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Received 18 May 2007, revised 5 July 2007, accepted 5 July 2007 Published online 26 September 2007

PACS 61.48.+c, 76.30.Pk, 78.30.Jw

We synthesized a series of Mg_xC_{60} samples with nominal composition of x between 1 and 6 via solid state reaction between C_{60} and Mg powder. For x = 5 a two dimensional structure was found. The polymer phase is unusually stable up to high temperatures, it remains unchanged at 823 K for 20 minutes as confirmed by ESR. The mid-infrared absorption spectrum suggests that the polymer sheets contain single bonded fulleride ions. Both the spin susceptibility and microwave conductivity measurements show that Mg_sC_{60} is metallic for T > 200 K. The transition from metallic to insulating states around 200 K may be attributed to Anderson localization.

phys. stat. sol. (b) 244, No. 11, 3853-3856 (2007) / DOI 10.1002/pssb.200776133





Paper

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1 Introduction

Only one alkaline earth intercalated fullerene polymeric structure has been recognized until now [1], which is remarkable if compared with the variety of polymeric phases present in alkali metal doped systems. Theoretical calculations [2] suggest that C_{60}^{n-} polyanions are stable preferring single bond formation for n > 3 if one neglects counterion size effects. Ca_xC_{60} and Ba_xC_{60} were largely studied because of their superconductivity and no polymeric phase was found. In a previous paper [1] a systematic study of the Mg_xC₆₀ system was presented and a 2D polymer structure with lattice parameters a = b = 0.922 nm and c = 2.525 nm was reported for x = 4.

An improved synthesis method allowed us to reconsider the Mg_xC_{60} system and to point out that the stoichiometric composition of this structure is 5 rather than 4. We studied the phase purity of the sample with both X-ray diffraction and ESR. For stoichiometries different from x = 5 the samples are heterogeneous showing multiple ESR absorption lines at the highest frequency. The thermal stability was also studied with ESR in a wide temperature range. To gain more information about the nature of the bonds (single or double) we measured the infrared and Raman spectra. Microwave conductivity measurements were also performed in order to study the electronic properties.

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2 **Experimental**

The samples were prepared by solid state reaction between stoichiometric amounts of pure C_{60} and Mg powders in a carbon steel tube in a glove box at temperatures between 380 °C and 450 °C. Several intermediate grindings were performed to improve the homogeneity of the samples. The progress of the reaction was followed by X-ray diffraction. Electron spin resonance at 9 GHz was performed with a commercial Bruker Elexsys E 500 spectrometer between 4-330 K on about 10 mg of Mg₅C₆₀ powder mixed with the ESR reference Mn:MgO in a 1:1 ratio. The samples were sealed in a quartz tube under 200 mBar He. The high-frequency ESR spectra were recorded on the same samples with a home built spectrometer operating at 225 GHz (which corresponds to 8.1 T for g = 2). Microwave resistivity was measured by a cavity perturbation technique [3] measuring the quality factor of a cavity operating at 10 GHz in the TE011 mode between 130 K and 400 K. The characteristic grain dimensions were much smaller than the penetration depth. In this limit the microwave losses in the cavity are directly proportional to the resistivity of the sample. The Mg_5C_{60} grains were separated by SnO oxide powder in order to avoid percolation currents among them. Raman spectra were collected using a T64000 Jobin-Yvon spectrometer in triple grating configuration with spectral resolution below 3 cm⁻¹. The excitation light was the 532 nm line of a frequency-doubled Nd-Yag laser. The diameter of the spot was 100 µm corresponding to a nominal irradiance of about 150 W/cm². Infrared spectra were recorded on pressed KBr pellets with a Bruker IFS 28 FTIR spectrometer under dynamic vacuum.

3 Results and discussion

The IR and Raman spectra of Mg_5C_{60} are shown in Fig. 1. The IR spectrum shows many lines as expected for symmetry lowering due to polymerization. The $T_{1u}(1)$, $T_{1u}(2)$, $T_{1u}(3)$ modes are clearly visible at 523 cm⁻¹, 576 cm⁻¹ and 1193 cm⁻¹, respectively. The intensity of the $T_{1u}(4)$ mode is instead suppressed and a mode visible also in the Raman spectrum appears at 1480 cm⁻¹. This absorption line can be attributed to the Raman active $A_p(2)$ mode blue shifted by approximately 10 cm⁻¹ with respect to



Fig. 1 Infrared and Raman spectrum of Mg_5C_{60} . The $A_g(2)$ mode at 1480 cm⁻¹ is clearly visible in both spectra. The infrared peak around 800 cm⁻¹ is typical of interfullerene single bonds.

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Fig. 2 ESR spectrum at 225 GHz and 150 K of Mg_5C_{60} . The orthorhombic KC_{60} fulleride polymer line is an intensity reference.

the neutral C_{60} molecule. A similar effect has been observed in C_{60} monolayers on metal surfaces (Pt, Cu, Au) [4, 5] and has been related to the formation of metal- C_{60} covalent bonds. We consider this as proof of covalent bonding between Mg atoms and C_{60} molecules, where charge is transferred from the fullerene to the d-orbitals of the metal. This scenario is also supported by the similar values of the ionization potentials of the Mg atom and the C_{60} molecule. The presence of the absorption peak at around 800 cm⁻¹ in the IR spectrum is a signature of single interfullerene bonds, seen in single-bonded polymers (Na₄C₆₀, Na₂RbC₆₀ [6]) and dimers (RbC₆₀)₂ [7], (C₅₉N)₂ [8].

The ESR spectrum at 225 GHz, Fig. 2, shows a single Lorentzian absorption line with line width $\Delta H = 2$ mT at all temperatures confirming the phase purity of the Mg₅C₆₀ samples. High frequency ESR allows in fact to see distinctly the absorption lines of phases with very similar *g*-factors. The slight distortion of the absorption line cannot be fitted with the characteristic line form of the *g*-factor anisotropy and is probably due to the inhomogeneity arising from the imperfect diffusion of the Mg atoms during the synthesis.

The temperature dependence of the spin susceptibility obtained by integrating the 9 GHz ESR signal is shown in Fig. 3 left. On the same figure the microwave conductivity is also reported. At temperatures higher than 200 K the susceptibility has a Pauli-like behavior while the conductivity decreases with temperature as usual in metals. For T < 200 K the susceptibility follows the Curie law and the conductivity increases with temperature.

The temperature dependence of the ESR line width at different frequencies is shown in Fig. 3 right. The ESR line width is dominated at high magnetic fields by a inhomogeneous broadening and it is tem-



Fig. 3 Left: Temperature dependence of the spin susceptibility (squares) and microwave conductivity (points) of Mg_sC_{60} . Right: ESR line width of Mg_sC_{60} versus temperature at 9 GHz (squares) and 225 GHz (circles).

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perature independent for T > 200 K. With the lowering of the temperature the line broadens due to the localization of the spins in the disordered crystal. At 9 GHz the intrinsic line width contribution is dominant and its temperature dependence is linear for T > 200 K as in metals in which the main relaxation mechanism is due to electron-phonon scattering [9]. For T < 200 K the line width becomes constant with temperature.

Both ESR and microwave conductivity show a continuous transition from a metallic to an insulating state with localized magnetic moments around 200 K. This behavior can be explained as an Anderson-like electron localization due to a disorder of the lattice. This disorder induces a mobility edge E_c in the electron band. If the Fermi energy is lower than the mobility edge the ground state is insulating but for temperature higher than E_c/k_B electrons became gradually delocalized.

We studied the thermal stability of the polymer phase by measuring the room temperature ESR spectrum after annealing in a furnace and quenching in water. The polymer phase was stable up to at least 823 K for 30 minutes. At higher temperatures the color of the quartz sample holder and the ESR spectrum change indicating a diffusion of the Mg atoms into the silica structure. The change was irreversible with temperature. We thus conclude that Mg_5C_{60} is stable up to very high temperatures, a reaction with the silica of the sample holder prevented us to measure the depolymerization temperature. These temperatures are also too high to allow IR or X-ray diffraction to study the depolymerization of Mg_5C_{60} .

4 Summary

 Mg_5C_{60} is a 2D fulleride polymer with a slight inhomogeneity in the distribution of Mg atoms. IR and Raman spectra show the coexistence of single bonds between C_{60} molecules and C_{60} -Mg atom covalent bonding but the determination of the exact crystalline structure needs a further investigation. The polymer is metallic for temperatures higher than 200 K. At this temperature the system becomes insulating, which we attribute to a disorder-driven, Anderson-like electron localization. Mg_5C_{60} is stable to at least 823 K where the sample reacts with the silica sample holder.

Acknowledgements The authors gratefully acknowledge the help of G. Oszlányi (Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences) with X-ray diffraction measurements and structural analysis. This work was supported by the Hungarian Scientific Research Fund (OTKA) through grants Nos. T049338, T046700, TS049881, F61733, and NK60984.

References

- [1] F. Borondics, G. Oszlányi, G. Faigel, and S. Pekker, Solid State Commun. 127, 311 (2003).
- [2] S. Pekker and G. Oszlányi, Synth. Met. 103, 2411 (1999).
- [3] B. Nebendahl, D. N. Peligrad, M. Požek, A. Dulčić, and M. Mehring, Rev. Sci. Instrum. 72, 1876 (2001).
- [4] P. D. P. Rudolf, R. Raval, and G. Williams, Appl. Phys. A 75, 147 (2002).
- [5] C. Cepek, A. Goldoni, and S. Modesti, Phys. Rev. B 53, 7466 (1996).
- [6] G. Klupp, Master's thesis, L. Eötvös University (2002).
- [7] K. Kamarás, D. B. Tanner, and L. Forró, Fullerene Sci. Technol. 5, 465 (1997).
- [8] N. Tagmatarchis, H. Shinohara, T. Pichler, M. Krause, and H. Kuzmany, J. Chem. Soc., Perkin Trans. 2, 2361 (2000).
- [9] Y. Yafet, Solid State Phys. 14, 1 (1963).