February, 1974] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(2), 641—644 (1975) 641

Physico-chemical Properties of Selenium-Tellurium-Sulfur Crystals

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(Received May 17, 1974)

The temperature dependence of electric conductivity and Vickers hardness of Selenium-Tellurium-Sulfur (Se–Te–S) crystals were studied. The conductivity decreased with an increase in sulfur content, remaining almost constant when the sulfur content was 40—80 atomic % at 20 and 30 atomic % of tellurium content. When tellurium content was 10%, both conductivity and hardness decreased abruptly when sulfur content exceeded 10%. It was found by means of X-ray diffraction that a hexagonal crystal structure with size twice the lattice constant of Se–Te crystals is formed when the sulfur content is 20% at 10% of tellurium content. When sulfur content exceeds 80%, the crystal structure becomes similar to that of pure sulfur (orthorhombic) at 20 and 30% of tellurium.

Hansen[1] reported that the phase diagram of Se–S system is of a complicated peritectic type, that of Se–Te system a basic solid solution type and that of Te–S system a eutectic type with a eutectic point at *ca.* 98—99 atomic % sulfur content. Many reports have appeared on the properties of Se–S, Se–Te, and Te–S systems.[2~5] The phase diagram of the Se–Te–S system has been reported,[6] but not its properties.

In this study, Se–Te–S crystals were prepared by heating amorphous Se–Te–S at 95 °C. The electric conductivity and Vickers hardness were measured. The results were discussed on the basis of X-ray diffraction data.

Experimental

Materials. Selenium (99.999%, Showa. Kagaku Co., Ltd.) and tellurium (99.999% Yokozawa Kagaku Co., Ltd.) were used. Sulfur of special grade was recrystallized twice.

Procedure. Three mixtures of powdered selenium and tellurium (Te, 10, 20 and 30 atomic %) were sealed separately in glass tubes under 10^{-3} Torr and melted at 470 °C. The glass tubes were exposed to the air for quenching. The products were powdered, and various amounts of sulfur were added. The mixtures were sealed separately in glass tubes, melted at 250—300 °C and quenched. The samples were crystallized at 95 °C for 2—24 hr. Specimens for measurement (4×4×7 mm) were cut out and left in the dark for *ca.* 24 hr. Electric conductivity was measured by the voltage drop method under 50 V. Vickers hardness was measured with a micro hardness tester of MVA type (Akashi Co.) under a load of 25~200 g for 1 min. X-ray diffraction was studied by the powder method with a Geigerflex (Rigaku Denki Co.) by means of CuKα line.

Results

Electric Conductivity (σ). The temperature dependence of electric conductivity of three Se–Te–S crystals with tellurium contents (a) 10%, (b) 20% and (c) 30% was studied in the range from room temperature to 95 °C. The relation between log σ and $1/T$ shows a nearly straight line. The relation between electric conductivity and sulfur content at 30 °C is shown in Fig. 1. The conductivity decreases with an increse in sulfur content. In (a), the conductivity decreases abruptly when the sulfur content exceeds 10%. In (b) and (c), the conductivity gradually decreases with an increase in sulfur content up to *ca.* 40%, remains almost constant, and decreases abruptly when

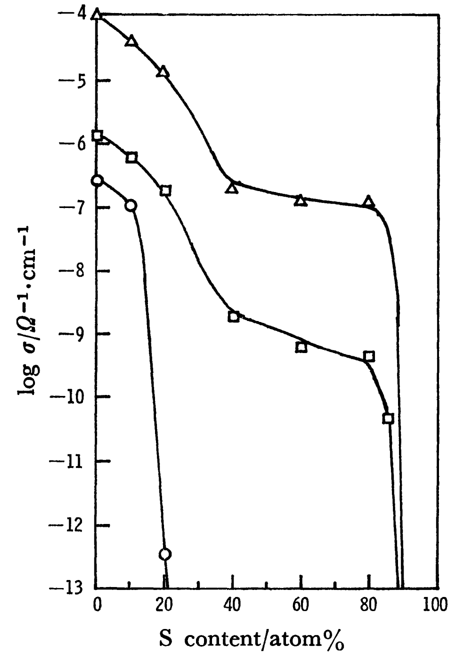


Fig. 1. Electric conductivity of Se-Te-S crystals n 30 °C.
Te content/atom% ○: 10, □: 20, △: 30.

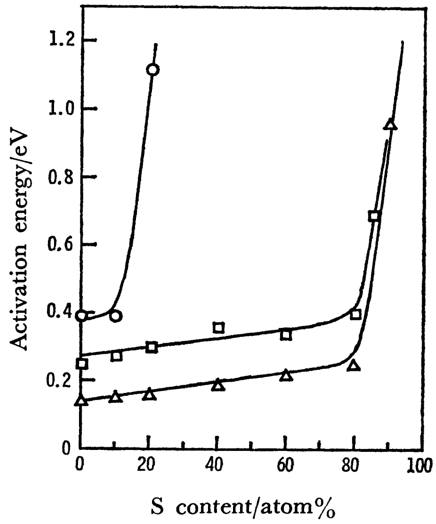


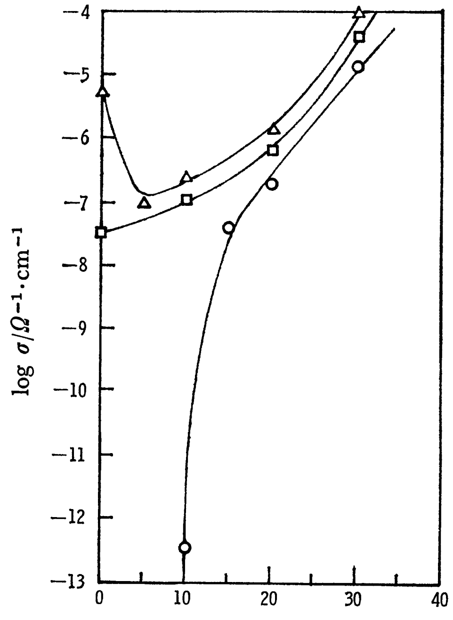
Fig. 2. Activation energy of the electric conductivity of Se-Te-S crystals.
Te content/atom% ○: 10, □: 20, △: 30.

the sulfur content exceeds 80%. The greyish black color of Se–Te crystals turned reddish brown in (a), brown in (b) and (c) at the sulfur concentration at which electric conductivity decreases abruptly.

Figure 2 shows the relation between sulfur content and activation energy. The activation energy was calculated by

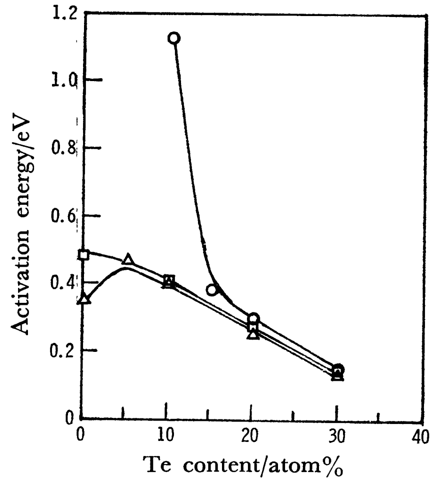
$$\sigma = \sigma_0 \exp(-E/kT),$$

where σ and σ_0 are electric conductivities, E activation energy, k the Boltzmann constant, and T absolute temperature. The activation energy remains almost constant in (a) for sulfur content up to 10%, but increases abruptly when it exceeds 10%. The results seem to be the reverse of that for conductivity (Fig. 1). In (b) and (c), the activation energy increases abruptly when sulfur content exceeds *ca.* 80%. Activation energy above 80% sulfur approaches 1.52 eV,[7] the energy of pure sulfur.



Te content/atom%

Fig. 3. Electric conductivity of Se-Te-S crystals at 30 °C.
S content/atom% △: 0, □: 10, ○: 20.

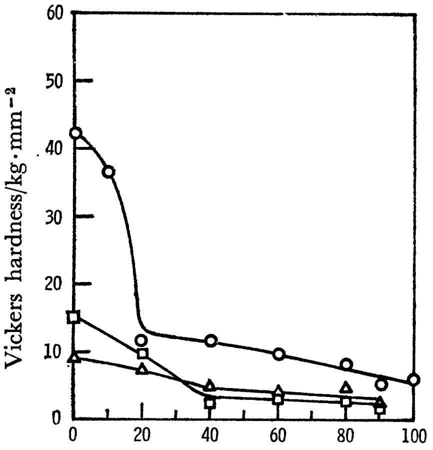


Te content/atom%

Fig. 4. Activation energy of the electric conductivity of Se-Te-S crystals.
S content/atom% △: 0, □; 10, ○: 20,

The relation between the electric conductivity of Se–Te–S crystals and tellurium content is shown in Fig. 3. When no sulfur is contained, the conductivity decreases with an increase in tellurium content up to ca. 5%, but increases above 5%. When sulfur content is 10%, the conductivity increases with an increase in tellurium content. When sulfur content is 20%, the conductivity abruptly decreases with a decrease in tellurium content below 15%. The relation between activation energy and tellurium content is shown in Fig. 4. The results seem to be the reverse of those for conductivity (Fig. 3).

Hardness. The relation between sulfur content and Vickers hardness of Se–Te–S crystals (a), (b) and (c) is shown in Fig. 5. The hardness decreases abruptly with an increase in sulfur content up to *ca.* 20% in (a) and decreases gradually above 20%. The rapid lowering of hardness corresponds to the decrease in conductivity (Fig. 1). The hardness of selenium crystallized at 95 °C is *ca.* 90 kg/mm², decreasing abruptly with an increase in tellurium content up to *ca.* 20% and decreases gradually above 20%. There is no change in hardness when sulfur content exceeds 80% in (b) and (c).



S content/atom%

Fig. 5. Vickers hardness of Se-Te-S crystals.
Te content/atom% ○: 10, □: 20, △: 30.

X-Ray Diffraction. The X-ray diffraction patterns for (a), shown in Fig. 6, are nearly the same for the 0 and 10% sulfur contents. When sulfur content is 20%, the diffraction pattern of 0% sulfur disappears, a different pattern appearing. For the samples with sulfur contents 40 and 60%, the diffraction pattern corresponding to 20% sulfur content appears accompanied by a different pattern. The diffraction pattern for 60% sulfur is similar to that of the SeS compound.[8] For 90% sulfur, it is similar to that of pure sulfur. The diffraction patterns for (b) (Fig. 7) are sharper than those for (a). When sulfur content is 10%, the diffraction pattern of 0% sulfur appears, its peaks shifting slightly towards small angles; it partly disappears when sulfur content is 20%, a new pattern appears differing

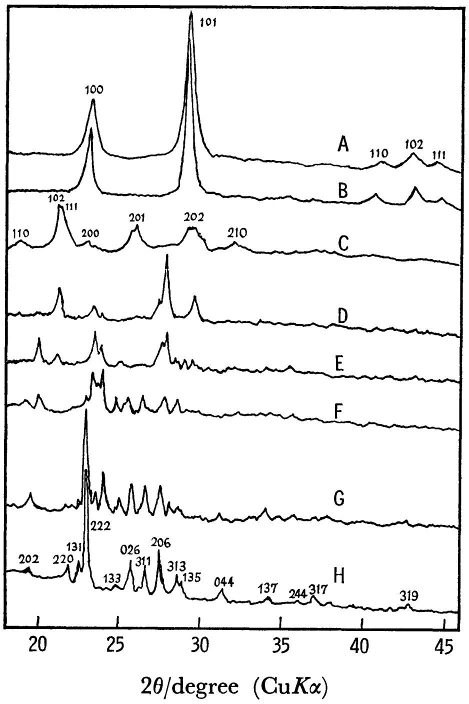


Fig. 6. X-ray diffraction patterns of Se-Te-S crystals containing 10 atom% of tellurium.
S content/atom%
A: 0, B: 10, C: 20, D: 40, E: 60, F: 80, G: 90, H: Pure sulfur (orthorhombic).

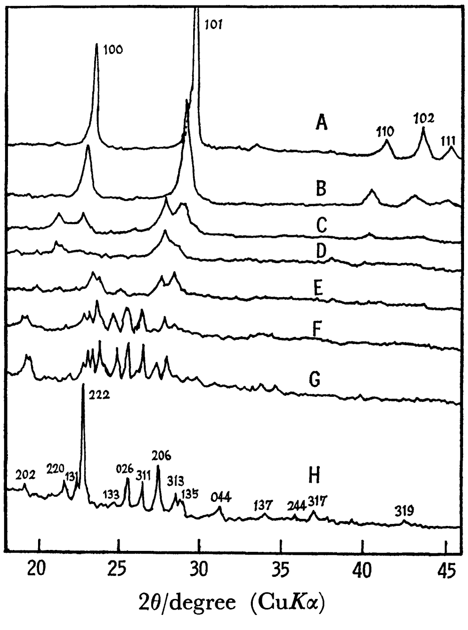


Fig. 7. X-ray diffraction patterns of Se-Te-S crystals containing 20 atom% of tellurium.
S content/atom%
A: 0, B: 10, C: 20, D: 40, E: 60, F: 80, G: 90, H: Pure sulfur (orthorhombic).

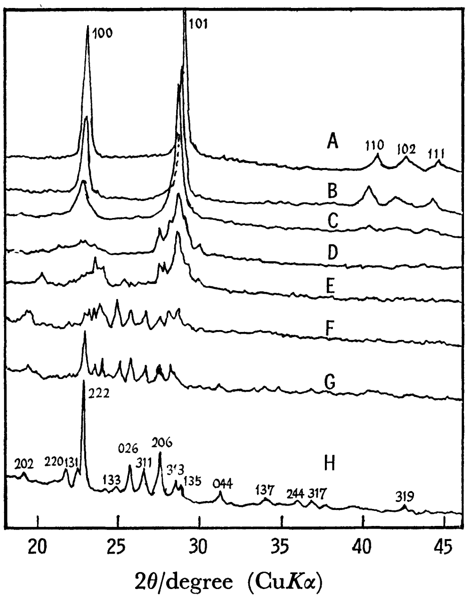


Fig. 8. X-ray diffraction patterns of Se-Te-S crystals containing 30 atom% of tellurium.
S content/atom%
A: 0, B: 10, C: 20, D: 40, E: 60, F: 80, G: 90, H: Pure sulfur (orthorhombic).

from that of (a) with 20% sulfur. The diffraction patterns for 40 and 60% sulfur differ from the pattern for 20% sulfur. The diffraction patterns for 80 and 90% sulfur differ from those for 40 and 60% sulfur, being similar to that of pure sulfur. The diffraction patterns for (c) are shown in Fig. 8. When sulfur content is 20%, the diffraction pattern of 0% sulfur partly remains the peaks shifting slightly towards small angles as in (b). The diffraction pattern of 0% sulfur partly remains in those of the Se–Te–S crystals with sulfur contents 40 and 60%. When sulfur content exceeds 80%, the diffraction pattern becomes similar to that of pure sulfur.

Discussion

In (a), the diffraction pattern for 20% sulfur differs entirely from that of the systems with 0 and 10% sulfur. Electric conductivity, activation energy and hardness indicate characteristic behavior when sulfur content exceeds 10%. It can be assumed that the diffraction pattern for 20% sulfur is due to the hexagonal crystal which has a unit cell with size twice Se–Te crystals lattice. Tellurium is substituted into a fixed position of the selenium crystal lattice and sulfur is substituted into a fixed position of the selenium of this lattice. The lattice constant of the new lattice is twice that of Se–Te crystal. It is possible to assign the diffraction pattern (Fig. 6, C). In Se–S crystal, the diffraction pattern differs from that of selenium when sulfur content exceeds *ca.* 7%.[2] In this Se–Te–S crystal (S= 20%), electric conductivity increases abruptly with an increase in tellurium content when tellurium content is below 15% (Fig. 3). For 10% sulfur, no rapid lowering in electric conductivity was observed in the presence of tellurium. No such phenomenon appears when tellurium content exceeds 20% (Figs. 7 and 8). This is due to the fact that sulfur and tellurium form eutectic crystals for large tellurium content. When sulfur content exceeds 80%, the diffraction patterns resemble that of pure sulfur (orthorhombic). It seems that this causes the electric conductivity to decrease abruptly with an increase in sulfur content when the sulfur content exceeds 80% in (b) and (c).

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