Unusual Crystallization Behavior of Selenium in the Presence of Organic Molecules at Room Temperature

Tsukio Ohtani,* Norihiro Takayama, Kazuaki Ikeda, and Masako Araki
Laboratory for Solid State Chemistry, Okayama University of Science, Ridai-cho 1-1, Okayama 700-0005

(Received October 21, 2003; CL-030999)

Amorphous Se was converted into fibrous crystals of hexagonal Se or polyhedral crystals of α-monoclinic Se when exposed to organic fluids at room temperature for several days. The growth phase was dependent upon the dielectric constant of the organic liquids. It is notable that hexagonal Se and α-monoclinic Se formed under vapors of *d*- and *l*-camphor, respectively. It is proposed that the organic compounds do not act as solvents, but play a catalytic role in the reactions.

Elemental Se is used in many applications. For example, amorphous Se is used in the photoconversion layer of solid-state image sensors such as highly sensitive camera tubes.[1] Many polytypes of Se exist, including hexagonal (*h*-Se),[2] α-monoclinic (α-*m*-Se),[3] β-monoclinic,[4] γ-monoclinic,[5] rhombohedral,[6] orthorhombic,[7] amorphous (*a*-Se),[8,9] etc. The *h*-Se is obtained by slowly cooling molten Se,[2] and the monoclinic phases form by evaporation from CS_2 solution.[3,4] The *h*-Se is thermodynamically the most stable form. Other phases convert to *h*-Se by warming. The *h*-Se consists of parallel chains of Se atoms arranged in helical spirals along the crystalline *c* axis.[2] All of the monoclinic phases are molecular crystals composed of building blocks of Se_8 molecules arranged in a crown shape.[3–5] The structure of *a*-Se is built from disordered helix-like Se chains with a minor contribution from Se_8 rings.[10] All the phases are scarcely soluble in most organic liquids at room temperature.

Recently we prepared Cu and Ag chalcogenides using a sonochemical method.[11] In the course of that study, we found that the *a*-Se form was transformed into *h*-Se crystals when allowed to stand in methanol at room temperature. In addition, over 100 years ago, Saunders reported that Se underwent a phase change from *a*-Se to hexagonal or monoclinic Se (the type of monoclinic phase was not identified) when placed in various organic solvents at ordinary temperature.[12] The origin remained unclear, and no further investigations on these phenomena have been reported since Saunders. In the present study, we investigated these reactions in detail using various organic compounds and modern analytical techniques.

Commercial *a*-Se shots (99.9999% purity: Rare Metallic Co., Ltd) were ground into powder in an agate mortar. Approximately 0.3 g of *a*-Se powder was placed into 7-mL organic liquid in a glass capsule, and was allowed to stand at room temperature for a certain period of time. In addition, the Se powder was exposed to a saturated vapor of organic compound in a desiccator at room temperature. In these experiments, various organic liquids and solids of commercial grade were utilized. Samples were analyzed by X-ray diffraction (XRD) using a Rigaku RINT 2500 instrument. The morphology of the samples was observed by scanning electron microscopy (SEM) using a JEOL JXA-8900 instrument.

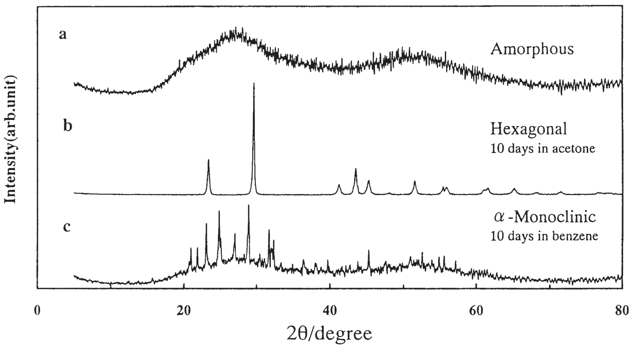

Figure 1. XRD patterns of Se: (a) amorphous Se (*a*-Se) starting material; (b) Se obtained by exposing *a*-Se to acetone at room temperature for 10 days; (c) Se obtained by exposing *a*-Se to benzene at room temperature for 10 days.

Figure 1a shows the XRD pattern of the starting *a*-Se, which exhibits a typical amorphous structure. Figures 1b and 1c show XRD patterns of Se obtained by exposing *a*-Se to acetone and benzene, respectively, at room temperature for 10 days. The patterns of Figures 1b and 1c were successfully analyzed on the basis of the hexagonal structure[2] and the α-monoclinic structure,[3] respectively. SEM images of Se particles are shown in Figure 2, where (a), (b), and (c) correspond to Figures 1a, 1b, and 1c, respectively. The *a*-Se particles possess an angular and irregular

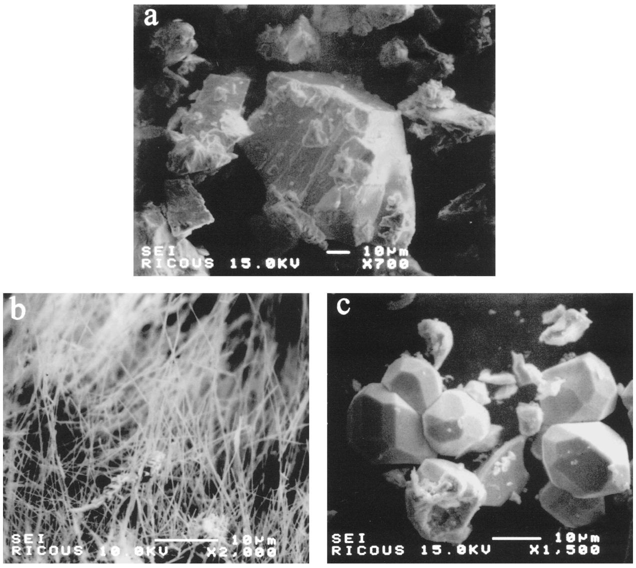

Figure 2. SEM images of Se particles: (a) amorphous Se (*a*-Se) particles; (b) Se particles obtained by exposing *a*-Se to acetone at room temperature for 10 days; (c) Se particles obtained by exposing *a*-Se to benzene at room temperature for 10 days.

polyhedral form with a mean size of 20–30 μm. The *h*-Se sample is composed of multiple fibrous single crystals with ca. 50-μm length and 0.1-μm diameter. The α-*m*-Se sample consists of many-faceted polyhedral crystals with mean diameter of ca. 10 μm. *h*-Se crystals with fibrous or needle-like morphology were obtained in acetone, pyridine, 2-propanol, acetonitrile, diethyl ether, benzylamine, piperidine, aniline, quinoline, acetophenone, or benzonitrile. Polyhedral α-*m*-Se crystals were grown in benzene, toluene, cyclohexane, or hexane. In methanol, ethanol, tetrahydrofuran, or dimethyl sulfoxide, the *h*-Se dominated. No reaction occurred in pure water. The shapes of the crystals grown are nearly identical to those obtained by other methods,[13–15] while the fibrous crystals have not been reported previously. The *a*-Se was entirely transformed into *h*- or α-*m*-Se form within 30 days at room temperature. The *h*- and the α-*m*-Se forms showed a tendency to be stable at high and low temperatures, respectively. Our observations differ from those of Saunders[12] for some organic compounds. The discrepancies seem to be mainly due to a lack of diffraction techniques in Saunders' experiments. It is known that *a*-Se is transformed into *h*-Se under illumination.[16,17] In the present case, the reaction rate did not change even in the absence of light, indicating that the reaction is not photoinduced.

When α-*m*-Se crystals, grown in benzene, were exposed to acetone at room temperature for 10 days, the polyhedral α-*m*-Se crystals became covered with needle-like *h*-Se crystals as shown in Figure 3a. In addition, spiral-shaped *h*-Se crystals occasionally grew, as shown in Figure 3b.

A clear relation exists between the type of phase grown and dielectric constant, ε, of the organic liquid. *h*-Se was obtained in liquids with an ε greater than 4.0. Liquids with an ε less than 3.0, such as benzene, toluene, cyclohexane, and hexane, caused a transformation to α-*m*-Se. This result would originate from the higher dielectric constant possessed by *h*-Se along the c axis ($\varepsilon \mathbin{//} c = 10\text{–}13$) compared with that of α-*m*-Se ($\varepsilon = 6\text{–}7$).[18]

Fibrous or needle-like crystals of *h*-Se formed under vapors of organic liquids or solids, i.e. acetone, methanol, 2,4-dichloroaniline, methyl *m*-nitrobenzoate, or *d*-camphor; while polyhedral crystals of α-*m*-Se grew under vapors of hexane, naphthalene, *l*-menthol, ethyl *p*-nitrobenzoate, or *l*-camphor. Crystals of two phases were obtained under vapors of benzene, toluene, cyclohexane, acetonitrile, 2-propanol, or ethanol. It is interesting to note that the type of crystal grown depended upon the camphor chirality.

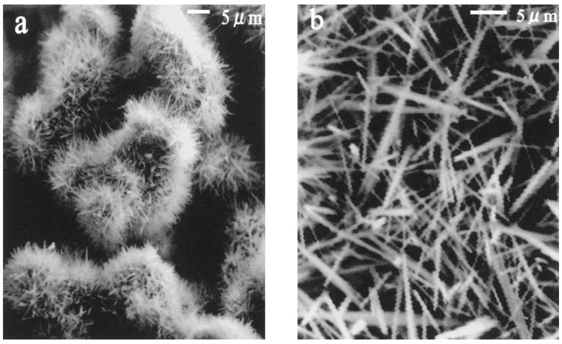

Figure 3. SEM images: (a) hexagonal Se (*h*-Se) crystals obtained by exposing α-monoclinic Se (α-*m*-Se) crystals to acetone for 10 days; (b) spiral *h*-Se crystals obtained by exposing α-*m*-Se crystals to acetone for 10 days.

Recently, *h*-Se crystals were obtained by precipitation from various organic solutions under solvothermal conditions at 453 K.[14] In the present study, however, the crystallization also occurred under saturated vapors of organic liquids and solids. We also observed that crystallization proceeded even under vacuum after a short exposure to organic fluids. Thus, it is most likely that organic compounds do not act as solvents, but the organic molecules adsorbed on the surfaces of Se particles play a catalytic role in crystal growth. Once the reaction begins, crystallization likely proceeds in an autocatalytic manner.

In conclusion, hexagonal and α-monoclinic Se crystals were grown from *a*-Se under quite mild conditions, which were entirely reproducible. The similar reactions would be observed for Te, that have the same structure with *h*-Se. The present results will open a path to a new area of surface reactions between organic and inorganic substances.

We are grateful to Dr. A. V. Powell and Prof. K. Tamura for fruitful suggestions and advice.

References

1 Y. Takiguchi, H. Maruyama, M. Kosugi, F. Andoh, T. Kato, K. Tanioka, J. Yamazaki, K. Tsuji, and T. Kawamura, *IEEE Trans. Electron Devices*, **44**, 1783 (1997).
2 P. Cherin and P. Unger, *Inorg. Chem.*, **6**, 1589 (1967).
3 P. Cherin and P. Unger, *Acta Crystallogr.*, **B28**, 313 (1972).
4 R. E. Marsh, L. Pauling, and J. D. McCullough, *Acta Crystallogr.*, **6**, 71 (1953).
5 O. Foss and V. Janickis, *J. Chem. Soc., Dalton Trans.*, **4**, 624 (1980).
6 Y. Miyamoto, *Jpn. J. Appl. Phys.*, **19**, 1813 (1980).
7 K. Nagata, H. Tashiro, and Y. Miyamoto, *Jpn. J. Appl. Phys.*, **20**, 2265 (1981).
8 E. H. Henninger, R. C. Buschert, and L. Heaton, *J. Chem. Phys.*, **46**, 586 (1967).
9 H. Krebs, *Z. Anorg. Allg. Chem.*, **265**, 156 (1951).
10 M. A. Popescu, "Non-Crystalline Chalcogenides," Kluwer, Dordrecht (2000), p 11.
11 T. Ohtani, T. Nonaka, and M. Araki, *J. Solid State Chem.*, **138**, 131 (1998).
12 A. P. Saunders, *J. Phys. Chem.*, **4**, 423 (1900).
13 F. Eckart, in "Recent Advances in Selenium Physics," ed. by European Selenium-Tellurium Committee, Pergamon Press, Edinburgh (1965), p 85.
14 J. Lu, Y. Xie, F. Xu, and L. Zhu, *J. Mater. Chem.*, **12**, 2755 (2002).
15 G. B. Abdullayev, Y. Asadov, and K. P. Mamedov, in "The Physics of Selenium and Tellurium," ed. by W. C. Cooper, Pergamon Press, Edinburgh (1969), p 179.
16 J. Dresner and G. B. Stringfellow, *J. Phys. Chem. Solids*, **29**, 303 (1968).
17 K. Ishida and K. Tanaka, *Phys. Rev.*, **B56**, 206 (1997).
18 "Landolt-Bornstein (New series)," ed. by O. Madelung, Springer-Verlag, Berlin, Heidelberg, etc. (1983), Vol. 17, p 86.

Published on the web (Advance View) February 5, 2004; DOI 10.1246/cl.2004.100