Enantioselective crystallization of amorphous Se in the presence of chiral organic molecules

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We have previously obsereved that when amorphous Se (a-Se) was exposed to organic fluids, the a-Se was transformed into a hexagonal Se (h-Se) or an α monoclinic Se (α-m-Se), corresponding to the dielectric constant of organic fluids. In the present study we found that the a-Se was enantioselectively crystallized into the h-Se or the α-m-Se by being exposed to chiral 2-octanol at room temperature; the h-Se was obtained in (R)-(-)-2-octanol, and the α-m-Se in (S)-(+)-2-octanol. Similar behaviors were observed under the vapors of 2-octanol as well as proline. This phenomenon is hardly explained, because the enantiomers have the same chemical and physical properties with each other, except for the optical rotation. The optical rotation is not responsible for this phenomenon, because this phenomenon was observed even in the absence of light. The phenomenon was also observed when the samples of various makers were employed, indicating that the quality of the samples has not responsibility for it. The origin is not cleared yet. If this phenomenon is intrinsic nature to the present system, this could be the answer to the "Ozma problem" proposed by Gardner, which inquires the way to communicate the meaning of "left or right" only by a language to the aliens.

1. Introduction

Elemental selenium has many polymorphs: amorphous (a-Se)[1,2], hexagonal (or trigonal) (h-Se)[3], α-monoclinic (α-m-Se)[4], β-monoclinic, γ-monoclinic, rhombohedral, orthorhombic, etc. The h-Se phase is the most stable phase, which can be obtained by slowly cooling molten Se. The α-m-Se phase is obtained as a metastable phase by evaporation from CS_2 solution, and easily converts to the h-Se phase by warming. Because of the high photoconductivity, the elemental selenium has been widely used in many applications such as photocells, xerography, electrical rectifiers, etc. The Se is also used for coloring glasses red or reddish yellow. Recent important use of the Se is a high sensitive camera tubes using HARP (High-gain Avalanche Rushing amorphous Photoconductor) imaging devices[5].
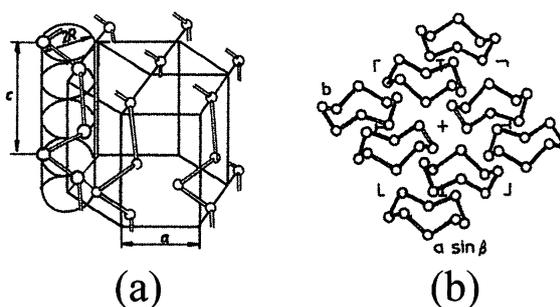
Figure 1. Crystal structures of Se: (a) hexagonal selenium (h-Se); (b) α-monoclinic selenium (α-m-Se).

Figure 1 gives schematic crystal structures of the h-Se (a) and the α-m-Se (b). The h-Se crystal consists of parallel infinite chains of Se atoms, where Se atoms are arranged in screw-like spirals along the

crystalline c axis[3]. The chains can be right-hand screws or left-hand screws, bringing about the chirality to the crystal. The α-m-Se phase is a molecular crystal, being composed of building blocks of Se_8 molecules arranged in a crown shape[4]. The h-Se is a semiconductor and the α-m-Se an insulator[6].

We have previously found that the a-Se was crystallized into the h-Se or the a-m-Se, when exposed to various organic fluids at room temperature for about 10 days[7, 8]. Figure 2 (a) shows the X-ray diffraction (XRD) pattern of the a-Se. When the a-Se was exposed to acetone liquid at room temperature for 10 days, the a-Se transformed to the h-Se, as shown in Fig. 2 (b). The a-m-Se was crystallized from the a-Se in benzene liquid, as shown in Fig 2 (c).

Scanning electron microscopy (SEM) images of a-Se, h-Se and a-m-Se are given in Fig. 3 (a), (b) and (c), respectively. The a-Se possesses angular and irregular morphology. In acetone, the a-Se was crystallized into multiple fibrous single crystals of the h-Se with ca. 50 μm of length and ca. 0.1 μm of diameter (Fig. 3 (b)). In benzene the a-Se was transformed to the a-m-Se crystals with many-faced polyhedral morphology with mean diameter of 10 μm (Fig. 3 (c)). The selective crystallization of the a-Se was observed for many other organic liquids. No reaction occurred in water. This phenomenon was also observed even in the absence of light.

A clear relation exists between the type of grown phase and the dielectric constant ε of the organic fluids. The h-Se crystals were grown in the liquids with an ε greater than ca. 4, e.g. acetone ($\varepsilon = 20.7$), methanol ($\varepsilon = 32.63$), ethanol ($\varepsilon = 24.55$), acetonitrile ($\varepsilon = 37.5$), benzonitrile ($\varepsilon = 25.20$), pyridine ($\varepsilon = 12.3$), quinoline ($\varepsilon = 9.00$), aniline ($\varepsilon = 6.89$), piperidine ($\varepsilon = 5.8$), diethyl ether ($\varepsilon = 4.3$), etc. The a-m-Se crystals formed in the liquids with an ε less than ca. 3, e.g. benzene ($\varepsilon = 2.27$), hexane ($\varepsilon = 1.89$), cyclohexane ($\varepsilon = 2.02$), toluene ($\varepsilon = 2.38$), etc.

More than 100 years ago, Saunders found similar selective crystallization of the a-Se in various organic liquids[9]. His results, however, are different from ours for some organic compounds, probably because of the lack of X-ray diffraction method in his experiments. He claimed that the precipitation from the organic solution causes the crystal growth of Se. Since Saunders' work, there has been no report on this phenomenon until our publication.

In this method we were able to obtain fibrous crystals of h-Se. These nanowires were found to show the electrical resistivity highly sensitive to the volatile organic gases, leading to the development of a gas sensor capable of detecting various organic gases at room temperature[10, 11].
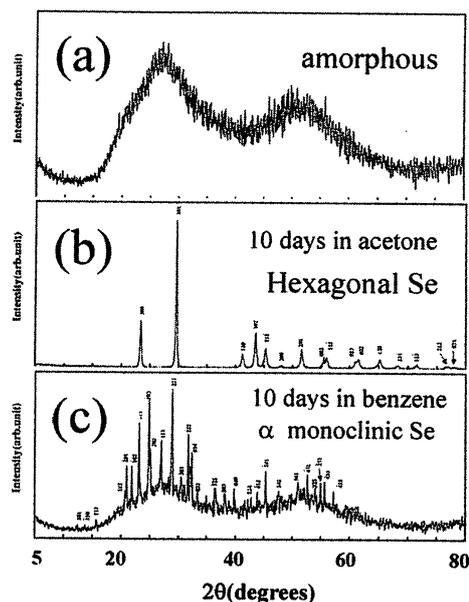
Figure 2. XRD patterns of Se: (a) starting amorphous Se (a-Se); (b) the h-Se obtained by exposing the a-Se to acetone at room temperature for 10 days; (c) the a-m-Se obtained by exposing the a-Se to benzene at room temperature for 10 days.
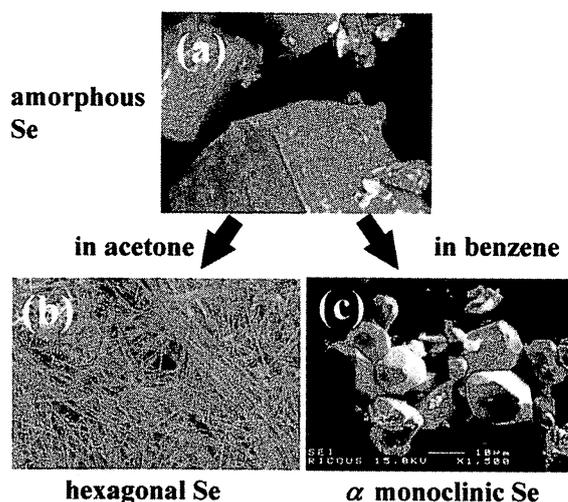
Figure 3. SEM images of Se particles; (a), (b) and (c) in the figure corresponds to Fig. 2 (a), (b) and (c), respectively: (a) the a-Se; (b) the h-Se; (c) the a-m-Se.

The present reactions took place even under the vapors of organic liquids or solids, suggesting that organic fluids do not act as solvent, but the adsorbed organic molecules play a catalytic role for the crystal growth. Such a situation is schematically illustrated in Fig. 4. If adsorbed organic molecules have the higher dielectric constant, the strong electrostatic field would be locally induced by the adsorbed molecules on the surface of Se particles. Such strong electrostatic field would act to stimulate the crystallization of h-Se, because h-Se has a relatively high dielectric constant along the c axis (ε // c = 10-13)[12].

In the present study we have observed the enantioselective crystallization of the a-Se in the presence of chiral organic molecules of 2-octanol and proline.
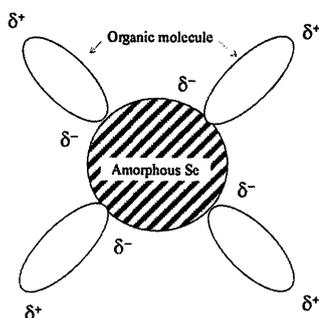
Figure 4. Schematic illustration of adsorbed organic molecules on the surface of amorphous Se.

2. Experiments

The experimental setups are illustrated in Fig. 5. The a-Se powder was placed into organic liquid in a glass capsule, and was allowed to stand at room temperature for a certain period of time (Fig. 5 (a)). The a-Se shots (Rare Metallic Co. Ltd, 99.9999% in purity) were ground into powder form by using an agate mortar. In order to investigate the enantiomeric effects on the crystallization of the a-Se, the experiments were carried out using the chiral secondary alcohols such as the 2-octanol (Sigma-Aldrich Corporation, 99% in purity). In addition, the a-Se powders were exposed to the vapors of chiral organic liquids or chiral organic solids as shown in Fig. 5 (b). Obtained samples were analyzed by an X-ray diffraction (XRD) technique using a Rigaku RINT 2500 instrument with CuKα radiation. The morphology of the samples was observed by SEM using a JEOL JXA-8900 instrument.
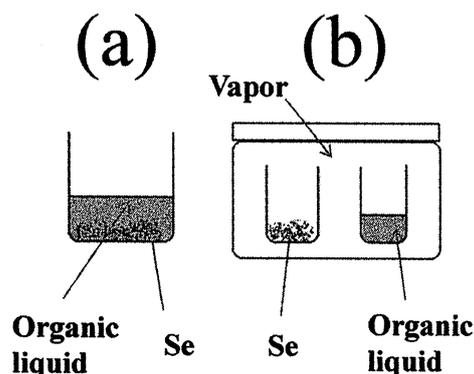
Figure 5. Schematic illustration of experimental setup for the crystallization of a-Se in organic liquid (a), and under the vapor of organic compound (b).

3. Results

3-1 Crystallization of Se in the presence of chiral secondary alcohols

The enantiomeric configuration of the secondary alcohols is represented in Fig. 6, where the asymmetric carbon atom is designated by the asterisk.
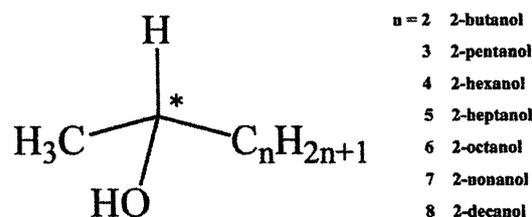
Figure 6. Enantiomeric configuration of secondary alcohols. The asymmetric carbon atom is designated by the asterisk.

Figure 7 shows XRD patterns for Se obtained by exposing the a-Se to chiral secondary alcohols (2-butanol, 2-pentanol, and 2-hexanol) for 10 days at room temperature. The a-Se was transformed into the h-Se for all cases. Figure 8 shows the results for 2-heptanol, 2-octanol and 2-nonanol. In the (S)-2-heptanol, the h-Se was dominantly grown, while the reaction was scarcely observed in the (R)-2-heptanol. For the 2-octanol, the h-Se was grown in the (R)-2-octanol and the α-m-Se in the (S)-2-octanol, being opposite to those of the 2-heptanol. For the 2-nonanol, the α-m-Se phase was dominantly obtained for both enantiomers.

We carried out the experiments for the 2-heptanol

and the 2-octanol for longer time. Figure 9 shows XRD patterns for Se obtained by exposing the a-Se to the 2-heptanol for 2 years at room temperature. The h-Se crystals were obtained for both enantiomers. SEM images of corresponding samples are given in Fig. 10; the fibrous single crystals of h-Se were grown in (S)-2-heptanol, and the needle like h-Se crystals in (R)-2-heptanol. For the 2-octanol, the same results shown in Fig. 8 were observed after 2 years, which will be described in more detail in the next section. For the 2-nonanol, the α–m-Se was obtained after 2 years.

Figure 9. XRD patterns of Se obtained by exposing the a-Se to chiral 2-heptanol for 2 years at room temperature.

Figure 7. XRD patterns for Se obtained by exposing the a-Se to the secondary alcohols for 10 days at room temperature: (a) (S)-2-butanol, (S)-2-pentanol, and (S)-2-hexanol; (b) (R)-2-butanol, (R)-2-pentanol, and (R)-2-hexanol.
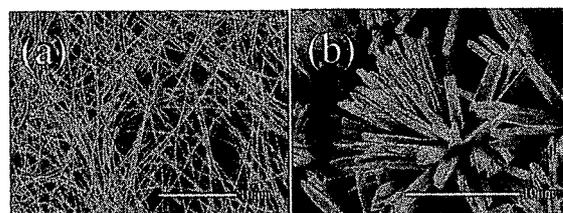
Figure 10. SEM images of Se obtained by exposing the a-Se for 2 years at room temperature to (S)-2-heptanol (a) and (R)-2-heptanol (b).

3-2 Enantioselective crystallization of amorphous Se in the presence of chiral 2-octanol

Figure 11 shows SEM images of Se crystals obtained in the 2-octanol for 10 days at room temperature: (a) in the (S)-2-octanol, (b) in the (R)-2-octanol. In the (S)-2-octanol, the a-Se was scarcely reacted, while fibrous and needle like crystals were grown in (R)-2-octanol, which are parallel to XRD observations shown in Fig. 8.

Figure 8. XRD patterns of Se obtained by exposing the a-Se to the chiral secondary alcohols (2-heptanol, 2-octanol, 2-nonanol) for 10 days at room temperature: (a) S-configuration, (b) R-configuration.
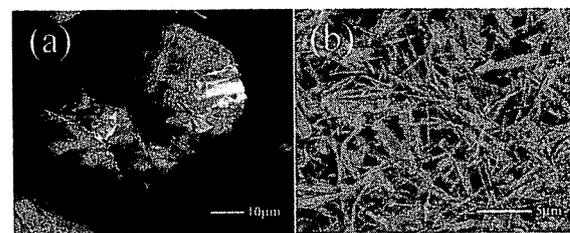
Figure 11. SEM images of Se obtained by exposing the a-Se to the 2-octanol for 10 days at room temperature: (a) in (S)-2-octanol, (b) in (R)-2-octanol.

Figure 12 shows XRD patterns of Se obtained by exposing the a-Se to the chiral 2-octanol for 30 days.

The h-Se phase was almost completely crystalized in (R)-2-octanol, while in the (S)-2-octanol the crystallization was scarcely progressed yet. XRD patterns of Se after 150 days of dipping in 2-octanol and the corresponding SEM images are shown in Figs. 13 and 14, respectively. The crystallization of the α-m-Se phase is progressed in the (S)-2-octanol.
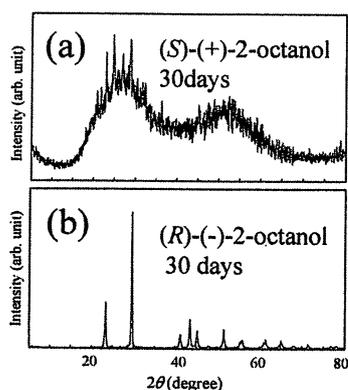
Figure 12. XRD patterns of Se obtained by exposing the a-Se to (S)-2-octanol (a) and (R)-2-octanol (b) for 30 days at room temperature.
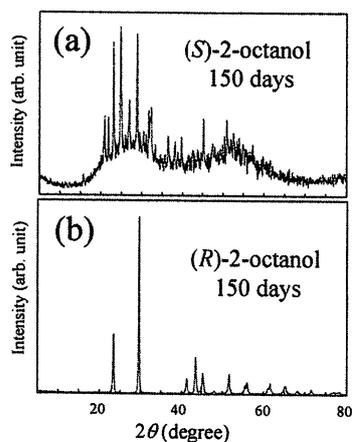
Figure 13. XRD patterns of Se after exposing the a-Se for 150 days to (S)-2-octanol (a) and to (R)-2-octanol (b).
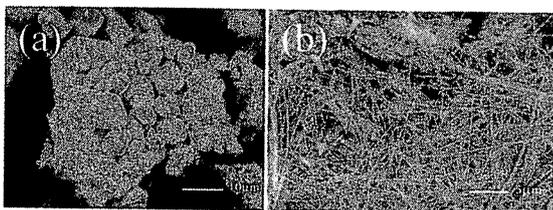
Figure 14. SEM images of Se. The samples correspond to those in Fig. 13.
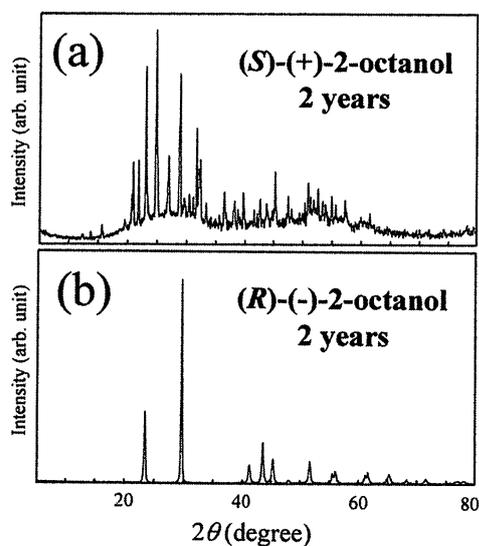
Figure 15. XRD patterns of Se crystals after exposing the a-Se to the 2-octanol at room temperature for 2 years: (a) in the (S)-2-octanol, (b) in the (R)-2-octanol.
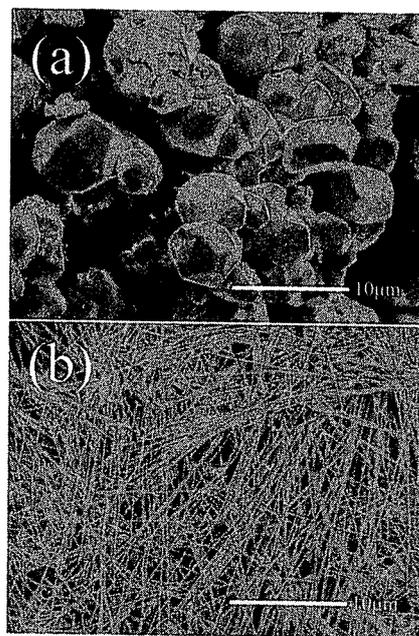
Figure 16. SEM images of Se crystals obtained by exposing the a-Se to 2-octanol for 2 years: (a) a-m-Se crystals in the (S)-2-octanol; (b) h-Se crystals in the (R)-2-octanol.

Figure 15 gives XRD patterns for Se samples obtained by exposing the a-Se to the chiral 2-octanol for 2 years. The large amount of the a-Se phase was transformed to the α-m-Se phase in the (S)-2-octanol, although the a-Se phase still remains. Figure 16

shows the SEM images of corresponding samples shown in Fig. 15. The polyhedral α-m-Se crystals were grown in the (S)-2-octanol; the size of each crystal is about several μm in diameter. The multiple fibrous h-Se crystals were obtained for the (R)-2-octanol; more than 50 μm length and about 0.1 μm diameter. These observations of the enantioselectivity are parallel to the XRD patterns in Fig. 15.

The a-Se was transformed to the h-Se, when exposed to the achiral 2-octanol.

These observations may possibly be caused by the slight difference in the quality between each of enantiomers. We have performed, thus, the experiments using various combinations of the a-Se and the 2-octanol made in different makers: the a-Se; Sigma-Aldrich Corporation, Wako Pure Chemical Industries, Rare Metallic Co., and Nacalai Tesque, Inc.: the 2-octanol; Sigma-Aldrich Corporation and Wako Pure Chemical Industries. Figure 17 shows XRD patterns of Se obtained by using the a-Se (Nacalai Tesque, Inc.) and the chiral 2-octanol (Wako Pure Chemical Industries) for 10 days at RT. The reaction was scarcely observed in the (S)-2-octanol. In the (R)-2-octanol the h-Se phase dominantly appeared, accompanied by a small amount of the α-m-Se phase. These results are essentially identical to the results obtained by using the a-Se (Rare Metallic Co. Ltd.) and the 2-octanol (Sigma-Aldrich Corporation). In other combinations of starting samples of different makers the similar results were obtained.

3-3 Enantioselective crystallization under the vapors of 2-octanol and proline

Figure 18 gives SEM images of the Se samples obtained by exposing the a-Se to the vapors of enantiomers of 2-octanol for 300 days at room temperature. The α-m-Se crystals and the h-Se crystals were obtained under the vapor of the (S)-2-octanol and (R)-2-octanol, respectively. These results were identified by the XRD measurements, while the small amount of h-Se phase coexists with the majority of α-m-Se phase under the vapor of (S)-2-octanol.
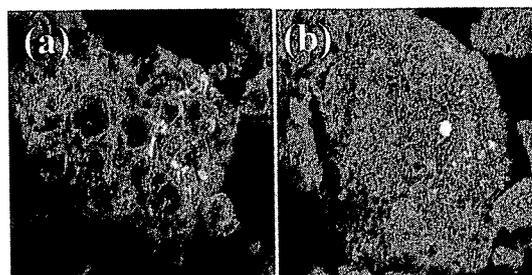
Figure 18. SEM images of the Se obtained by exposing the a-Se to the vapor of chiral 2-octanol at room temperature for 300 days: (a) in (S)-2-octanol; (b) in (R)-2-octanol.

The enantioselective crystal growth was also observed in the vapor of proline. Figure 19 gives XRD patterns of Se crystals obtained by exposing the a-Se to the vapor of a pair of enantiomers of proline for 410 days. Figure 20 exhibits SEM images of Se crystals corresponding to the samples given in Fig.19: (a) in the L-(-)-proline and (b) in the D-(+)-proline. The α-m-Se and h-Se crystals were grown for the vapor of L-proline, and D-proline, respectively.

Figure 17. XRD patterns of Se obtained by exposing the a-Se (Nacalai Tesque, Inc.) to the chiral 2-octanol (Wako Pure Chemical Industries) for 10 days at room temperature.
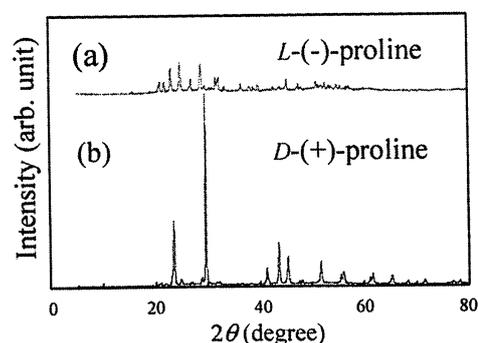
Figure 19. XRD patterns of Se crystals obtained by exposing the a-Se to the vapor of the proline for 410 days at room temperature: (a) L-(-)-proline, (b) D-(+)-proline.
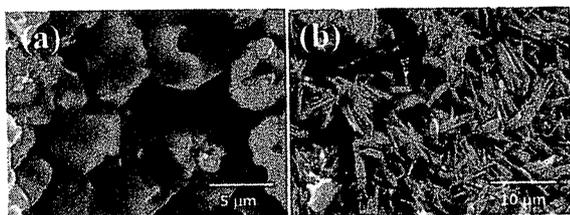
Figure 20. SEM images of α-m-Se crystals. Figs. (a) and (b) correspond to Fig. 19 (a) and (b), respectively.

It is to be interested that the chiral proline is used as an enantioselective organocatalyst, which works as the chiral catalyst in an Aldol reaction[13], although the mechanism is different from that of the present reactions.

It was sometimes observed that the h-Se and the α-m-Se crystals were grown under the vapor of (+)-camphor and (-)-camphor, respectively. The enantioselectivity was not observed in under the vapors of chiral organic solids such as aspartic acid, alanine, serine, menthol, tartaric acid, galactose, limonene, Noe's reagent, etc. The α-m-Se crystals were obtained in all cases.

4. Discussion

The a-Se was observed to show the enantioselective crystallization by being exposed to the chiral 2-octanol at room temperature. The similar enantioselective crystallization was observed under the vapors of chiral 2-octanol as well as chiral proline. The origin of this phenomenon is quite hardly explained, because the enantiomers have the same chemical and physical properties with each other, except for the optical rotation. This phenomenon was also observed in the absence of light, indicating that the optical rotation is excluded from the candidate of the origin.

As mentioned above, the kind of grown phase depends on the dielectric constant ε of the organic molecules. The strong electrostatic field locally induced by the adsorbed organic molecules on the surface of a-Se could stimulate the crystallization of the h-Se phase having the higher ε value. The ε value of the secondary alcohol is 16.72, 13.20, 11.06, 9.25, 7.80, and 6.66 for 2-butanol, 2-pentanol, 2-hexanol, 2-heptanol, 2-octanol and 2-nonanol, respectively. The ε value of 7.80 of the 2-octanol is situated near the border of the criterion for crystal growth of the h-Se or the α-m-Se. This could be the necessary con-

dition for the present enantioselective crystal growth.

The most noticeable is that the crystallization rate of the α-m-Se in the (S)-2-octanol is quite slow, compared with that in other organic fluids producing the α-m-Se, such as benzene. The a-Se seems to be almost inert to the (S)-2-octanol. This would suggest that the electrostatic field induced by adsorbed (S)-2-octanol molecules on the surface of the a-Se particles is effectively suppressed by some causes. One of the causes would be that the alkyl chain direction of the (S)-2-octanol is not perpendicular to the surface of the a-Se particles, but parallel to it. The other is that the molecules of the (S)-2-octanol are adsorbed in antiparallel manner. Both mechanisms would act to diminish the local electrostatic field on the surface. But one cannot explain why such situations occur only for the S configuration. It is more plausible, thus, that the a-Se has any responsibility for this phenomenon. The unknown crystal structure of the a-Se would correlate with the chiral organic fluids, causing this phenomenon.

The modification of the a-Se consists of a complex combination of Se atoms forming chains and closed rings. It is believed that the short-range ordering of the chains is similar to the structure of h-Se and the rings resemble to those in the monoclinic Se[r4]. We recall here that the h-Se has the chirality originating from the helical chains. This leads us to consider that there would be a symmetry break in the h-Se like chains existing in the a-Se, bringing about the enantioselective crystallization, with correlating to the chiral organic molecules. We have carried out, thus, the following examinations, focusing on the careful preparations of the a-Se.

[Preparation of the a-Se by quenching the molten Se]

The present XRD measurements revealed that the commercial a-Se possesses the amorphous modification. But the commercial samples would contain an unknown characteristic structure, because we are not able to know the preparation method of them. We prepared, thus, the amorphous Se by quenching molten Se (the starting Se: Rare Metallic Co., Ltd.) from 673 K to 273 K. Using this a-Se, we carried out the experiments for the chiral 2-octanol. Figure 21 shows XRD patterns of Se obtained by exposing the prepared a-Se to the 2-octanol (Sigma-Aldrich Corporation) for 100 days at room temperature. Although the

α-m-Se phase coexists with the h-Se phase for the (S)-2-octanol, the results are essentially similar to those obtained by using the commercial a-Se. These results show that the present enantioselective crystallization does not depend on the sample preparation processes.
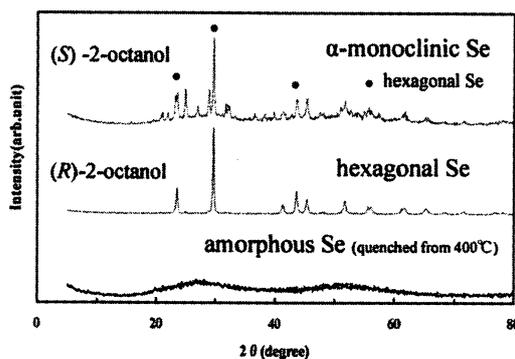
Figure 21. XRD patterns of Se obtained by exposing the a-Se to 2-octanol for 100 days at RT, using the a-Se prepared by quenching the molten Se from 673 K to 273 K.

[Effects of milling turn direction of the a-Se]

In the present study we obtained the powdered a-Se by clockwise milling of the Se shots using an agate mortar by hand. The one direction of the milling turn   would break the symmetry of h-Se like chains existing in the a-Se. The symmetry breaking by one direction of stirring was observed in aqueous solution of $NaClO_3$[15, 16]. We ground, thus, the a-Se shots clockwise or counterclockwise in the agate mortar.   Figure 22 shows XRD patterns of Se obtained by exposing the a-Se to the chiral 2-octanol for 66 days at room temperature, where the a-Se was previously milled in the agate mortar clockwise (a), and counterclockwise (b).   In both directions of turn the same results were obtained; the α-m-Se crystals were obtained in the (S)-2-octanol and the h-Se crystals in the (R)-2-octanol.

As a result, we were not able to find the origin of the present enantioselective crystallization of a-Se. Since we cannot know the detailed preparation processes of enantiomers of 2-octnol and proline, there still remains the possibility that the enantiomers of these organic compounds are slightly different in the quality with each other, causing the enantioselective crystallization. It is quite necessary for us to know the precise preparation methods of the enantiomers of 2-octanol and proline.
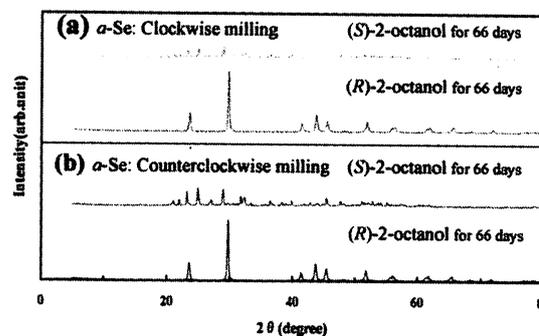
Figure 22. XRD patterns of Se obtained by exposing the a-Se to 2-octanol for 66 days, where the a-Se was milled in an agate mortar clockwise (a), and counterclockwise (b).

[Is this phenomenon an answer to the "Ozma problem"?]

If the present phenomenon is truly intrinsic nature to this system, we have obtained the new means to distinguish the chirality of organic compounds without observation equipment. In addition, we can communicate the concept of right or left to any person only by a language. Gardner proposed the "Ozma problem", which asks the way to communicate the meaning of "left or right" only by a language to the aliens living in faraway space[17]. This problem was solved by the observations of non-preservation of the parity in the β-decay of Co^{60} atoms[18]. This is the solution by the physics. The present observation of enantiosectivity would be the answer to this problem from the field of chemistry. We can inform the aliens the exact concept of the left as follows. "Expose the amorphous Se to each of enantiomers of 2-octanol, and observe the optical rotation of the chiral 2-octanol, which produced the hexagonal Se. The observed rotation direction is the left."

The communication to the aliens would be also possible in the following case. If the starting enantiomers of the 2-octanol (or proline) and the a-Se are well identified including possibly existing impurities, the present observations can be always reproduced. If the aliens are informed of the same preparation processes of 2-octanol (or proline) and a-Se as ours, they can know the exact concept of right or left only by a language from us. The detailed preparation method of present organic compounds should be needed again.

discussion and advices.

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