る。紫外線照射により ϵ' が減り、 ϵ'' がかなり増大する。これに対する一つの可能な説明は、非架橋酸素イオンが架橋イオンに変わるため、網目構造の連結度が増し、その固有振動の周波数が低下したので、 10^6 Hz 以上の高周波域にある変形損失のピーク位置が低周波側へずれ、ピークの裾が 10^6 Hz 以下の周波域へ現われたというものである。 10^6 Hz 付近では、網目変形の振動形態の一部は、交流電界に追いつかなくなり、 ϵ' へ寄与しなくなるため、 ϵ' が減る。

われわれのガラス試料の誘電特性を測定し、また結果について貴重な見解を示された電気試験所並河洋氏に深く謝意を表す。

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Thermal Expansion of Arsenic-Sulfur Glasses

By

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As-S 系 ガ ラ ス の 熱 膨 脹

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Some properties and the structure of the glasses in the system As-S have previously been reported^{1)~3)}.

However its thermal properties have not been studied yet. The purpose of this note is to report the thermal expansion of the As-S glasses and how the result can be explained with the structural models for the As-S glasses described in the previous paper³⁾.

The composition of glasses chosen for study are as follows, $\text{As}_2\text{S}_{2.7}$, $\text{As}_2\text{S}_{2.85}$, As_2S_3 , As_2S_4 , As_2S_6 , As_2S_7 , As_2S_9 , As_2S_{12} . The glasses were prepared by melting together high purity elements in evacuated, sealed Pyrex tubes which were placed in a rocking furnace at 600°C for several hours.

A tube-type vitreous-silica dilatometer and differential gaging electronic comparator were used to measure the thermal expansion and the softening temperature (A_t), transformation temperature (T_g) and linear coefficients of thermal expansion from room temperature to T_g and T_g to A_t (α_1 and α_2 , respectively) were determined from the expansion curves.

Before the measurement the specimen, a bar of about $(3-4) \times (3-4) \times (20-25)$ mm, was annealed at near the transformation temperature for one hour and cooled gradually to room temperature in the furnace. The heating rate in the measure-

ment was controlled to be about $2^\circ\text{C}/\text{min}$. The results are shown in Fig. 1 and 2.

As can be seen from the figures, each value does not change linearly in proportion to S content but maxima in T_g and A_t and minimum in α_1 were observed on the point of As_2S_3 . These phenomena can be interpreted qualitatively as follows.

According to the structural informations for the As-S glasses previously reported³⁾, $-\text{As}-\text{S}-\text{As}-$ linkages are replaced with $-\text{As}(\text{S})_n-\text{As}-$ linkages with increasing S content above As_2S_3 and the structure of glass approaches to that of plastic S with further addition of S. On the other hand S in $-\text{As}-\text{S}-\text{As}-$ linkages is eliminated and $-\text{As}-\text{As}-$ bonds are formed with decreasing S content below As_2S_3 . While the bond strengths of both S-S bond (33.4 ± 4.8 kcal/mole) and As-As bond (32.1 kcal/mole) are considerably lower than that of As-S bond (61 kcal/mole). Therefore T_g and A_t show the maxima in As_2S_3 composition and their values decrease as the S content increases or decreases.

The increase in α_1 with an increase of S content above As_2S_3 is probably attributed to that S has large thermal coefficient of linear expansion. However with decreasing S content below As_2S_3 , α_1 is found to increase again.

For this phenomenon the following interpretation may be considered. With decreasing S content below As_2S_3 , $-\text{As}-\text{As}-$ bonds are formed in the glass network and this causes the deformation of layer structure and at the same time the expansion of interlayer distance. Consequently it becomes easy for the glasses with lower S content than that of As_2S_3 to expand thermally.

The relationships of composition and A_t , T_g , α_1 or α_h have already been reported over the glass forming region of the As-S system⁹⁾. However between the present work and that by Tanaka et al. there is an essential discrepancy in the composition range of lower S content than that of As_2S_3 . This could be attributed to the structural difference of glasses depending on the glass preparation because in the case of Tanaka et al. the glass specimens are prepared by the distillation method. This view may be supported by Maruno's result⁶⁾ that glassy films of As_2S_x ($2.7 < x < 2.9$) prepared by evaporation contain As_2S_2 (or As_4S_4) component and are a microheterogeneous system consisting of mixed aggregates of As_2S_3 and As_2S_2 (or As_4S_4).

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Fig. 1. T_g (●) and A_t (○) of As-S glasses and T_g (△) of plastic S⁹⁾.

Fig. 2. α_1 (○) and α_h (●) of As-S glasses.

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The Thermal Conductivity of Aluminum Nitride

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窒化アルミニウムの熱伝導度

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The thermal conductivity of aluminum nitride samples was measured from 1250°C to 1630°C on electron beam method^{1)~3)}.

The thermal diffusivity κ was calculated from measured phase difference of the temperature fluctuations between two faces of the slab, and

according to Wheeler's equation of first approximation,

$$\kappa = \frac{2.9 l^2 \omega}{2 \pi \Delta \theta} \quad \dots \dots \dots (1)$$

where ω is the modulation frequency of electron beam, l is the thickness of the slab and $\Delta \theta$ is