman modes observed are listed in Table I for all samples. In the } Ba_{3}C_{60} \text{ spectrum, there are about 13 strong Raman lines observed, some of which are doublets. The low-and high-frequency } A_{g} \text{ derived modes are located at 506 and } 1430.8 \text{ cm}^{-1}, \text{ respectively. The position of } A_{g}(2) \text{ pentagonal pinch mode is identical to that of } K_{6}C_{60}, \text{ suggesting that the charge transfer from Ba to } C_{60} \text{ is complete, also being consistent with } \sim 6.3 \text{ cm}^{-1} \text{ redshift per electron relative to neutral } C_{60}. \text{ However, the up-shift of 13 cm}^{-1} \text{ for the radial } A_{g}(1) \text{ mode is larger than that for } K_{6}C_{60} \text{ (9 cm}^{-1}). \text{ It is to be pointed out that the Raman spectrum of } Ba_{3}C_{60} \text{ is amazingly similar to that of } K_{6}C_{60} \text{ except for the relative intensities between } A_{g}(2) \text{ and } H_{g}(2) \text{ modes.}

\text{In the case of } K_{3}Ba_{3}C_{60} \text{ and } Rb_{3}Ba_{3}C_{60}, \text{ the similar Raman lines to } Ba_{3}C_{60} \text{ are observed. However, the strongest line is } A_{g}(2) \text{ mode, similarly to the case of } K_{6}C_{60} \text{ with bcc structure. It is worth pointing out that the } K_{3}Ba_{3}C_{60} \text{ and } Rb_{3}Ba_{3}C_{60} \text{ spectra are essentially identical to each other. These spectra are relatively insensitive to the choice of alkali-metal ion species. This behavior is similar to the case of } A_{3}C_{60} \text{ and } A_{6}C_{60} \text{ (A=K, Rb) compounds, where this behavior is explained both by a weak coupling between } C_{60} \text{ and alkali cations and by a complete charge transfer from the alkali-metals to } C_{60} \text{ molecules. However, an anomalous Raman shift for the two } A_{g} \text{-derived modes is observed in } K_{3}Ba_{3}C_{60} \text{ and } Rb_{3}Ba_{3}C_{60}. \text{ The first thing to be noted is the } A_{g}(2) \text{ mode observed at 1425.5 (1424.1) cm}^{-1} \text{ in } K_{3}Ba_{3}C_{60} \text{ (} Rb_{3}Ba_{3}C_{60} \text{). The relative down-shift of } A_{g}(2) \text{ mode measured from that of } Ba_{3}C_{60} \text{ is only 5.3 and 6.7 cm}^{-1} \text{ for } K_{3}Ba_{3}C_{60} \text{ and } Rb_{3}Ba_{3}C_{60}, \text{ respectively. These values are much smaller than that expected basing on the established empirical relation between the formal } C_{60} \text{ valence and the Raman shift. Another anomaly is found in the radial } A_{g}(1) \text{ mode, which shows a downshift of 8.6 and 10.5 cm}^{-1} \text{ relative to } Ba_{3}C_{60} \text{ for } K_{3}Ba_{3}C_{60} \text{ (} Rb_{3}Ba_{3}C_{60} \text{),} \]
respectively. Such a large downshift upon alkali metal doping displays a sharp contrast with the case of $A_xC_{60}$ (A=K, Rb) where a slight upshift is observed with increasing alkali metal. Low frequency $H_g$ modes also show complicated and characteristic behavior. The $H_g(2)$ mode of cubic $Ba_3C_{60}$ is single peak at $432 \text{ cm}^{-1}$, while it shows a splitting into two peaks both in $K_3Ba_3C_{60}$ and $Rb_3Ba_3C_{60}$. The splitting of $H_g(3)$ mode is observed in all samples in Fig.2, and the splitting is smaller in the alkali-doped ternaries, while the center of doublet remains unchanged.

Room temperature Raman spectra of the samples $Sm_{2.75}C_{60}$ and $K_{3.25}Sm_{2.75}C_{60}$ are shown in Fig.3. For $Sm_{2.75}C_{60}$, an anomalously broad distribution of vibrational structures for the low frequency $H_g$ modes and around the $A_g(2)$ mode is observed, which could be related to the complexity of $Sm_{2.75}C_{60}$ structure. The low frequency $H_g(1)$ and $H_g(2)$ modes are asymmetric. $H_g(2)$ mode has to be fitted with four components. It suggests that the degeneracy $H_g(2)$ mode is lifted. This splitting may be attributed to the symmetry lowering due to the orthorhombic superstructure of this material. A similar behavior has been observed in single crystal $K_3C_{60}$ at 80 K and in $Ba_4C_{60}$ and $Ba_6C_{60}$ at room temperature. A bunch of lines appears around $700 \text{ cm}^{-1}$ which are likely to be assigned to the $H_g(3)$ and $H_g(4)$ modes. It is to be pointed out that the pinch $A_g(2)$ mode occurs at $1432.8 \text{ cm}^{-1}$, indicating that Sm is divalent, and the charge transfer is complete according to $6.3 \text{ cm}^{-1}$ redshift per electron relative to neutral $C_{60}$. The position of the radial $A_g(1)$ is also consistent with that of $A_6C_{60}$ (A=K, Rb). This definitely confirms divalent Sm by Raman scattering, being consistent with the results of near-edge and extended X-ray absorption fine structure in $Yb_{2.75}C_{60}$.

The top of Fig.3 shows the spectrum of $K_{3.25}Sm_{2.75}C_{60}$, which is amazingly similar to $A_3Ba_3C_{60}$ although the Raman spectra of the intercalation host materials are different. Table I shows that even the positions of all corresponding modes are almost the same between $K_{3.25}Sm_{2.75}C_{60}$ and $A_3Ba_3C_{60}$ compounds. This surprising result strongly indicates that Raman spectrum is insensitive to the metal ion species either in the intercalation host or as an intercalation guest, suggesting a weak coupling between the $C_{60}$ and the metal ions and
a complete charge transfer from metal cations to $C_{60}$ molecules.

Raman shift of the radial $A_g(1)$ and $A_g(2)$ pinch modes as a function of the nominal charge transfer simply derived from the chemical formula for $Ba_3C_{60}$, $Sm_{2.75}C_{60}$, $A_3Ba_3C_{60}$ ($A$=K, Rb), and $K_{3.25}Sm_{2.75}C_{60}$ are plotted in Fig.4. For comparison, the results of $Ba_xC_{60}$ ($x$=4, 6) recently reported by us [5], $K_xC_{60}$ ($x$=3, 6) reported by Duclos et al. [6], and $KBa_2C_{60}$ and $KBaCs_{60}$ reported by Yildirim et al. [7] are also plotted in the figure. For the $A_g(2)$ mode, there is a boundary at charge transfer of 6 electrons. Below which, the relation between the Raman shift of $A_g(2)$ mode and charge transfer is linear. They follow the characteristic shift of $\sim 6.3$ cm$^{-1}$ redshift per elementary charge for the all samples including $Ba_3C_{60}$ and $Sm_{2.75}C_{60}$. However, when the charge transfer exceeds six, the pinch $A_g(2)$ mode does not follow the simple characteristic relation, showing a complicated behavior. In other words, although there exist a systematic relation between Raman shift and charge transfer for the "$t_{1u}$ band" fullerenes, the "$t_{1g}$ band" fullerenes are quite different. The charge transferred from metal to $C_{60}$ molecules were -9, -15, and -7 for the $Ba_4C_{60}$, $Ba_6C_{60}$, and $K_3Ba_3C_{60}$ ($K_{3.25}Sm_{2.75}C_{60}$), respectively, if charge transfer was derived according to 6.3 cm$^{-1}$ redshift per elementary charge. This is much larger (less) than the nominal charge transfer for $Ba_xC_{60}$ ($x$=4 and 6) ($K_3Ba_3C_{60}$ and $K_{3.25}Sm_{2.75}C_{60}$). If the charge transfer from Ba to $C_{60}$ molecules is complete, the redshift per elementary charge is about 9 cm$^{-1}$, being much larger than $\sim 6.3$ cm$^{-1}$. In addition, an anomalous Raman shift for the $A_g$ derived modes takes place in the ternary $A_3Ba_3C_{60}$ ($A$=K, Rb) and $K_{3.25}Sm_{2.75}C_{60}$, the down-shift is only about 6 cm$^{-1}$ for the nominal charge transfer of three electrons relative to $Ba_3C_{60}$ and $Sm_{2.75}C_{60}$.

Let us switch to the arguments on the radial $A_g(1)$ mode. A continuous up-shift of the $A_g(1)$ mode with increasing charge transfer until six electrons observed as shown in Fig.4. This mode-stiffening has been explained by electrostatic interactions which produces sufficient stiffening to encounter the softening of the mode expected on the basis of charge transfer effects. [5] It is to be noted that the Raman shift of the radial $A_g(1)$ for $Sm_{2.75}C_{60}$ with $t_{1u}$ states falls on the linear line of $K_xC_{60}$ with $t_{1u}$ states. In contrast, in the $t_{1g}$ fullerenes, the frequency of the $A_g(1)$ mode almost remains unchanged for $Ba_xC_{60}$, while
it decreases with increasing charge transfer in the ternaries $A_3Ba_3C_{60}$ and $K_{3.25}Sm_{2.75}C_{60}$. It is worth noting that both $A_g(1)$ and $A_g(2)$ modes show complicated behavior in the $t_{1g}$ bands.

In the case of Ba derived fullerides, a strong hybridization between the Ba atoms and the $\pi$-type functions of the $C_{60}$ network may be responsible for the behavior of the $A_g$ derived modes as discussed in Ref.15. The charge transfer is complete in the intercalation hosts of $Ba_3C_{60}$ and $Sm_{2.75}C_{60}$, following the characteristic relation between Raman shift and charge transfer, while the introduction of alkali metals leads to an anomalous Raman shift for the two $A_g$ derived modes in the ternary $A_3Ba_3C_{60}$ and $K_{3.25}Sm_{2.75}C_{60}$.. However, the Raman shift of $A_g(2)$ pinch mode follows the characteristic shift of $\sim 6.3 \text{ cm}^{-1}$ per elementary charge transfer for the co-intercalated $C_{60}$ of $ABa_2C_{60}$ (A=K, Rb, and Cs) and $KBaCsC_{60}$ with $t_{1u}$ states. It suggests that the anomalous Raman shift of the $A_g$ mode could be related to the "$t_{1g}$" band electrons. In fact, some other differences between the "$t_{1u}$" and "$t_{1g}$" superconductors have been found. In the $t_{1u}$ band, superconductivity occurs only at $(C_{60})^{-3}$ state which corresponds to the half-filling of the $t_{1u}$ band. However, the reported "$t_{1g}$" superconductors are $B_4C_{60}$ (B=Ba, Sr), $A_3Ba_3C_{60}$, and $Ca_5C_{60}$. which have the molecular valences of -8, -9, and -10, respectively. Such tolerance for the molecular valence in $t_{1g}$ superconductor makes a striking contrast with the strict constraint for the valence state in the case of "$t_{1u}$" superconductors. Another difference to be pointed out is that the "$t_{1u}$" superconductivity appears only in fcc or related structures. In the case of $t_{1g}$ band, superconductivity is observed in various structures, even orthorhombic structure. To completely understand the physical properties and superconducting mechanism of fullerides, it is necessary to further investigate $t_{1g}$ fullerides, and to explain the difference between $t_{1u}$ and $t_{1g}$ fullerides.

In summary, the Raman scattering study has been carried out in the two fulleride families of $A_xBa_3C_{60}$ (x=0, 3; A=K, Rb) and $K_xSm_{2.75}C_{60}$ (x=0, 3.25). The results definitely show some differences between $t_{1u}$ and $t_{1g}$ fulleride for Raman shift of the two $A_g$ modes. For $t_{1u}$ fullerides, the down-shift of the $A_g(2)$ mode and the up-shift of $A_g(1)$ mode can be explained
by charge transfer and the electrostatic interactions upon doping, respectively. In contrast, the $t_{1g}$ fullerides show a complicated behavior for Raman shift of the two $A_g$ modes. The Raman shifts of the two $A_g$ modes, observed in the tenaries $A_3Ba_3C_{60}$ and $K_{3.25}Sm_{2.75}C_{60}$, significantly differ from that of the binary fullerides $Ba_4C_{60}$ and $Ba_6C_{60}$. It is also found that Raman spectra of $A_3Ba_3C_{60}$ and $K_{3.25}Sm_{2.75}C_{60}$ are identical to each other, indicating a weak coupling between the $C_{60}$ and metal cations, and the same charge transfer to $C_{60}$ molecules. However, the anomalous Raman shift could not be explained only by the charge transfer.

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TABLE I. Positions and linewidths (in parentheses) for the Raman modes in $Ba_3C_{60}$, $A_3Ba_3C_{60}$ ($A=K$ and Rb), $Sm_{2.75}C_{60}$, and $K_{3.25}Sm_{2.75}C_{60}$

| $I_h$ mode | $Ba_3C_{60}$ | $K_3Ba_3C_{60}$ | $Rb_3Ba_3C_{60}$ | $Sm_{2.75}C_{60}$ | $K_{3.25}Sm_{2.75}C_{60}$ |
|------------|--------------|-----------------|-----------------|-----------------|-----------------|
| $A_g(1)$   | 505.9 ( 4.2 ) | 497.3 ( 2.4 )   | 495.4 ( 3.7 )   | 498.3 ( 6.9 )   | 496.8 ( 5.0 )   |
| $A_g(2)$   | 1430.8 ( 13.0) | 1425.5 ( 6.3 ) | 1424.1 ( 11.1 ) | 1432.8 ( 22.6 ) | 1424.7 ( 14.3 ) |
| $H_g(1)$   | 273 ( 5.3 )   | 266.3 ( 11.9 )  | 266.6 ( 4.5 )   | 264.7 ( 23.3 )  | 265.6 ( 10.4 )  |
|            | 278.7 ( 4.6 ) | 276.5 ( 3.0 )   | 272.8 ( 5.7 )   | 283.0 ( 3.1 )   | 276.0 ( 6.6 )   |
| $H_g(2)$   | 432.3 ( 5.3 ) | 414.9 ( 2.3 )   | 417.8 ( 3.7 )   | 344.5 ( 38.3 )  | 415.0 ( 3.9 )   |
|            | 422.9 ( 2.8 ) | 424.8 ( 2.9 )   | 400 ( 48.8 )    | 422.7 ( 18.0 )  | 415.0 ( 18.0 )  |
|            |                |                |                 | 427.0 ( 10.2 )  |                 |
| $H_g(3)$   | 648.2 ( 8.5 ) | 653.5 ( 5.6 )   | 655.3 ( 5.8 )   | 647.9 ( 25.0 )  | 653.3 ( 7.2 )   |
|            | 681.6 ( 7.8 ) | 673.3 ( 4.8 )   | 674.3 ( 4.2 )   | 683.4 ( 31.0 )  | 672.1 ( 12.9 )  |
| $H_g(4)$   | 760.7 ( 8.4 ) | 757.7 ( 4.2 )   | 758.7 ( 5.6 )   | 756.7 ( 23.0 )  | 757.5 ( 7.8 )   |
| $H_g(5)$   | 1091.7 ( 18.5)| 1086.0 ( 15.3) | 1086.7 ( 16.4)  | 1085.5 ( 22.3)  | 1088.0 ( 25.2)  |
|            | 1117.3 ( 12.8)|                |                 | 1112.4 ( 12.8)  |                 |
| $H_g(6)$   | 1227.6 ( 16.1)| 1229.0 ( 9.8)   | 1227.9 ( 13.1)  | 1226.2 ( 20.9)  | 1227.6 ( 16.7)  |
| $H_g(7)$   | 1322.1 (34.6) | 1314.0 ( 20.6)  | 1315.5 ( 18.0)  | 1317.9 ( 27.1)  |                 |
|            | 1388.1 ( 15.3)| 1377.4 ( 8.9)   | 1373 ( 23.5)    | 1387 .8 ( 46 )  | 1378.2 ( 11.5 ) |
| $H_g(8)$   | 1474.4 (26.1) |                |                 |                 |                 |


FIGURE CAPTIONS

Figure 1:
Powder X-ray diffraction patterns of $Sm_{2.75}C_{60}$ and $K_{3.25}Sm_{2.75}C_{60}$. The two peaks marked by arrows cannot be indexed with a body-centered-cubic cell with lattice parameter $a=11.093$ Å.

Figure 2:
Room temperature Raman spectra of $Ba_3C_{60}$, $K_3Ba_3C_{60}$, and $Rb_3Ba_3C_{60}$.

Figure 3:
Room temperature Raman spectra of $Sm_{2.75}C_{60}$ and $K_{3.25}Sm_{2.75}C_{60}$.

Figure 4:
Charge transfer-Raman shift relation for the radial $A_g(1)$ and $A_g(2)$ pinch modes. Squares represent the current experimental results, circles refer to the experimental results of $Ba_xC_{60}$ reported by us (Ref.15), up-triangles are from the results of $K_xC_{60}$ reported by Duclos et al. (Ref.5), and down-triangles refer to the results of $KBa_2C_{60}$ and $KBaCsC_{60}$ reported by Yildirim et al. (Ref.16).
Fig. 1

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Fig. 2

The diagram shows Raman spectra for different compounds: Rb$_3$Ba$_3$C$_6$O, K$_3$Ba$_3$C$_6$O, and Ba$_3$C$_6$O. The x-axis represents the Raman shift in cm$^{-1}$, and the y-axis represents the intensity in arbitrary units.
Fig. 3

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Fig. 4

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