Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis of M_1C_{60} (M = Rb,Sr, Y) Compounds by Electrolysis

Hiraku Endo [a], Takashi Watanabe [a], Yoshiyuki Nagayama [a], Nobunari Yoshiyama [a] & Hiroshi Yamamoto [a]

[a] College of Sci. & Technol., Nihon University, 7-24-1 Narashinodai, Funabashi-shi, Chiba, 274, Japan

Version of record first published: 04 Oct 2006

To cite this article: Hiraku Endo, Takashi Watanabe, Yoshiyuki Nagayama, Nobunari Yoshiyama & Hiroshi Yamamoto (1998): Synthesis of M_1C_{60} (M = Rb,Sr, Y) Compounds by Electrolysis, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 316:1, 347-352

To link to this article: http://dx.doi.org/10.1080/10587259808044525

Mol. Cryst. Liq. Cryst., 1998, Vol. 316, pp. 347–352
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS OF M_1C_{60} (M=Rb,Sr,Y) COMPOUNDS BY ELECTROLYSIS

HIRAKU ENDO, TAKASHI WATANABE, YOSHIYUKI NAGAYAMA, NOBUNARI YOSHIYAMA and HIROSHI YAMAMOTO
College of Sci. & Technol., Nihon University, 7-24-1 Narashinodai, Funabashi-shi, Chiba 274, Japan

Abstract The C_{60} compounds with Rb, Sr and Y were synthesized in an electrolysis cell where 1.5mmol/l-C_{60} Toluene and 0.1mol/l-$M(ClO_4)x$ (x=1, M=Rb; x=2, M=Sr; x=3, M=Y), N,N-Dimethylformamide(DMF) were used. Though the as-prepared sample on the cathode was not crystallized, the post annealed samples showed several characteristic X-ray diffraction peaks. After annealing the slowly cooled sample had a body-centered orthorhombic structure and the rapidly cooled one revealed a face-centered cubic structure. The Sr_1C_{60} and Y_1C_{60} phases were newly observed similar to the Rb_1C_{60}.

Keywords C_{60}, Electrolysis, Rb_1C_{60}, Sr_1C_{60}, Y_1C_{60}, Polymeric phase

INTRODUCTION

Several groups have investigated a new class of A_1C_{60} (A=alkali metals) phase because of its characteristic crystallographic phase[1,2]. The Rb_1C_{60} phase reveals a structural transition driven by reversible formation and breaking of covalent bonds. It was anticipated in the polymeric phase that a quasi-one-dimensional metal conductivity is obtained and a Peierls transition takes place at 50K[3]. Also M. C. Martin *et al.*[4] discussed about

two types of conductivity of the RbC_{60} by optical measurements.

The A_1C_{60} has been synthesized by a thermal intercalation[5] or by a reaction in a toluene solution[6]. We have developed an electrolysis process to obtain such the M_1C_{60} compound. The results of the case of Rb_1C_{60} have been appeared in elsewhere[7]. In this work the further experiments have been done for new M_1C_{60} compounds with M=Rb, Sr and Y. The electrolysis process and the crystallographic structures of the obtained compounds were investigated.

EXPERIMENTAL

Figure 1 shows the electrolysis cell used for the synthesis of the compound. The cell was set in a dry box filled with N_2 gas. The cell had two parts; the cathode and the anode tube. The tubes were separated by an ion-exchange membrane. The solution in the cathode tube was the mixture of 1.5mmol/l-C_{60} Toluene. The solution in the anode tube was 0.1mol/l-$M(ClO_4)x$ (x=1, M=Rb; x=2, M=Sr; x=3, M=Y), N,N-Dimethylformamide (DMF). The cathode was a silver plate. The anode was a silver or gold plate. The reference electrode was Ag/Ag^+(BAS, RE-5). The bias voltage was kept at each the reduced potential of C_{60}; -0.8V for Rb, -1.2V for Sr and -2.2V for Y. The current was kept very small for 20h after applying the

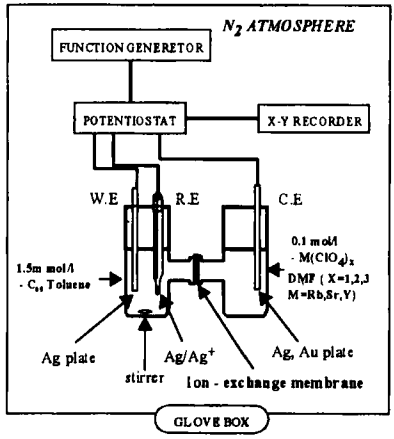


FIGURE 1 The used electrolysis cell and solution.

voltage and then was increased to about 0.05mA/cm^2. The reaction temperature was about 30℃. The potentiostat (HOKUTO DENKO, HA-301) was used for a cyclic voltammetry and the electrolysis.

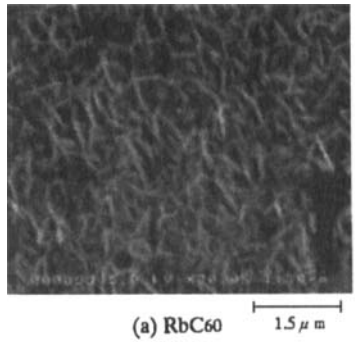
The morphological structure and the composition of local area were observed by Scanning Electron Microscope (SEM; HITACHI S-4500) and Energy Dispersive X-ray Spectrometer (EDX; KEVEX Inst.), respectively. The crystallographic structure was studied by the reflected X-ray Diffraction (XRD; RIGAKU, RAD-C).

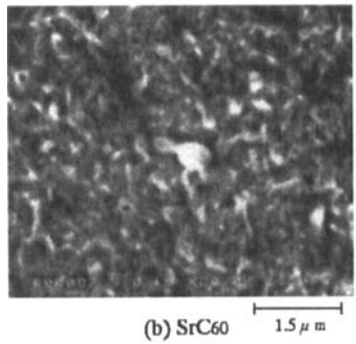
RESULTS AND DISCUSSION

A black thick film of the compound was formed on the cathode silver plate. The obtained compound was also annealed in a vacuum at 160℃ for 50h, and slowly or rapidly cooled to room temperature.

The SEM photographs of the compounds after the electrolysis of about 100h are shown in Fig. 2. The shape of the RbC60 particle was needle-like, and that of the Sr, YC60 was plate-like. The size of the particles was about 0.5 μm. The co-existence with each metals and C60 was confirmed by the composition analysis of the local area of the particles. A very high density of metal without C60 was also detected in small particles which were insulative and impurities.

Figure 3 shows the typical XRD patterns of the compounds. The as-prepared sample did not reveal any diffraction peaks from a C60 compound and was not crystallized. Then many diffraction peaks from impurities were observed. In the electrolysis process we should consider that solvation and/or mixing with various counter ions took place in the vicinity of the electrode. The post annealed sample showed several XRD peaks which indicated a crystallization of a C60 compound. The slowly cooled sample revealed features of a body-centered orthorhombic (bco) structure. The lattice parameters **a**, **b** and **c** of the Rb-C60 were estimated to be 9.07, 10.12 and 14.40 Å, respectively. As shown in Fig. 3(a) the observed XRD patterns of RbC60 system were in good agreement with those of the Rb1C60 reported by O.Chauvet *et al.*[8]. Almost same the crystal structures were synthesized also in the case of Sr and Y. These newly obtained M1C60





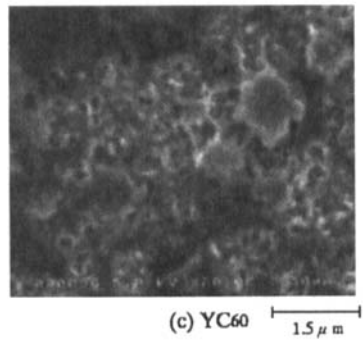


FIGURE 2 The SEM photographs of the compound of RbC60 (a), SrC60 (b) and YC60 (c). White particles were insulative and impurities.

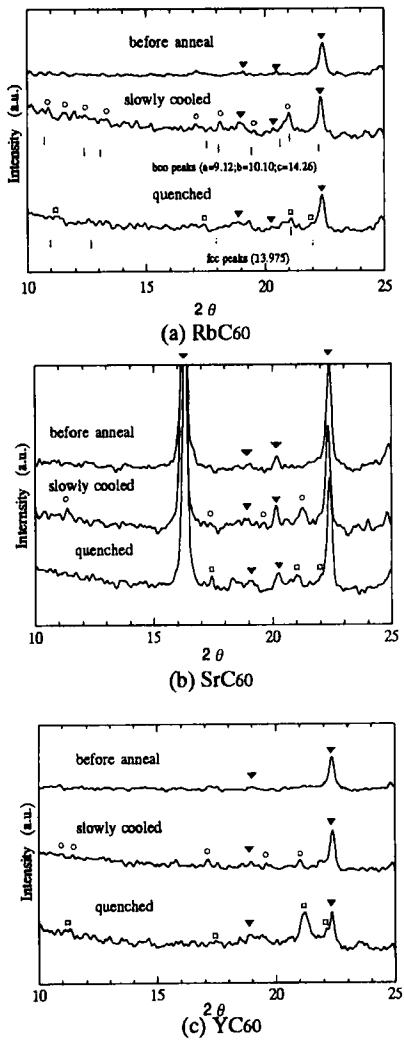


FIGURE 3 The XRD (Cu α) patterns of the compunds. The marked lines of the bco are the result by O.Chauvet et al.[8]. Where ▽, ○ and □ was impurities, the bco phase and the fcc phase, respectively. The lattice parameters were a=9.07, b=10.12, c=14.40Å in the bco phase of Rb1C60, and a=13.97Å in fcc; Sr1C60 a=9.04, b=9.89, c=15.26Å in bco, and a=13.98Å in fcc; Y1C60 a=9.07, b=10.34, c=14.92Å in bco, and a=13.89Å in

compounds were thought to be polymeric where the minimum bond length of neighboring C60 molecules was about 9.1 Å of which the value suggests covalent bonds between molecules.

On the other hand, the rapidly cooled sample revealed the features of a face-centered cubic (fcc) structure rather than the polymeric bco structure. The lower angle diffraction peaks became much smaller than the main diffraction peak at 2θ of about 21 degree. The lattice parameter **a** of Rb1C60, Sr1C60 and Y1C60 was estimated about 14.0, 14.0 and 13.9 Å, respectively. The lattice parameter was smaller than that of a fcc C60.
In this work the Sr1C60 or the Y1C60 was newly obtained similar to the Rb1C60. The two types of crystal phases were found in the all annealed samples including Rb, Sr and Y.

SUMMARY

The Rb1C60, Sr1C60 and Y1C60 compounds were synthesized by the electrolysis from solution. After post anneal the bco polymeric and the fcc phase were formed by slowly and rapid cooling, respectively. The obtained results suggest that a new class of the polymeric phase of C60 can be obtained even with a two or three valence metal. It will be very interesting to study the conductivity of such the polymeric compounds.

ACKNOWLEDGMENTS

The authors would like to thank the Advanced Materials Science Center in their College of Sci. & Technol., Nihon University for kept in the various analytical measurements of the samples.

REFERENCES

[1.] Q.Zhu, O.Zhou, J.E.Fischer, A.R.McGhite, W.J.Romanow, R.M. Strongin, M.A.Cichy and A.B.Smith III, Phys. Rev. B47, 13948(1993).
[2.] P.W.Stephens, G.Bortel, G.Faigel, M.Tegze, A.Janossy, S.Pekker, G.Oszlanyi and L.Forro: Nature 370, 636 (1994).

[3.] R.M.Fleming, M.J.Rosseinsky, A.P.Ramirez, D.W.Murphy, J.C.Tully, R.C.Haddon, T.Sigrist, R.Tycko, S.H.Glarum, P.Marsh, G.Dabbagh, S.M.Zahurak, A.V.Makhija and C.Hampton, Nature 352, 701(1991).

[4.] M.C.Martin, D.Koller, X.Du, P.W.Stephens and L.Mihaly, Phys. Rev. B49, 10818(1994).

[5.] J.Winter and H.Kuzumany: Solid Syate Commun. 84, 935(1992).

[6.] H.H.Wang, A.M.Kini, B.M.Savall, K.D.Carlson, J.M.Williams, M.W.Lathrop, K.R.Lykke, D.H.Parker, P.Wurz, M.J.Pellin, D.M.Gruen, U.Weip, W.-K.Kwik, S.Fleshler, G.W.Crabtree, J.E.Schirber and D.L.Overmyer, Inorg. Chem. 30, 2838(1991).

[7.] H.Endo, N.Yoshiyama and H.Yamamoto, Mol. Cryst. Liq. Cryst. 280, 289(1996).

[8.] O.Chauvet, G.Oszlanyi, L.Forro, P.W.Stephens, M.Tegze, G.Faigel and A.Janossy, Phys. Rev. Lett. 72, 2721(1994).