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High Pressure Synthesis of Alkali Metal Intercalated C_{60} Polymers

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Potassium and Rubidium doped A_xC_{60} (A = K, Rb; x = 1, 2, 3) were treated under a pressure of 5 GPa at 573 K. After the treatment, the AC_{60} samples (x = 1) were transformed into orthorhombic 1D-polymers. The A_2C_{60} samples were transformed into a mixture of fcc monomer phase and orthorhombic 1D-polymer. The fcc A_3C_{60} samples were unchanged even after the treatment. These changes are very different from those found in the high-pressure treatments of Li and Na doped C_{60} fullerides, which transformed into the rhombohedral LiC_{60} and NaC_{60} 2D-polymers, tetragonal Li_xC_{60} 2D-polymer ($x \geq 2$), and Na_xC_{60} monomer phase ($x \geq 2$). All of the polymers A_xC_{60} (x = 1; A = Li, Na, K, Rb) obtained by the high pressure treatment were semiconductors with the conductivities increasing in the order of Li<Na≪K<Rb-forms.

Keywords: C_{60}; alkali metal; polymer; high pressure

INTRODUCTION

Solid C_{60} is polymerized through [2+2] cycloaddition of carbon double bonds into orthorhombic (Orth) 1D-polymer, tetragonal (T) 2D-polymer, and rhombohedral (3R) 2D-polymer by treating under high-pressure and high-temperature conditions. [1, 2] Although the intercalation of alkali atoms into the C_{60} polymers may modify the electrical properties, it leads to the degradation of polymers into monomers if the intercalation reactions are carried out at

elevated temperatures. The AC_{60} (A = K, Rb, Cs) 1D-polymers [3, 4] linked by [2+2] cycloaddition and the Na_4C_{60} 2D-polymer [5] linked by carbon single bonds have been obtained by the reaction of C_{60} with alkali metals. It was also reported that the Na_2RbC_{60} transformed into 1D-polymer linked by carbon single bonds by cooling slowly to low temperatures [6]. Recently, we have synthesized 3R 2D-polymers intercalated with Li and Na by treating A_xC_{60} (A = Li, Na; x = 1 - 3) fullerides under high pressure [7]. In this study, K and Rb doped C_{60} fullerides are treated under a high-pressure and high-temperature condition to synthesize new alkali metal doped C_{60} polymers.

EXPERIMENTAL

C_{60} and alkali azide AN_3 (A = Li, Na, K, Rb) were mixed in molar ratios of AN_3/C_{60} = 1, 2, 3, and heated at 523 - 533 K, 663 - 713 K, 753 K, and 783 K for A = Li, Na, K, Rb, respectively, in evacuated glass tubes to decompose the azides to metals. High-pressure (HP) treatments were performed under 5 GPa at 573 K for 1 h using a cubic anvil press according to the method described elsewhere [7]. The samples were characterized by a powder X-ray diffractometer and an infrared (IR) spectrometer. Electrical conductivity was measured by d.c. four-probe method in a temperature range of 200 - 300 K in vacuum.

RESULTS AND DISCUSSION

All of the A_xC_{60} samples were soluble in toluene before the HP treatment. Powder X-ray diffraction (XRD) patterns of LiC_{60} and NaC_{60} before the HP treatment were indexed on the basis of fcc unit cells with lattice parameters a = 14.18 Å and 14.20 Å, respectively [7, 8]. The KC_{60} and RbC_{60} prepared in this study were mixtures of fcc and Orth phases. All of these samples became insoluble in toluene after the HP treatment. The XRD patterns of the HP treated samples $(AC_{60})_{HP}$ (A = Li, Na, K, Rb) are compared in Figure 1. The $(C_{60})_{HP}$, $(LiC_{60})_{HP}$, and $(NaC_{60})_{HP}$ were 3R 2D-polymers [7] with lattice parameters a = 9.26 - 9.31 Å and c = 24.2 - 24.7 Å, as shown in Table 1. The Li and Na atoms are intercalated between the C_{60} layers polymerized in the (111) plane of the fcc lattice. On the other hand, the XRD patterns of $(KC_{60})_{HP}$ and $(RbC_{60})_{HP}$ were indexed with orthorhombic unit cells. The lattice parameters a are 9.28 Å and 9.45 Å for A = K and Rb, respectively, which are smaller than the distance (10.02 Å) between the centers of fcc packed C_{60} molecules. This indicates the contraction of the intermolecular distance in the [110] direction of the fcc

lattice. As shown in Figure 2, the IR spectra of $(KC_{60})_{HP}$ and $(RbC_{60})_{HP}$ are different from those of pristine C_{60} and 3R 2D-polymers, but similar to that of the RbC_{60} 1D-polymer reported by Kamarás *et al.* [9] These results suggest that the $(KC_{60})_{HP}$ and $(RbC_{60})_{HP}$ consist of Orth 1D-polymers of C_{60}.

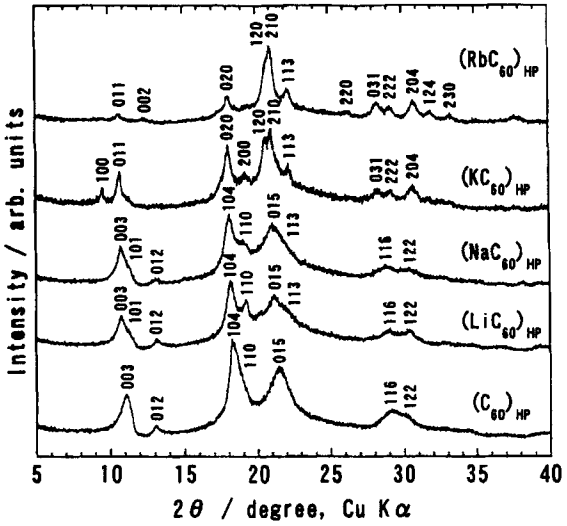

FIGURE 1 Powder XRD patterns of $(AC_{60})_{HP}$ (A = Li, Na, K, Rb). The indexes of the peaks are based on the unit cells listed in Table 1.

TABLE 1 Lattice parameters of $(AC_{60})_{HP}$ phases synthesized under 5 GPa at 573 K.

Phases	Symmetry	Lattice constants			
		a (Å)	b (Å)	c (Å)	V (Å^3)
$(C_{60})_{HP}$	Trigonal	9.31(3)	—	24.22(7)	606
$(LiC_{60})_{HP}$	Trigonal	9.26(2)	—	24.68(5)	611
$(NaC_{60})_{HP}$	Trigonal	9.31(1)	—	24.68(3)	618
$(KC_{60})_{HP}$	Orthorhombic	9.28(4)	9.69(3)	14.93(7)	671
$(RbC_{60})_{HP}$	Orthorhombic	9.45(7)	9.74(4)	14.72(7)	677

Temperature dependence of the electrical conductivities of the $(AC_{60})_{HP}$ polymers is shown in Figure 3. The conductivity of the 3R $(C_{60})_{HP}$ 2D-polymer was smaller than 10^{-8} $\Omega^{-1}cm^{-1}$, whereas all of the $(AC_{60})_{HP}$ polymers were semiconductors with the conductivities of 2×10^{-4}, 2×10^{-2}, 3×10^{0}, and 1×10^{1}

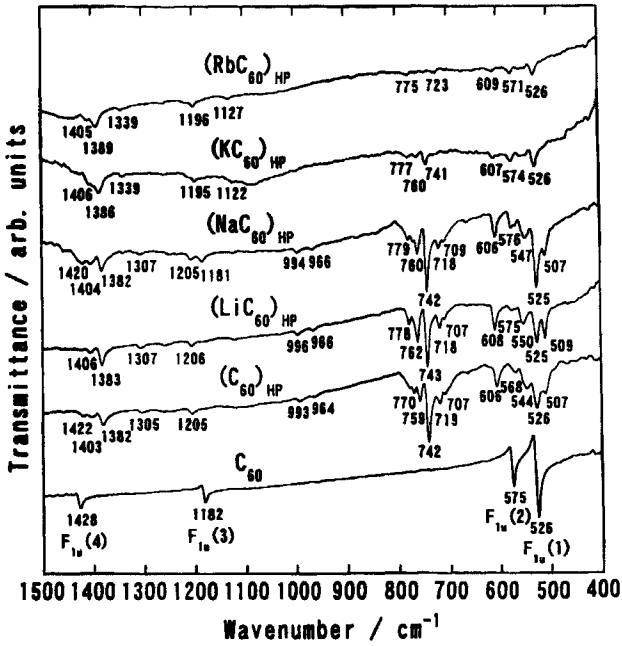

FIGURE 2 IR spectra of pristine C_{60} and $(AC_{60})_{HP}$.

$\Omega^{-1}cm^{-1}$ at room temperature for A = Li, Na, K, and Rb, respectively. The conductivity increases in the order of $(LiC_{60})_{HP} < (NaC_{60})_{HP} < (KC_{60})_{HP} < (RbC_{60})_{HP}$ polymers. The activation energy for the conductivity decreases in the same order. The deviation from a linear relation observed at 265 K for the $(LiC_{60})_{HP}$ sample is probably due to a phase transition [7]. Okada *et al.* [10] pointed out from the energy band calculation that the 3R C_{60} 2D-polymer was a semiconductor with an indirect band gap of 0.35 eV and the electronic structure around the gap was affected by the strong π interaction between the layers. They predicted that the material could become a metal by electron doping [10]. The insulating property of the 3R $(C_{60})_{HP}$ polymer is due to an absence of the carriers. Although the intercalation of Li or Na introduces a large number of electrons into the C_{60} polymers, it also brings about the increase in the basal spacing, as shown in Table 1. The weakened π interaction between the layers may lead to a thermally activated conduction of the electrons. As for AC_{60} (A = K, Rb, Cs) 1D-polymers, it was reported from the a.c. and d.c. conductivity measurements that the KC_{60} 1D-polymer was a metal whereas the RbC_{60} and CsC_{60} 1D-polymers were semiconductors [4, 11].

Bommeli *et al.* [4] explained this difference in terms of an increase in the interchain distance in the order of K<Rb<Cs. The semiconducting behavior observed for the Orth $(RbC_{60})_{HP}$ 1D-polymer agrees with that for the RbC_{60} 1D-polymer [4, 11]. The Orth $(KC_{60})_{HP}$ 1D-polymer was also found to be a semiconductor. The $(KC_{60})_{HP}$ has an orthorhombic structure with a lower symmetry than that of the KC_{60} 1D-polymer[12], as judged from the existence of (100) reflection in the XRD pattern of $(KC_{60})_{HP}$. The XRD patterns measured after the HP treatments in this study were all broadened compared to those before the HP treatments, indicating a low degree of polymerization or the existence of the distorted polymers. It cannot be ruled out that a large fraction of distorted structure between or within the polymers may result in the semiconducting behavior.

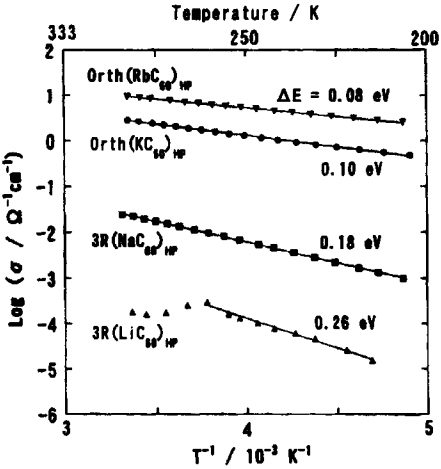

FIGURE 3 Temperature dependence of the electrical conductivity of $(AC_{60})_{HP}$.

TABLE 2 Phases formed by HP treatment under 5 GPa at 573 K.

x	Li	Na	K	Rb
1	3R	3R	Orth	Orth
2	3R+T	3R+A	Orth+B	Orth+B
3	3R+T	3R+A	B	B

3R: 3R AC_{60} 2D-polymer, T: Tetragonal Li_xC_{60} 2D-polymer,
Orth: Orthorhombic AC_{60} 1D-polymer,
A: Na_xC_{60} monomer phase, B: fcc A_3C_{60} monomer phase

The phases formed by the HP treatments of A_xC_{60} (A = Li, Na, K, Rb; x = 1, 2, 3) are summarized in Table 2. For the $(Li_xC_{60})_{HP}$ and $(Na_xC_{60})_{HP}$ with x = 2 and 3, the T 2D-polymer and non-polymerized phases intercalated with Li and Na, respectively, were formed with the corresponding 3R 2D-polymers, and the relative quantities of the former phases increased with increasing x [7] . There existed the fcc monomer phases and the Orth 1D-polymers in the $(K_2C_{60})_{HP}$ and $(Rb_2C_{60})_{HP}$ samples. The $(K_3C_{60})_{HP}$ and $(Rb_3C_{60})_{HP}$ were mainly composed of the fcc monomer phases with lattice parameters a = 14.253 Å and 14.431 Å, and showed superconducting transitions at 19.5 K and 30.0 K, respectively, which are in good agreement with the values for K_3C_{60} and Rb_3C_{60} reported by Fleming *et al.* [13] It appears that the K_3C_{60} and Rb_3C_{60} are not polymerized by the HP treatments under 5 GPa at 573 K.

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