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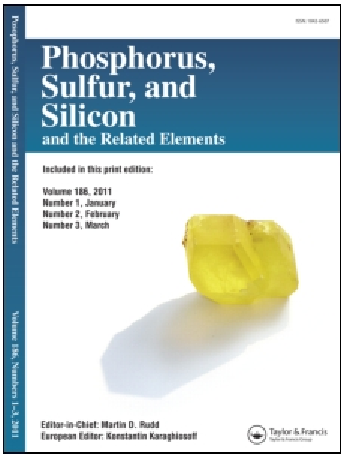

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EFFECT OF ULTRASONIC WAVE IRRADIATION ON THE ELECTRICAL CONDUCTIVITY OF THE UNDOPED AND DOPED MOLTEN SULFUR WITH SOME INORGANIC MATERIALS

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The electrical conductivity and the activation energy of conduction were measured up to 340°C for undoped sulfur melts and doped sulfur melts with 5 mol% LiF, 5 mol% NaF, 13.4 mol% NaCl, 1 and 5 mol% KCl, 5 mol% NaBr, 5 mol% Se, 5 mol% NaBr + 5 mol% Se, 5 mol% Na_2SO_4*, 5 and 10 mol% Na. The effect of irradiation of ultrasonic waves of 20 kHz was studied. The electrical conductivity generally increased with increasing temperature above 200°C with a variety of temperature dependencies. The addition of NaBr, Se, LiF,* Na_2SO_4*, NaBr + Se, and KCl caused an increase in conductivity in this order by max. two orders of magnitude. For sulfur melts doped with 5 and 10 mol% Na, a wide jump of electrical conductivity occurred at 245°C, giving exceedingly high electrical conductivities above this temperature. By the irradiation of ultrasonic waves, the electrical conductivity was raised together with the formation of jump for Se, NaBr + Se, 5 mol% Na, LiF,* Na_2SO_4*, NaBr, and NaF. The largest irradiation effect was observed for 10 mol% Na, for which the jump temperature was 190°C. The activation energies classified into low, medium, and high groups were obtained. The assumption of microscopic temperature was proposed, which was found to explain the electrical conductivity of irradiated melts.*

Keywords: Sulfur melt; electrical conductivity; activation energy; ultrasonic wave; sodium polysulfide

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One of the effects of ultrasonic waves is to decompose compounds. The sonochemical decomposition has been studied by a number of researchers.[1] It is known that CCl_4 is decomposed into elemental chlorine by the application of ultrasonics.[2] Significant sonolytic decomposition of alkanes,[3] metal nitrobenzene,[4] and metal carbonyls[5] has also been reported. According to Entezari et al.,[6] although irradiation of 900 kHz ultrasound to CS_2 did not produce any noticeable change, the ultrasound of lower frequency of 20 kHz caused to decompose this compound resulting in formation of a heterogeneous mixture of black particles in a yellow solution. Such low frequency ultrasound produces more violent cavitation which leads to give higher localized temperatures and pressures at the cavitation sites.[7] The hot-spot theory of ultrasonic waves claims that the temperatures of above 5000 K and pressures higher than 500 atm are calculated to be produced in the localized hot spots.[8]

Sulfur has many allotropes. The room temperature stable α-sulfur contains S_8 molecules (cyclo-S_8) with orthorhombic crown structure. At 95.3°C, this α-S_8 transforms into monoclinic β-sulfur. The melting point of α-S_8, which is metastable above 95.3°C, is 112.8°C, while that of β-sulfur (β-S_8) is higher, viz. 119.6°C.[9] There are other forms in sulfur: They are monoclinic γ-sulfur, rhombohedral ε-sulfur having cyclo-S_6 structure, S_7, cyclo-S_{10}, cyclo-S_{12}, cyclo-S_{18}, cyclo-S_{20}, polycatena sulfur, etc.[10] On temperature rise to 159.4°C, the concentration of polymeric S_∞ in a sulfur melt very rapidly increases, which are known to cause the change in the various properties of the melt almost discontinuously. The chain length of the polymeric sulfur exceeds 2×10^5 S atoms at 180°C. This length decreases if the temperature is further raised, although the atom number still remains $\approx 10^3$ at 400°C.[10]

According to the reports on the behavior in liquid sulfur, the velocity of the ultrasonic waves decreases with increasing temperature in a range from 120°C to 300°C without any marked change at the 159.4°C transition temperature.[11,12] As for attenuation of ultrasonic waves of 5.8, 12, and 15 MHz, a slow rise beginning at 160°C was detected.[12] In the attenuation curve at 1 MHz, however, no such increase was observed to occur.[13] Instead, two small peaks emerged between 100°C and 120°C. The above discrepancies are assumed to be related with the type (structure and reactivity) of sulfur used for the measurements.

The effect of ultrasonic waves of low frequencies on sulfur melt does not seem to have been reported. However, in view of the above reports on decomposition of organic substances by ultrasonic waves, some degrees of sonolysis is expected to occur also for polymerized sulfur molecules in the melt. If the sulfur-sulfur bond in $S_\propto$ is disruptured forming smaller molecules by the irradiation of ultrasonics, the electrical conductivity of sulfur melt would be increased.

In this work, the electrical conductivity, κ, of sulfur melt was measured as a function of temperature with and without irradiation of ultrasonic waves of 20 kHz frequency. The effect of ultrasonics was studied in coupling with that of doping of various chemical materials to sulfur.

EXPERIMENTAL

Materials Used

Sublimed sulfur of analytical grade purity was purchased from Waco Pure Chemical Ind. Ltd., and was used as received. Its purity was 99.9%. The x-ray powder diffraction pattern of this sulfur is shown in Figure 1, in comparison with the α-S pattern of JCPDS No. 8-247 (orthorhombic). The crystallinity of the sulfur used is good, showing that it is almost exclusively composed of α-S.[13]

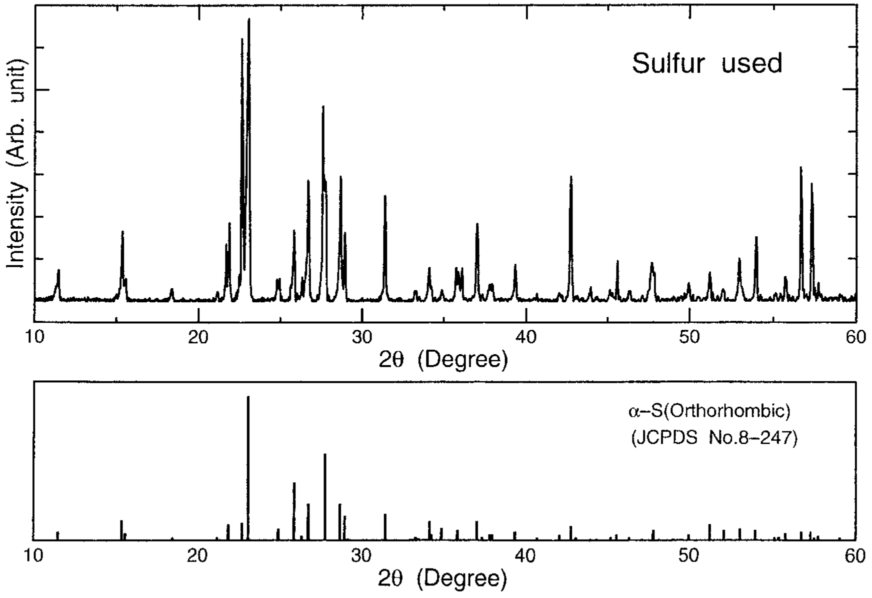

FIGURE 1 X-ray powder diffraction pattern of the sulfur used in comparison with the α-S pattern of JCPDS No. 8-247 (lower). Rigaku RAD-IC diffractometer; CuKα radiation monochromatized with curved pyrolytic graphite (40 kV, 20 mA); Slit = 0.5°–0.5°–0.05 mm–0.6 mm.

Sodium metal (purity: 99.95%) was that obtained from Nippon Soda Co., Ltd. in a form of small blocks sealed in an argon gas ampoule. The hydroxide and hydrocarbons on the metal surface were removed before use by the treatment with dehydrated ethanol and acetone in an argon glove box where the oxygen and moisture levels were maintained both below 1 ppm by circulating the gas throuth a purifier in which oxygen and moisture were removed by hot-copper and molecular shieve 5A respectively.

Selenium of 99.9% purity was obtained from Wako Pure Chemical Ind. Ltd. Guaranteed grade reagents of Na_2SO_4 (99%), LiF (99.9%), NaF (99%), NaCl (99.5%), KCl (99.9%), and NaBr (99.9%) were purchased from the same company. Nitrogen gas of 99.99% purity was supplied from Nihon Sanso Co. Ltd.

Conductivity Cell

Figure 2 shows a sketch of conductivity cell. The stainless steel can of 70 mm diameter and 80 mm long has a screw cap with a 40 mmϕ

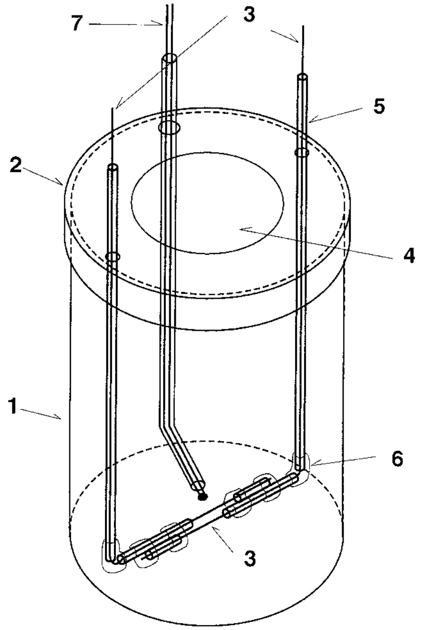

FIGURE 2 Sketch of conductivity cell. 1: Stainless steel can; 2: Stainless screw cap; 3: Mo lead wires for conductivity measurement; 4: Hole for horn tip insertion into sulfur melt; 5: Sintered Al_2O_3 tube for electric shield; 6: Sauereisen cement; 7: Thermocouple (K-type).

center hole for ultrasonic tip and three small holes near the edge. Close to the bottom of the can, was set the measuring part of electrical conductivity which consists of two parallel Mo wires of 0.5 mmϕ fixed with Sauereisen Cement. On ultrasonic experiments, the horn tip was immersed vertically into the sulfur melt, directed to the measuring part for exposure of ultrasonics. The electrical shield of the two Mo lead wires were accomplished by using sintered Al_2O_3 tube. Since the electrical conductivity of Sauereisen Cement was not so low as to certify no effect on sulfur conductivity, the cement fixed a wire to the Al_2O_3 tube was pasted not to touch to another wire as shown in Figure 2. The Mo wires in the Al_2O_3 tubes were separately led out from the two small holes drilled through the can lid. The electrical conductivity was read with an Advantest Model 8430 ultra-high resistancemeter of which the input impedance was above 10^{16} Ω. Since the conductivity did not change in a range of frequencies between 1 and 10 kHz, measurements were made using 1 kHz frequency in this work. The cell constant for electrical conductivity was obtained by measuring the resistance of 0.1 M KCl aqueous solution at room temperature. As the standard specific resistance of this solution, the reference data[14] was used after correcting the temperature.

A K-type thermocouple was inserted into the can through another small hole of the cap to measure the temperature of the sulfur near the measuring part of electrical conductivity.

Ultrasonic Equipment

The emission equipment of Nihon Seiki Co., Model US-600NCVP consists of a generator, a transducer and a horn. The generator converges the 50 Hz input frequency into 19.6 ± 0.5 kHz electric energy of maximum output 600 W. The output of the energy was controlled with V-level current and tuning dials. The transducer contains the piezoelectric element which converges the electric energy into a vibrating mechanical energy of the same frequency. The cylindrical horn is made with Inconel 300 of 36 mm diameter and 640 mm long. On experiment, the horn tip was submerged into sulfur melt in the stainless steel can. In order to be resistant against corrosion during the experiments at high temperatures above 300°C, the horn was made of Inconel.

Measuring Procedure

The weighed amount (usually about 70 g) of sulfur with or without doping materials was put in the stainless steel can, which was then placed at the center of the Pyrex reaction tube in a vertical tube furnace.

In some experiments without ultrasonics irradiation, the samples of smaller amounts of about 35 g were also used. The reaction tube was fitted to the metal adaptor of the furnace with two neoprene “O” rings. The atmosphere of the reaction tube was changed to nitrogen by flushing the gas for about 20 min. Subsequently, the electric current was passed throuth the nichrome wires of the tube furnace to raise the temperature. The furnace temperature was controlled with a Pt-13% Rh/Pt thermocouple placed outside the stainless steel can. In the case of ultrasonic wave irradiation, the horn tip was lowered to submerge into sulfur after it melted.

The amplitude of the ultrasonics was nearly linearly related with the V-level indicator value as shown in Figure 3, but it slightly levels off at higher currents. The relation may be expressed by an equation, $A = 6.25 \times 10^{-2}\ C + 2.7 \times 10^{-1}\ C^{1/2}$, where A($\mu$m) and C($\mu$A) are the amplitude and V-level current respectively.

RESULTS AND DISCUSSION

The electrical conductivity and viscosity of molten sulfur largely affect the performance of sulfur battery cells. The reduction of viscosity has been reported to be achieved by adding the substances that break the bonding chains between sulfur atoms.[15] In a review of Sudworth and Tilley,[16] varieties of materials, viz. halogens, selenium,[17] tetracyanoethylene,[18] etc. are introduced as that which could be used for this purpose.

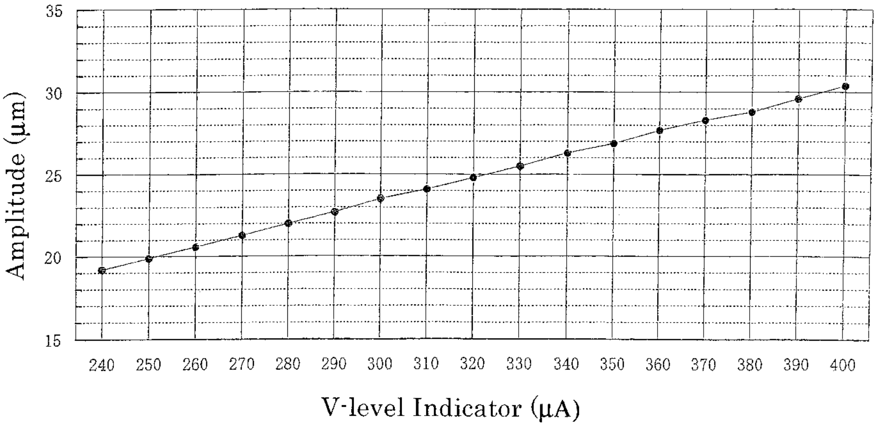

FIGURE 3 Relation between the amplitude of ultrasonic waves (μm) and V-level value (μA).

In this article, we first describe the result of the electrical conductivity measurements of undoped sulfur. Then, study is made for the effect of addtion of alkali halides such as LiF, NaF, NaCl, KCl, and NaBr to sulfur. After that, the doping effect of the other materials than alkali halides, but were thought to be possibly effective for rising the electrical conductivity, was studied. They are Se, NaBr + Se, and Na_2SO_4. Selenium has been pointed out to decrease markedly the viscosity of sulfur melt,[17] which could enhance the electrical conductivity according to the conduction theory of liquids. Lastly, sodium polysulfide was prepared by adding sodium metal slowly to the sulfur melt in a dry box filled with purified argon, and the conductivity of the mixed melt of sodium polysulfides and sulfur was measured.

An experimental run of electrical conductivity data acquisition consists of measurements in heating process and cooling process which followed immediately after heating. Repeated runs were carried out using the samples of the same composition which were either new or already used for measurements. These results give information about the heating history of the sample, which influences the electrical conductivity as possibly be associated with sluggishness for attaining equilibrium of allotropic transformation of the sulfur melt.

In the heating process experiments, the sample temperature was raised in vertical resistance tube furnace with or without irradiation of ultrasonic waves. The furnace heating rates were rather low; 1–1.3 K/min (0.017–0.022 K/sec). On the other hand, when the ultrasonic irradiation was overlapped with the furnace heating, the heating rates drastically increased to 0.2–0.8 K/sec as a result of sonic energy absorption by sulfur.

Figure 4 shows the rate of the melt temperature rise on ultrasonic irradiation to undoped sulfur melt and sulfur melts doped with 5 and 10 mol% Na metal. These samples were selected as an example showing typical behavior of the sulfur melts. The results for the sulfur melts doped with the other chemical materials used in this work were similar.

To discuss about the effect of the amplitude of ultrasonics on the heating rate, we use the experimental results for two undoped sulfur samples irradiated by ultrasonic waves of different amplitude. The circles in Figure 4 indicate the rates for undoped sulfur under the ultrasonics irradiation with a V-level value of 140 μA (amplitude 11.9 μm from the equation described in sec.2.4.) and a tuning transducer dial of 120, which will be referred to as 140/120 hereafter. The diamonds show those of 200/120 (amplitude 16.3 μm). For these two experiments there seems to be no significant difference in the rate with amplitude, showing that the transduction of ultrasonic energy into the melts has already been saturated below 140 μA. On this basis, since all ultrasonic

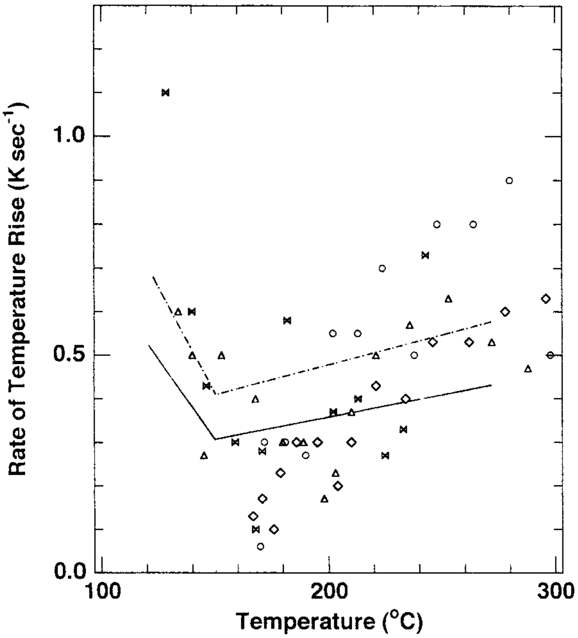

FIGURE 4 Rate of temperature rise of sulfur melt on irradiation of ultrasonic waves plotted against temperature. ○: Undoped sulfur, intensity of ultrasonics 140/120; ◇: Undoped sulfur, intensity of ultrasonics 200/120; △: 5 mol% Na doped sulfur, intensity of ultrasonics 200/120; ⋈: 10 mol% Na doped sulfur, intensity of ultrasonics 200/200.

waves used in this work had the energies higher than 140 μA, the ultrasonics of the energies between 140 and 200 μA as V-level values were regarded as the same, i.e., essentially unvaried with amplitude, with respect to the rate of temperature rise. The ▲ and ⋈ marks in the figure are the rate values for the sulfur melts with 5 and 10 mol% Na dopants respectively. Their ultrasonic levels were 200/120 and 200/200 respectively. The effect of ultrasonics on these melts is seen to be nearly the same as that on the undoped sulfur melts.

The rate data plotted in Figure 4 manifest a characteristic trend that the rate of the temperature rise decreases at first with increasing temperature below 150°C or 160°C, whereas it increases above that temperature. This behavior could be explained as related with the change of heat capacity. The heat capacity of sulfur melt, c_p , gradually increases as the temperature increases from 115°C (31.79 J K^{-1} mol^{-1}) to 150°C (34.73 JK^{-1} mol^{-1}). It discontinuously jumps into 48.41 J K^{-1} mol^{-1} at the latter temperature, above which c_p decreases with increasing temperature up to 402°C (32.92 J K^{-1} mol^{-1}).[19,20] Note that the polymerization temperature of sulfur is 150°C in the above thermodynamic data which differs from 159.4°C of Meyer.[10] The solid and broken lines in Figure 4 show the rates calculated by using the literature c_p values on the assumption that the transmitted ultrasonic energies into the melts are 15 and 20 W respectively. These calculated lines are seen to represent fairly well the change of the rate with temperature, though the slopes at temperatures above 150°C are somewhat lower. In the above cases, the absorbed ultrasonic energy was thought to be unchanged with temperature. But if it is assumed that highly polymerized sulfur melt absorbs the sonic energy to a smaller extent, the rate of temperature rise would be more increased at higher temperatures than 150–160°C due to the decomposition of the polymers, resulting in better agreement with the experimental data.

The electrical conductivity measurement in the cooling process was carried out for the sample which is freely cooled after the current supply to the furnace for the heating process measurement was just stopped. In the case of the ultrasonic experients, irradiation was stopped simultaneously. The cooling rates of the samples after heated to near 300°C were 0.1–0.13 K/sec and 0.25–0.3 K/sec (with ultrasonics irradiation when heating) in the early stage of cooling. The reason of higher rates of the latter would be that that temperature of the melts under ultrasonic irradiation was significantly higher than those of the stainless steel can and Pyrex reaction tube near the melts because the ultrasonic wave quickly heated only the melts. When the sample was cooled to as low as ca. 200°C, the rates were lowered to 0.05–0.07 K/sec. These cooling rates were the same for the unirradiated and irradiated samples.

UNDOPED SULFUR

Figure 5 shows the electrical conductivity, κ, of undoped sulfur. The open and filled marks in the figure indicate the conductivities measured in the heating and cooling processes respectively. For comparison, the change of electrical conductivities retrieved from the article by Cleaver et al.,[21] is shown lower right of the figure as a bold solid curve. This curve is lower than the present values by more than two orders of magnitude. The most possible explanation for this difference is to ascribe it to the impurities migrated in the sulfur. It is generally considered that the electrical conductivity is increased by the presence of a small amount of impurity. Fehér et al.[22] have measured the electrical conductivity of sulfur melts after purified them by various techniques.[23–26] The conductivities reported by Fehér et al.[22] were in fact very low in a range

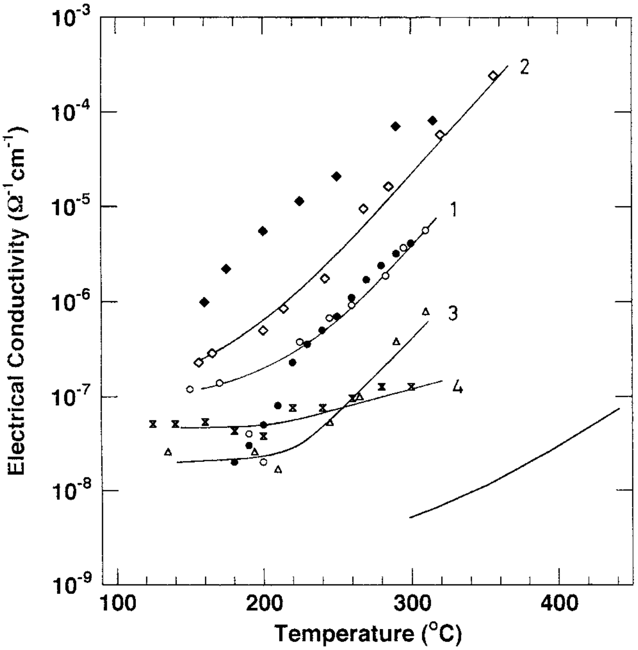

FIGURE 5 Electrical conductivity of undoped sulfur (no ultrasonic irradiation). ○, ●: Experiment 1 using new sample; ◇, ◆: Experiment 2 using new sample; △: Experiment 3 using once heated sample; ⧗: Experiment 4 using twice heated sample; Bold solid line shows the reference curve.[21] Open and filled marks show the conductivities in the heating and cooling processes, respectively.

from 1×10^{-13} to 2.3×10^{-12} $\Omega^{-1}cm^{-1}$ at temperatures between 130°C and 180°C. These values are still much lower than those of Cleaver et al.[21] At this point, the question arises as to what impurity could enhance the electrical conductivity of sulfur melt so largely. In the same article by Fehér et al.,[22] they report that doping of 0.02% benzil, 0.015% bromine, or 0.2% bromine is in effective for enhancing the κ values. The conductivities remained as low as 10^{-13}–10^{-10} $\Omega^{-1}cm^{-1}$ for these melts in the above temperature range. These results indicate that the materials which cause to increase the electrical conductivity are rather restricted. It becomes interesting to search for such materials, on the contrary.

Experiments 1 and 2 in Figure 5 were made using new samples. Some discrepancies in the conductivity are seen for these two curves measured under nearly the same conditions. That is to say, the electrical conductivity of sulfur melt has the properties which are very condition sensitive, sometimes resulting in change of the κ values in orders of magnitude.

The slope of curves 1 and 2 are close at temperatures above 220°C. Curve 3 is for the sample which was once heated and cooled in experiment 2. This curve is lowered below curve1, but three curves 1, 2, and 3 are alike in shape. Curve 4 shows the electrical conductivity of the sample which was used for experiment 3. For this curve, the slope above 220°C is considerably gentler, but the conductivity in the low temperature region of 130–250°C is somewhat higher than that of experiment 3. The melt clearly changes its transport properties during the repeated cycles of heating and cooling measurements.

The electrical conductivity measured in the cooling process is almost the same as that in the heating process above 220°C for experiment 1. However, it decreases rapidly with decreasing temperature below that temperature, bringing about a considerable difference in κ from that of the heating process when the temperature is lowered to 180°C. The cooling process conductivity of experiment 2 is, on the other hand, higher than the κ value in the heating process at all temperatures studied.

Figure 6 show the electrical conductivity versus temperature curves for irradiated sulfur with ultrasonic waves (heating process). A large difference from unirradiated sulfur (Figure 5) is observed in the shape of the curves although the conductivities at high temperatures near 300°C do not differ largely. Namely, curves 5, 6, and 7 in Figure 6 increase very steeply when the temperature is raised to about 160°C, and after this jump they gradually level off. New samples were used for experiments 5, 6, and 7. The sample of curve 8 is that which was once used for heating (without ultrasonics) and cooling experiment. The electrical conductivity of curve 8 is markedly low, suggesting the large effect of heating history of the sample to the electrical conductivity when the sample is irradaited with ultrasonics. This curve also shows the rapid increase of κ, but the jump temperature is shifted to a higher temperature of 220°C.

The electrical conductivity for the cooling process is much lower than that for the heating process in all experiments 5, 6, and 7. This is typical of the electrical conductivities when ultrasonic wave is applied in the heating process as can be seen also for doped sulfur melts. During the irradiation of ultrasonic waves, the sulfur molecules are in a state of higher localized temperatures and pressures at the cavitation sites as explained by the theories of ultrasound of low frequencies.[7,8] As soon as the irradiation is stopped, the excited molten sulfur returns to the ordinary state, giving the electrical conductivities of the cooling process which are lower than those of the heating process.

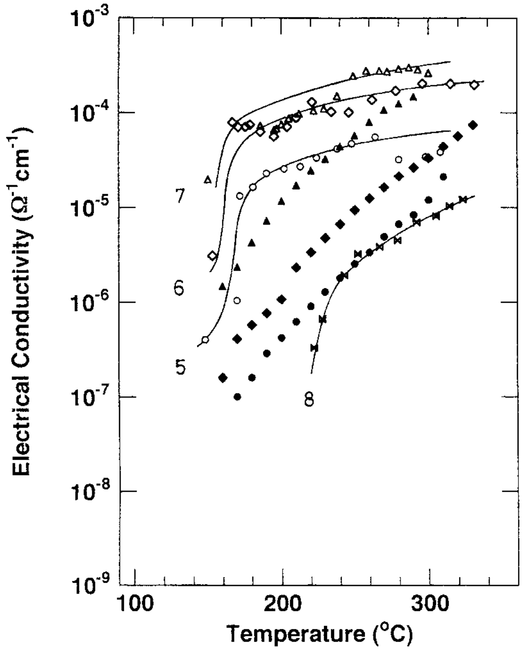

FIGURE 6 Electrical conductivity of undoped sulfur (ultrasonic irradiation). ○, ●: Experiment 5 using new sample; ◇, ◆: Experiment 6 using new sample; △, ▲: Experiment 7 using new sample; ⋈: Experiment 8 using once heated sample. Open and filled marks show the conductivities in the heating and cooling processes, respectively.

On the other hand, when the sample is heated without ultrasonic irradiation (Figure 5), the molten sulfur is nearly in equilibrium with the indicated temperature. But when the temperature is turned into decrease, the cooling rate is higher than the heating rate by 5–8 times in the initial stage and it is still higher by about three times at 200°C, which is considered to be the reason for higher electrical conductivities obtained in the cooling process experiments. A supporting evidence is that the electrical conductivities in the cooling processes are in the same range of 10^{-7} – 10^{-5} Ω^{-1}cm^{-1} at 200°C both for Figures 5 and 6. As already described, the cooling rate is settled to the same rate at this temperature both for unirradiated and irradiated samples.

Plots of log κ against 10^3/T for the experiments of Figure 5, which were carried out without ultrasonic waves, are shown in Figure 7. The experimental points for experiments 1, 2, and 3 below $10^3/T \approx 2.0$ (above ~230°C) give the straight lines of virtually the same slope yielding an activation energy of conduction, 98.9 kJ/mol. For experiment 4, a

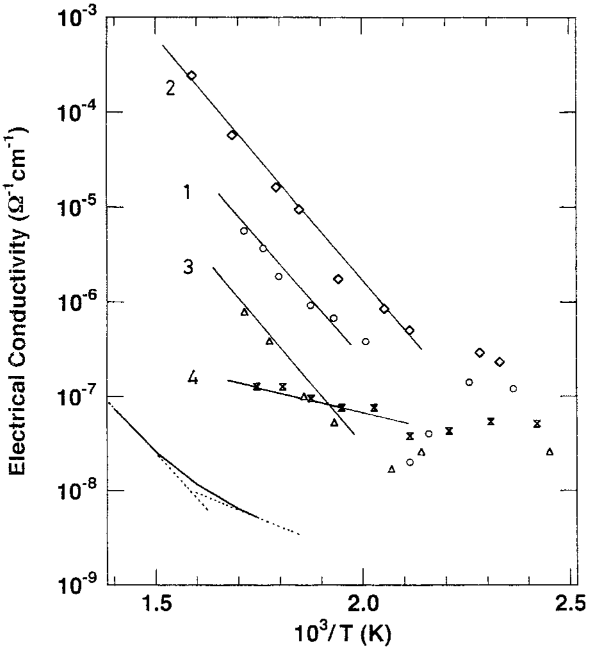

FIGURE 7 Logarithm of electrical conductivity plotted against 10^3/T for undoped sulfur (no ultrasonic irradiation, heating process). ○: Experiment 1 using new sample; ◇: Experiment 2 using new sample; △: Experiment 3 using once heated sample; ⧗: Experiment 4 using twice heated sample. Lines 1, 2, and 3: Activation energy 98.9 kJ/mol; Line 4: Activation energy 20.3 kJ/mol. Bold solid line shows the reference curve;[21] Dotted straight lines were drawn for two extreme cases: Activation energies ~34 and ~94 kJ/mol.

straight line was also obtained, but the Arrhenius energy was much lower, viz. 20.3 kJ/mol. The conductivity of Cleaver et al.[21] shows a curvature which gives rise to at least two different activation energies. The slope at the lower temperature limit gives ~34 kJ/mol. This value is not so apart from the that of experiment 4. The slope at the higher temperature limit gives ~95 kJ/mol, which is close to the activation energy obtained for experiments 1, 2, and 3.

Figure 8 shows log κ vs. 10^3/T plots for the samples irradiated with ultrasonic waves. Lower activation energies were obtained for these samples. The energies for experiments 5, 6, and 7 (new samples) were between 3.6 and 28.1 kJ/mol above 180°C. On the other hand, the activation energy obtained for experiment 8, which was carried out using once heated sample, was higher (59.0 kJ/mol).

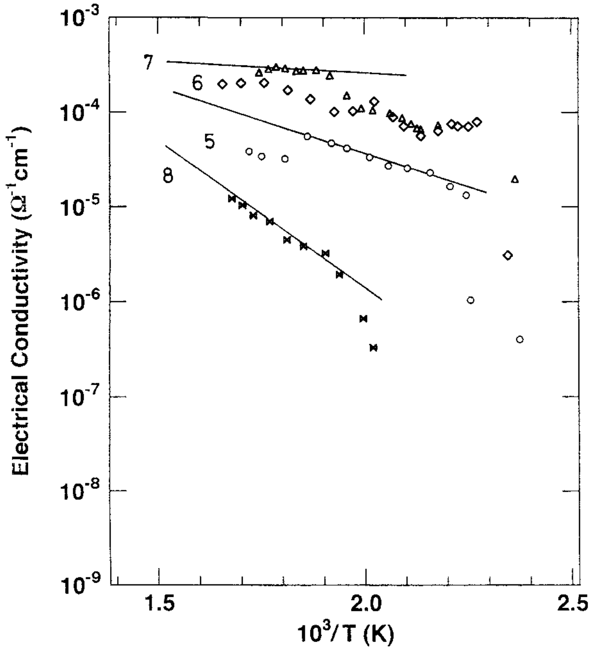

FIGURE 8 Logarithm of electrical conductivity plotted against 10^3/T for undoped sulfur (ultrasonic irradiation, heating process). ○: Experiment 5 using new sample; ◇: Experiment 6 using new sample; △: Experiment 7 using new sample; ⋈: Experiment 8 using once heated sample. Activation energies for experiments 5, 6, and 7: Between 3.6 and 28.1 kJ/mol; Activation energy for experiment 8: 59.0 kJ/mol.

Several Selected Dopants

Alkali Metal Fluorides (LiF and NaF)

The possibility of increase in electrical conductivity is expected by doping alkali metal halides (MX) on account of their strong tendency to dissociate into M^+ and X^- ions in sulfur melts. The effect of halogens has already been pointed out.[16]

Figure 9 shows the electrical conductivity of sulfur melt doped with 5 mol% LiF. Curve 1 indicates the conductivity change in the heating process using a new sample without ultrasonic waves, which is close to curve 1 of Figure 5 for undoped sulfur (without ultrasonic irradiation) above 180°C. There is a difference, however, that the LiF doped sulfur yields a shallow minimum of conductivity at ~160°C. This temperature is corresponding to the polymerization temperature of sulfur.

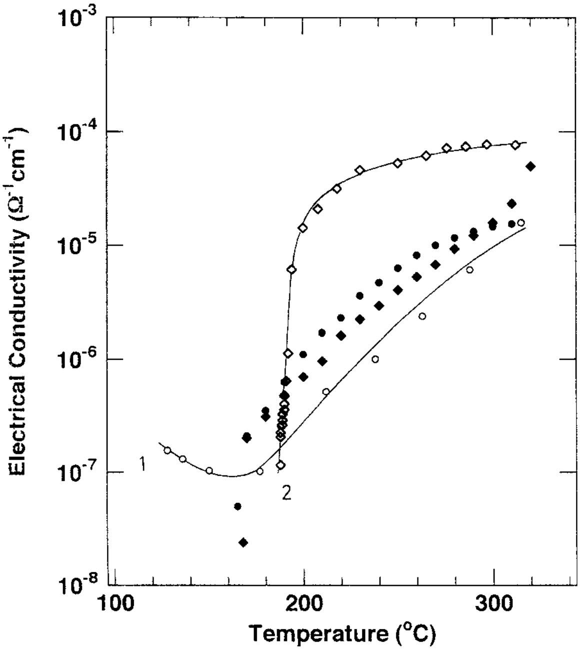

FIGURE 9 Electrical conductivity of 5 mol% LiF doped sulfur as a function of temperature. ○, ●: Experiment 1 using new sample without ultrasonic irradiation; ◇, ◆: Experiment 2 using once heated sample. Ultrasonic irradiation was carried out in the heating process. Open and filled marks show the heating and cooling processes, respectively.

The change of the electrical conductivity in the case of ultrasonics irradiation is shown by curve 2 of Figure 9. This is for the heating process experiment using once heated sample. The conductivity is shown to increase almost vertically from 10^{-7} to 10^{-4} Ω^{-1}cm^{-1} at 190°C. Such a jump has also been observed for undoped sulfur melts irradiated with ultrasonics (Figure 6), where the jump temperature was lower around 160°C.

As for the difference in the conductivities for the cooling and heating processes of experiments 1 and 2 of 5 mol% LiF doped sulfur, the same behavior was as undoped sulfur was seen.

The electrical conductivities plotted against temperature for sulfur melt doped with 5 mol% NaF are given in Figure 10. Curves 1 and 2 in the figure show the conductivity change in the heating process experiments without and with ultrasonic waves using new and once heated samples, respectively. These curves are in close resemblance to the curves of Figure 9. The effect of NaF on the electrical conductivity

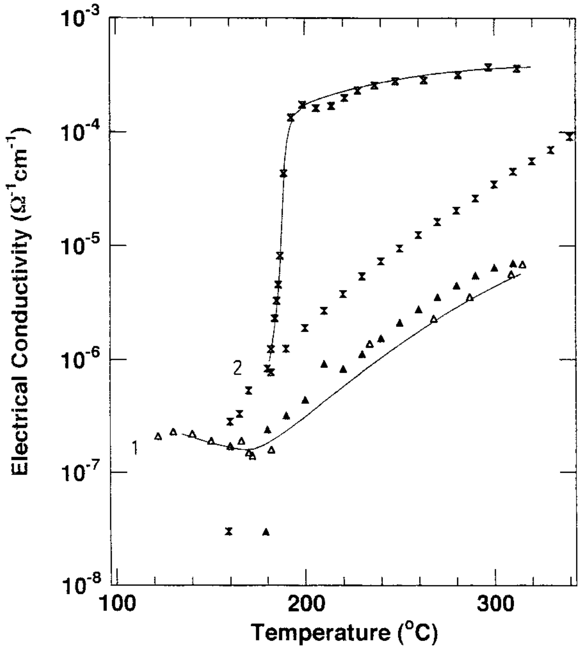

FIGURE 10 Electrical conductivity of 5 mol% NaF doped sulfur as a function of temperature. △, ▲: Experiment 1 using new sample without ultrasonic irradiation; ⧖, ⧗: Experiment 2 using once heated sample. Ultrasonic irradiation was carried out in the heating process. Open and filled marks show the heating and cooling processes, respectively.

is basically the same as that of LiF; there is no significant difference between Li and Na. The κ jump for irradiated melt (Figure 10, curve 2) occurs at 180–190°C for NaF. The Arrhenius plot of electrical conductivity is shown in Figure 11. For both the LiF and NaF doped sulfur melts, the activation energy without ultrasonic waves was obtained to be 75.0 kJ/mol from the slope of line 1 above 200°C. When the ultrasonic irradiation was made, the straight lines 2 and 3 were obtained above 200°C for LiF and NaF respectively. The slopes of these lines were nearly the same, giving an activation energy of 11.1 kJ/mol. This value is much lower than that for the unirradiated samples, and it is also in agreement with those of irraidated undoped sulfur.

Alkali Metal Chlorides (NaCl and KCl)

In Figure 12, is shown the electrical conductivity of sulfur melts doped with either NaCl or KCl. The concentration of NaCl in

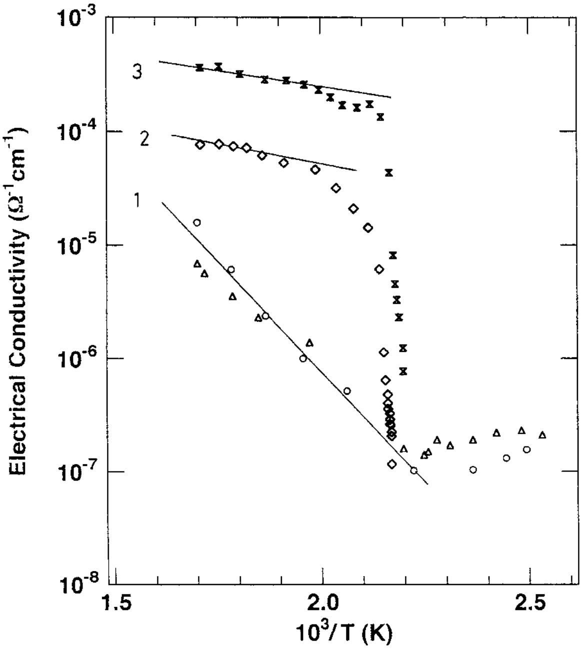

FIGURE 11 Logarithm of electrical conductivity of 5 mol% LiF doped sulfur and 5 mol% NaF doped sulfur plotted against 10^3/T. ○: New sample of 5 mol% LiF doped sulfur without ultrasonic irradiation; ◇: Once heated sample of 5 mol% LiF doped sulfur with ultrasonic irradiation; △: New sample of 5 mol% NaF doped sulfur without ultrasonic irradiation; ⧗: Once heated sample of 5 mol% NaF doped sulfur with ultrasonic irradiation. Line 1: Activation energy 75.0 kJ/mol; Lines 2 and 3: Activation energy 11.1 kJ/mol.

sulfur is 13.4 mol%, and those of KCl are 1 and 5 mol%. The right low open and filled circles in the figure show the κ values for unirradiated NaCl doped sulfur in the heating and cooling processes respectively. No increase from undoped sulfur is observed in the electrical conductivity by the addition of NaCl. The diamonds are for ultrasonic irradiation experements. The heating process electrical conductivity (open diamonds) does not give any jump in this case dissimilar to the sulfur melts added with LiF and NaF. The effect of ultrasonic irradiation cannot be observed here. The variation of κ with temperature for these unirradiated and irradiated experiments is shown together as curve 1.

The conductivities of the sulfur melt doped with KCl measured in the heating processes are given by curves 2, 3, and 4 in Figure 12. Curve 2

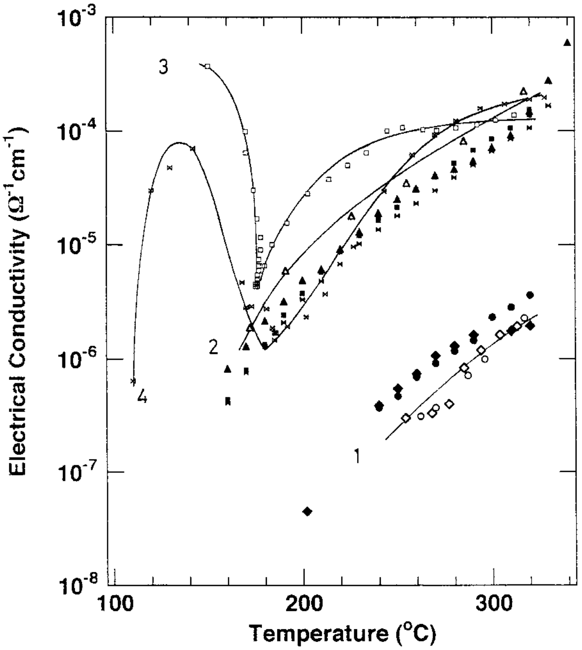

FIGURE 12 Electrical conductivity as a function of temperature for NaCl doped sulfur and KCl doped sulfur. o, ●: 13.4 mol% NaCl doped sulfur, new sample, without ultrasonic irradiation; ◇, ◆: 13.4 mol% NaCl doped sulfur, once heated sample, with ultrasonic irradiation; △, ▲: 5 mol% KCl doped sulfur, new sample, without ultrasonic irradiation; □, ■: 5 mol% KCl doped sulfur, once heated sample, with ultrasonic irradiation; ⋈, ⧓: 1 mol% KCl doped sulfur, new sample, with ultrasonic irradiation. Curve 1: Conductivity in heating process for 13.4 mol% NaCl doped sulfur; Curve 2: Conductivity in heating process for 5 mol% KCl doped sulfur, without ultrasonic irradiation; Curve 3: Conductivity in heating process for 5 mol% KCl doped sulfur, with ultrasonic irradiation; Curve 4: Conductivity in heating procees for 1 mol% KCl doped sulfur, with ultrasonic irradiation. Open and filled marks show the hating and cooling processes, respectively.

is for 5 mol% KCl doped sulfur without ultrasonics irradiation. Curves 3 and 4 are for the KCl concentrations of 5 and 1 mol%, respectively, obtained under ultrasonics irradiation. Curves 2, 3, and 4 are close in the temperature range above ~200°C. That is to say, the unirradiated KCl (5 mol%) doped melt gives the electrical conductivities higher than those of the undoped sulfur melts by about two orders and more than one order of magnitude at 200°C and 300°C respectively. The electrical conductivity of irradiated melts (1 mol% KCl and 5 mol% KCl) is not heightened from that of irradiated undoped sulfur melts in the temperature range 200–300°C.

Irradiation of ultrasonic waves does not increase the electical conductivity for KCl doped melts. However, it causes to produce a distinct minimum (curves 3 and 4 in Figure 12) at 175–180°C. When the measurement was started from a lower temperature of 110°C, a broad maximum at ~135°C could also be observed (curve 4). The κ values for experiments of 3 and 4 in the cooling process were lower than those in the heating process.

The electrical conductivities were plotted against $10^3/T$ in Figure 13. The lower and upper straight lines give the $1/T$ dependence of κ for the melts doped with NaCl and KCl in the high temperature range, respectively. The slopes of these lines are virtually the same above 200°C, yielding a high activation energy of 105.2 kJ/mol.

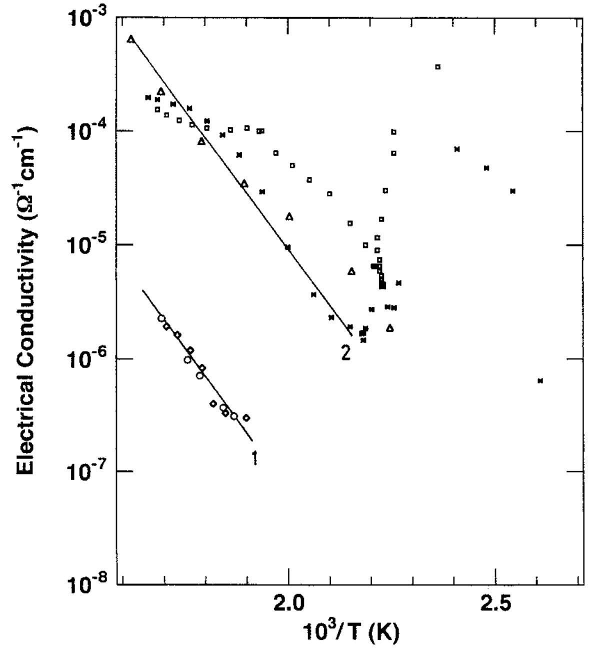

FIGURE 13 Logarithm of electrical conductivity plotted against $10^3/T$ for NaCl doped sulfur and KCl doped sulfur. ○: New sample of 13.4 mol% NaCl doped sulfur without ultrasonic irradiation; ◇: Once heated sample of 13.4 mol% NaCl doped sulfur with ultrasonic irradiation; △: New sample of 5 mol% KCl doped sulfur without ultrasonic irradiation; □: Once heated sample of 5 mol% KCl doped sulfur with ultrasonic irradiation; ⋈: New sample of 1 mol% KCl doped sulfur with ultrasonic irradiation.

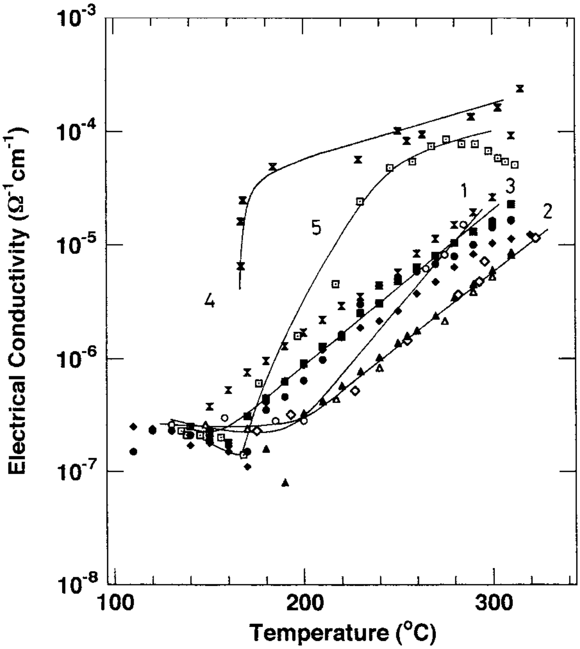

FIGURE 14 Electrical conductivity of 5 mol% NaBr doped sulfur as a function of temperature. ○, ●: New sample without ultrasonic irradiation; △, ▲: New sample without ultrasonic irradiation; ◇, ♦: Once heated sample without ultrasonic irradiation; ⧖, ⧗: Once heated sample with ultrasonic irradiation in the heating process; ⊡, ⊠: Twice heated sample with ultrasonic irradiation in the heating process; Curve 1 for ○; Curve 2 for △and ◇; Curve 3 for ⊠; Curve 4 for ⧗; Curve 5 for ⊡. Open marks and ⊡ show the heating process data, and filled marks and show the cooling process data.

Alkali Metal Bromide (NaBr)

The electrical conductivity as a function of temperature for sulfur melt with the addition of 5 mol% NaBr is shown in Figure 14. Here, curves 1 and 2 indicate the change of the conductivity in the heating process experiments without ultrasonics irradiation. Curve 1 is for a new sample. Since the two heating process measurements for a new sample (△) and a sample once heated (◇) gave the close κ values, their change was represented by one curve (curve 2). For the melts of this dopant, the difference of heating history of the sample (new and once heated samples) exersts only a small effect on the κ values. The addition of NaBr causes an increase in the electrical conductivity but to a small degree (about half of one order of magnitude) at temperatures 200–300°C. There is a possibility that the increase is in the scattering of measured values. The conductivity almost does not change with temperature below 200°C. Figure 14 also shows that the electrical conductivity in the cooling process is not so apart from that in the heating process unless ultrasonic irradiation is made.

Curves 4 and 5 in Figure 14 show the heating process conductivity when the sulfur melt was irradiated with ultrasonic waves. The samples were once heated and twice heated sulfur for curves 4 and 5 respectively. Curve 4 is close to curves 5, 6, and 7 of Figure 6 for irradiated undoped sulfur. The vertical change in curve 4 appears at 165°C. For curve 5, the rate of this increase is not so high, but the steep conductivity increase starts from the same temperature. The difference in the shape of curve 5 from curve 4 is to be ascribed to the heating history of the samples. The electrical conductivity of irradiated sulfur doped with NaBr is essentially unvaried from that of irradiated undoped sulfur at 200–300°C. Curve 3 shows the conductivity change in the cooling process of this sample. This curve is much lower than curve 5, in agreement with the results for the irradiated undoped sulfur, LiF, and NaF doped sulfur melts.

Figure 15 shows the electrical conductivity change as a function of $10^3/T$. The region of the straight change of the conductivity is not so clear except for the experimental points which comprise curve 2 in Figure 14. However, the obtained three lines in Figure 15 show nearly the same slopes which yield 84.8 kJ/mol as activation energy.

Se

The addition of Se has been reported to reduce the viscosity of sulfur melt.[17] Since it is generally accepted that the ion mobility in liquids is heightened by the lowering of viscosity, the electrical conductivity of sulfur melt is expected to be increased if Se is doped.

The electrical conductivity of the sulfur melt doped with 5 mol% Se is shown in Figure 16. Curves 1 and 2 are for the heating process experiments using new and once heated samples, respectively, without ultrasonics irradiation. No significant change in the electrical conductivity is seen to be take place by sample history. The electrical conductivity shown by these curves increases with increasing temperature with a higher slope below 180°C but the slope becomes much gentler above 200°C. As a result, the electrical conductivity of unirradiated sulfur melts doped with Se becomes higher than that of undoped sulfur by more than one order of magnitude at 200°C, and it is nearly the same as that of undoped sulfur at 300°C. The higher slope in the lower temperature range may be related with the decrease of viscosity caused by the addition of Se.

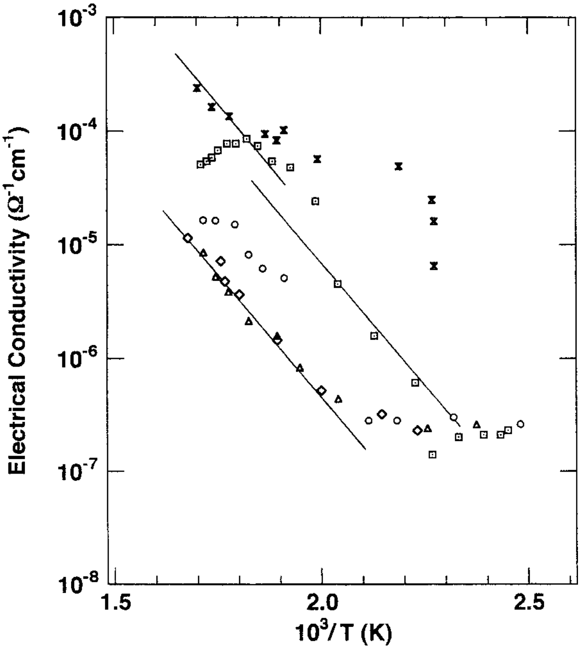

FIGURE 15 Logarithm of electrical conductivity plotted against 10^3/T for 5 mol% NaBr doped sulfur. ○: New sample without ultrasonic irradiation; △: New sample without ultrasonic irradiation; ◇: Once heated sample without ultrasonic irradiation; ⧗: Once heated sample with ultrasonic irradiation; ⊡: Twice heated sample with ultrasonic irradiation.

Curve 3 shows the change of κ measured under ultrasonics irradiation using a twice heated sample. The conductivity jump appears at 160°C which is the same as that for irradiated undoped sulfur (new samples). There is, however, a difference that the jump width is narrower. The electrical conductivity is not clearly increased from that of undoped sulfur by the addition of Se for the melt irradiated with ultrasonics. If the reduction of viscosity of the melts does not bring about the conductivity increase, a possibility may be postulated that a significant proportion of electronic conduction exists and contributes to conduction in addition to ionic conduction. It should be noted as a characteristic feature of the melts doped with Se that the heating history of the sample does cause evolution of large change in the electrical conductivity, in contrast to the other dopants.

As usual, the electrical conductivity measured in the cooling process after ultrasonic heating is much lower than that in

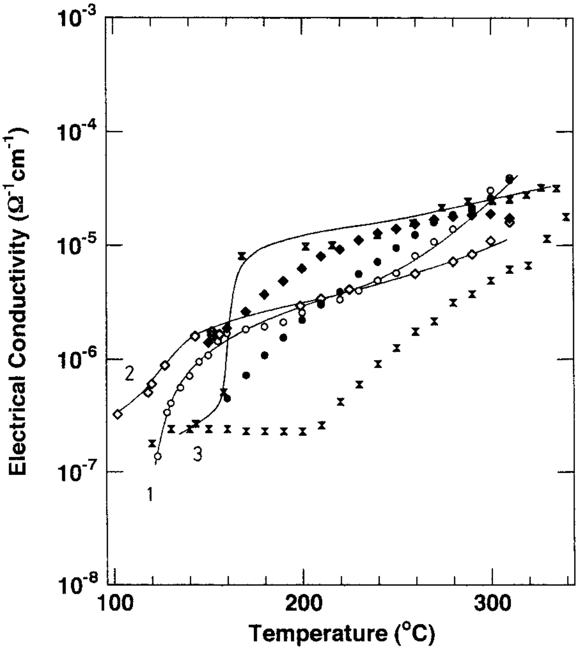

FIGURE 16 Electrical conductivity of 5 mol% Se doped sulfur as a function of temperature. ○, ●: Experiment 1 using new sample without ultrasonic irradiation; ◇, ◆: Experiment 2 using once heated sample without ultrasonic irradiation; ⌶, ⌶: Experiment 3 using twice heated sample. Ultrasonic irradiation was carried out in the heating process. Open and filled marks show the hating and cooling processes, respectively.

the heating process under ultrasonic irradiation. For the samples heated without ultrasonics irradiation, the conductivity in the cooling process measurements is closer to that in the heating process measurements.

In Figure 17, the electrical conductivities for unirradiated experiments are plotted against $10^3/T$. There are three regions of straight lines in the 1/T dependence: Below 150°C, 150–230°C and above 230°C. The activation energy in the region below 150°C is calculated to be 83.5 kJ/mol, whereas the activation energy in the second region (150–230°C) is as low as 15.2 kJ/mol. The energy in the third region above 230°C is again 83.5 kJ/mol. The conduction mechanism for the first and third regions is assumed to be the same. The activation energy for the melts irradiated with ultrasonics (15.2 kJ/mol at >170°C) is the same as the lowest of the above energies.

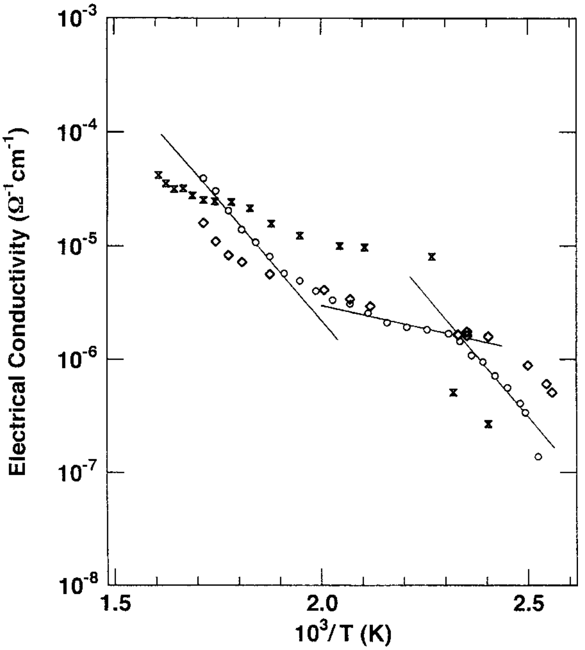

FIGURE 17 Logarithm of electrical conductivity plotted against 10^3/T for 5 mol% Se doped sulfur. ○: New sample without ultrasonic irradiation; ◇: Once heated sample without ultrasonic irradiation; ⧗: Twice heated sample with ultrasonic irradiation.

NaBr + Se

To our knowledge, no reports have been published regarding the synergistic effect of doping on the electrical conductivity of sulfur. Here, the combination of NaBr and Se was selected rather arbitrarily, and the electrical conductivity of doped sulfur was studied. The concentrations of added NaBr and Se were both 5 mol% in sulfur.

The variation of electrical conductivity is shown in Figure 18, where curves 1 and 2 indicate the κ values for the heating process experiments using new and once heated samples, respectively, without ultrasonic wave irradiation. Curve 1 has a feature significantly differed from curve 2 at temperatures below 200°C. It shows a minimum which is alike to those observed for LiF doped sulfur (Figure 9) and NaF doped sulfur (Figure 10) but is not seen for undoped sulfur. On the other hand, the electrical conductivity of curve 2 increases steadily with increasing temperature from 120°C to 320°C. Curves 1 and 2 are close above 240°C. The discrepancy in the two curves should be ascribed to the heating history of the samples. The unirradiated sulfur melts doped with

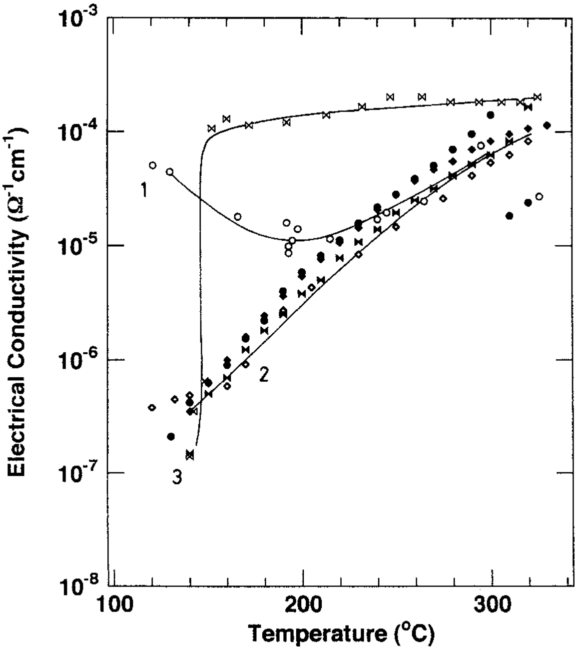

FIGURE 18 Electrical conductivity of NaBr (5 mol%) and Se (5 mol%) together doped sulfur as a function of temperature. ○, ●: Experiment 1 using new sample without ultrasonic irradiation; ◇, ◆: Experiment 2 using once heated sample without ultrasonic irradiation; ⋈, ⧗: Experiment 3 using twice heated sample. Ultrasonic irradiation was carried out in the heating process. Open and filled marks show the hating and cooling processes respectively.

NaBr + Se exhibit the electrical conductivity to some extent higher than the unirradiated undoped sulfur at temperatures 200–300°C. The enhancement is from one to one-half order of magnitude.

Curve 3 shows the conductivity change under ultrasonics irradiation measured using twice heated sample. The curve shows the conductivity jump at 145°C with a large jump width from 10^{-7} to 10^{-4} Ω^{-1} cm^{-1}. The electrical conductivity of the irradiated sulfur added with NaBr and Se combination dopant remains 1–2 × 10^{-4} Ω^{-1} cm^{-1} almost unchanged with increasing temperature above the jump temperature. It is basically the same as that of irradiated undoped sulfur at 200–300°C. The unirradiated electrical conductivity is regarded to increase a little more largely by the addition of NaBr + Se compared with the case where NaBr or Se is added. For irradiated melts, however, there seems to be no significant effect caused by the NaBr + Se addition.

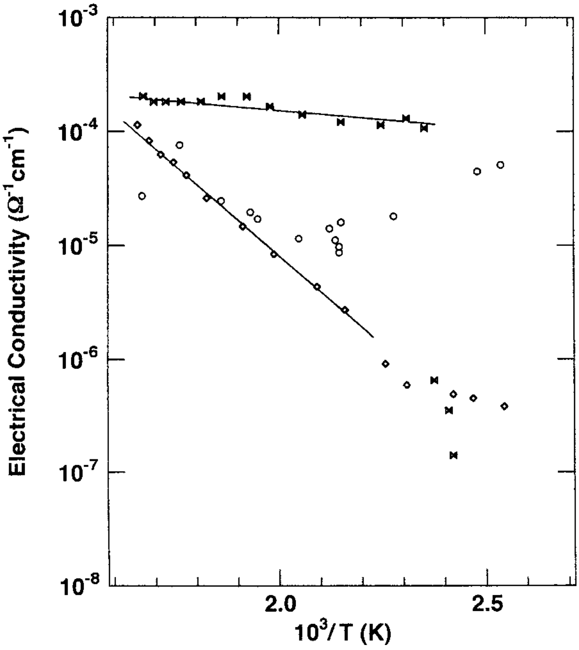

FIGURE 19 Logarithm of electrical conductivity plotted against 10^3/T for NaBr (5 mol%) and Se (5 mol%) doped sulfur. ○: New sample without ultrasonic irradiation; ◇: Once heated sample without ultrasonic irradiation; ⋈: Twice heated sample with ultrasonic irradiation.

Plots of the electrical conductivities against 10^3/T were made as shown in Figure 19. Experiment 2 gives a straight line in a fairly wide range of temperatures above ~170°C. This line yields an activation energy of 60.0 kJ/mol. In contrast, the activation energy for the irradiated sample is low, i.e. 6.0 kJ/mol above ~160°C.

Na_2SO_4

In order to have information on the behavior of anions of doped compounds in the melts with respect to electrical conductivity, the measurement of electrical conductivities of sulfur melts doped with Na_2SO_4 was carried out. Dissociation of ionic crystal Na_2SO_4 in sulfur melt is supposed to form Na^+ and SO_4^{2-}, from which the effect of replacement of X^- of sodium halides, NaX, by SO_4^{2-} could be studied. The concentration of Na_2SO_4 in sulfur here was 5 mol%.

Figure 20 shows the electrical conductivity as a function of temperature for the Na_2SO_4 doped sulfur melt added with Na_2SO_4. Curve 1

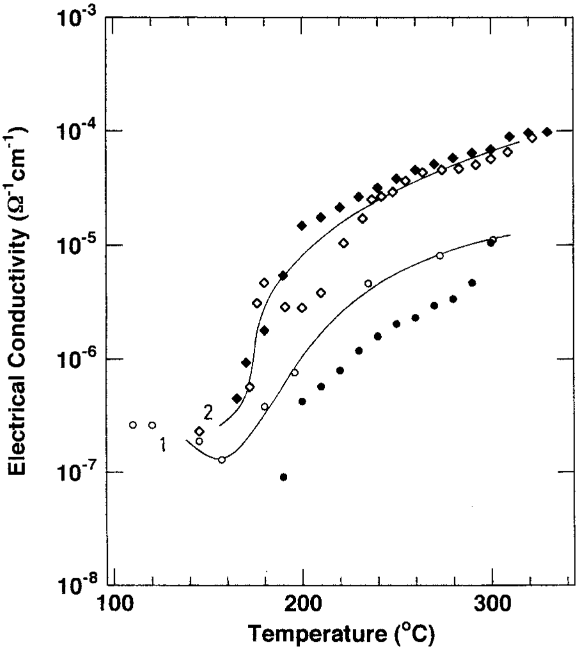

FIGURE 20 Electrical conductivity of 5 mol% Na_2SO_4 doped sulfur as a function of temperature. ○, ●: Experiment 1 using new sample without ultrasonic irradiation; ◇, ◆: Experiment 2 using once heated sample. Ultrasonic irradiation was carried out in the heating process. Open and filled marks show the hating and cooling processes respectively.

shows the change of κ in the heating process of experiment 1 which was made using new sample without ultrasonics irradiation. This curve is close in shape to those for 5 mol% NaF doped sulfur (curve 1 of Figure 10) and 5 mol% NaBr doped sulfur (curves 1 and 2 of Figure 14). The electrical conductivity of unirradiated sulfur melt doped with Na_2SO_4 is hihger than that of unirradiated undoped sulfur by more one order of magnitude at 200°C, and it is still higher though the difference is smaller at 300°C. Curve 1 of Figure 20 lowers with increasing temperature in a range of lower temperatures yielding a shallow minimum at ~160°C. This temperature is also very close to those of the LiF doped melt and NaF doped melt. Regarding the influence of anions on electrical conductivity, SO_4^{2-} ions seem to have fairly close similarities to F^- and Br^- ions.

As for the conductivites measured under ultrasonic irradiation, the conductivity shown by curve 2 for once heated sample is less similar. The jump temperature of this curve is about 180°C, which is near to

190°C for LiF doped sulfur (curve 2 of Figure 9) and NaF doped sulfur (curve 2 of Figure 10). However, the jump of the present curve is not wide. Also, the Na_2SO_4 curve increases with increasing temperature with a considerable slope after this jump, in contrast to the case of LiF and NaF doped melts, where the curves levelled off. In the melts doped with Na_2SO_4, the ultrasonic waves seem to cause to increase the electrical conductivity with reluctance. The conductivities for the cooling process measurements of experiment 2 (Figure 20) are almost the same as those for the heating process measurements where the ultrasonic waves were applied. This result may be in accordnce with the above trend seen for the heating process curve with ultrasoncis.

In the electrical conductivity vs. $10^3/T$ plots (Figure 21), the heating process measurement in experiment 2 gives a linear change at higher temperatures above 230°C. The activation energy in this range of temperature is calculated to be 33.2 kJ/mol. The activation energy for the unirradiated melt is near this value above 230°C.

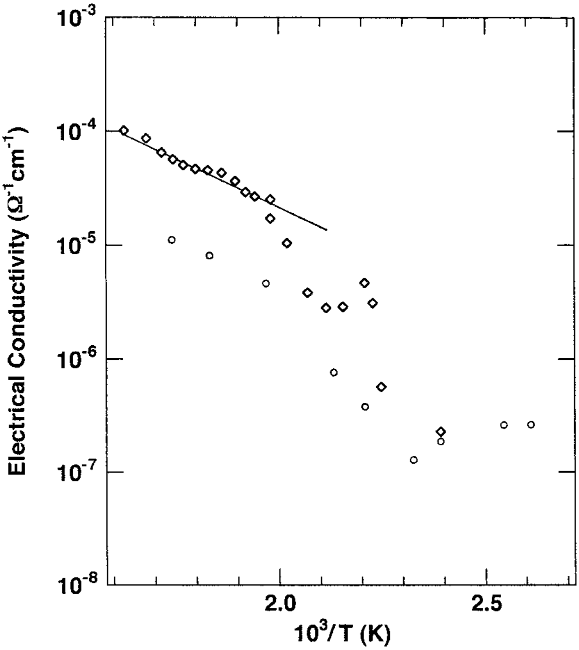

FIGURE 21 Logarithm of electrical conductivity plotted against $10^3/T$ for 5 mol% Na_2SO_4 doped sulfur. ○: New sample without ultrasonic irradiation; ◇: Once heated sample with ultrasonic irradiation.

Na Doped Sulfur

5 mol% Na Doped Sulfur

Alkali-metal polysulfides have been prapared by various methods. For the control of vigorous reaction between Na metal and sulfur, ingenious techniques to combine the elements in liquid ammonia or refluxing organic solvents such as tetrahydrofuran, dimethyl sulfoxide, etc. have been taken. The corrosion of container is greatly reduced by the use of the organic solvents.[27–29]

In this study, however, the sodium polysulfide was prepared by the direct reaction of Na metal with sulfur melt exclusively to avoid the migration of solvent in the product, since the solvent may, even if its amount is small, change electrical conductivity. The reaction was carried out by adding slowly a weighed amount of several small pieces of Na metal, which had been freshly cut from a block, into the sulfur melt heated in the stainless steel conductivity cell in an argon glove box. Because the reaction is highly exothermic, the sulfur melt was cooled to the initial temperature of 200°C by standing with occasional stirring after each piece of the Na metal was added. The conductivity measurement was started after the product was cooled to room temperature in the glove box.

Figure 22 shows the electrical conductivity as a function of temperature for the sulfur melt doped with 5 mol% Na metal. Curves 1, 2, and 3 in the figure show the change of κ in the heating processes of experiments 1, 2, and 3, respectively, which were carried out without ultrasonics irradiation. Curves 1 and 3 are for new samples, while curve 2 is for a twice heated sample. It should be noted that the temperature dependence of these three curves is very different from those of the other curves for unirradiated undoped and doped sulfur melts. The electrical conductivity is low at lower temperatures, being nearly the same as seen for sulfur melts doped with some other materials used in this work. The curves are nearly horizontal, and no anomaly is seen to exist between 150–200°C. The difference from the undoped sulfur is small. For example, the electrical conductivity is higher than that of undoped sulfur only by about one order of magnitude at 200°C. However, the present curves show a rapid increase in the electrical conductivity at 245°C. Namely, there is a conductivity jump though the melts are not irradiated with ultrasonics. The jump of this kind has not been observed for the molten sulfur with other dopants without ultrasonic irradiation. The κ values after this jump are much higher than those of the other melts. The electrical conductivity attains 10^{-3}–10^{-2} Ω^{-1} cm^{-1} at 300°C.

It is generally the case that the cooling process conductivity is higher than the heating process conductivity, but the discrepancy in Figure 22

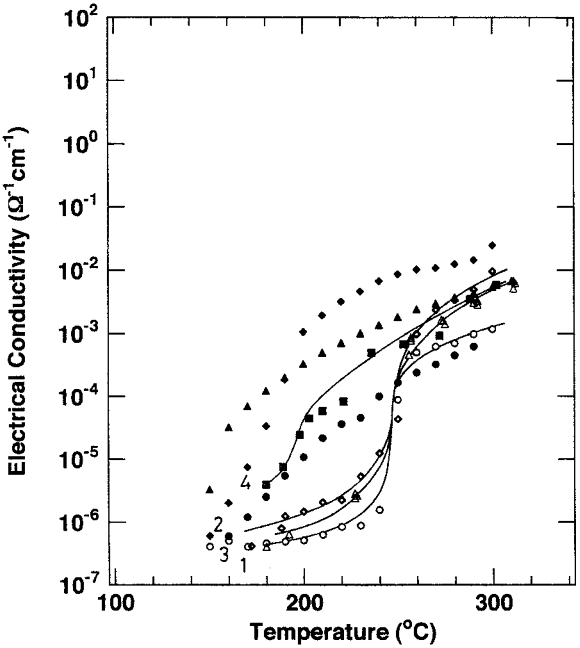

FIGURE 22 Electrical conductivity of 5 mol% Na doped sulfur as a function of temperature. ○, ●: Experiment 1 using new sample without ultrasonic irradiation; ◇, ♦: Experiment 2 using twice heated sample without ultrasonic irradiation; △, ▲: Experiment 3 using new sample without ultrasonic irradiation; ⊠: Experiment 4 (heating process experiment) using once heated sample with ultrasonic irradiation. Open and filled marks show the hating and cooling processes respectively.

between the open and filled marks looks like larger than that for the sulfur melts added with other dopants.

Curve 4 in Figure 22 depicts the heating process conductivity when the once heated sulfur melt doped with 5 mol% Na was irradiated with ultrasonic waves. Curve 4 shows a small unclear conductivity jump at 190–200°C. This temperature is close to those for the sulfur melts doped with LiF, NaF, or Na_2SO_4. In the present case, however, the jump width is too small. The electrical conductivity increases rather steeply as the temperature increases after this jump. Above around 260°C, the κ values of curve 4 are eventually the same as those of the unirradiated melts.

In Figure 23, the electrical conductivities are plotted against 10^3/T. The data of experiment 4 (with ultrasonic irradiation) and the conductivity change in the high temperature range of experiments 1, 2, and 3

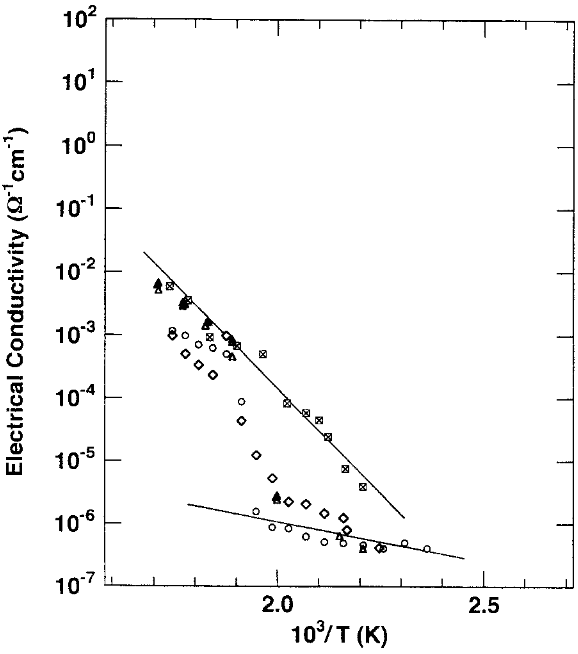

FIGURE 23 Logarithm of electrical conductivity plotted against 10^3/T for 5 mol% Na doped sulfur. ○: New sample without ultrasonic irradiation; ◇: Twice heated sample without ultrasonic irradiation; △: New sample without ultrasonic irradiation; ⊠: Once heated sample with ultrasonic irradiation.

(without ultrasonic irradiation) yield a high activation energy for the electrical conduction, i.e., 127.5 kJ/mol, while in the low temperature range of experiments 1, 2, and 3, the activation energy was as low; 25.2 kJ/mol.

10 mol% Na Doped Sulfur

The electrical conductivity of the unirrdiated sulfur melt doped with 10 mol% Na is shown in Figure 24. Curves 1, 2, and 3 in this figure are seen to be in close resemblance with curves 1, 2, and 3 of Figure 22 for the sulfur melt doped with 5 mol% Na with regard to the shape and the temperature dependence, but the κ values of the present curves of 1, 2, and 3 are higher than those of Figure 22 by about two or three orders of magnitude at high temperatures above 260°C. These high conductivities are considered to be resulted from the existence of higher concentration of sodium polysulfide ions in these sulfur melts. At lower temperatures around 150°C, however, the κ values are not so high. They

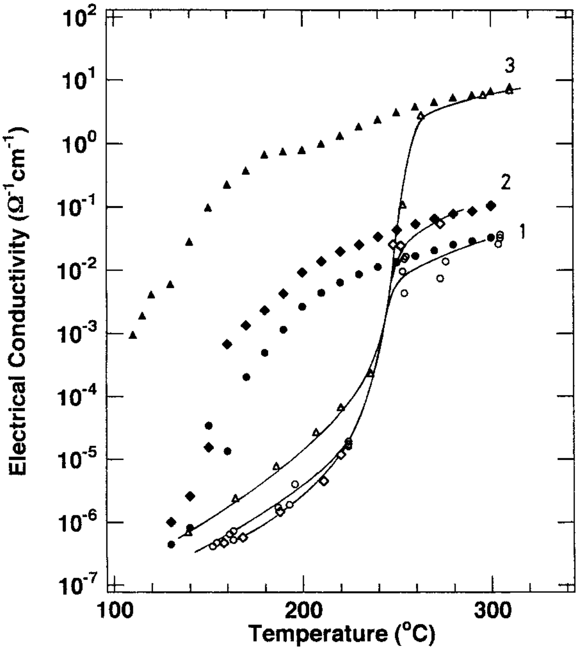

FIGURE 24 Electrical conductivity of 10 mol% Na doped sulfur as a function of temperature (no ultrasonic irradiation). ○, ●: Experiment 1 using new sample; ◇, ◆: Experiment 2 using once heated sample; △, ▲: Experiment 3 using three times heated sample. Open and filled marks show the heating and cooling processes respectively.

are in the same order of magnitude as the curves for 5 mol% Na doped sulfur.

On heating the melt, the electrical conductivity steeply increases at ~245°C (Figure 24). This jump temperature is the same as that of Figure 22 for 5 mol% Na.

The three curves (1, 2, and 3) of Figure 24 represent larger difference in the electrical conductivity at high temperatures after the jump, for which the heating history of the sample would be related. Experiments 1, 2, and 3 were carried out using new, once heated and three times heated samples, respectively. The electrical conductivity is higher for the melt that has already been used for heating experiment. It seems that the κ value increases as the number of heating times is increased. The conductivity for new sample is $4 \times 10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ and that for three times heated sample is $6 \times 10^{0}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 300°C. The same trend is also seen for sulfur melts doped with 5 mol% Na (Figure 22), but it is not in accord with the behavior of the sulfur melts added with the other doping materials used in this work, where the decrease is usual for electrical conductivity when the number of the heating (and cooling) times is increased.

The electrical conductivities of the cooling process experiments of 1, 2, and 3 shown by the filled marks in Figure 24 are much higher than those of the respective heating process experiments in a range of lower temperatures below the jump temperature. This behavior is the same for the sulfur melts doped with 5 mol% Na.

The electrical conductivities for 10 mol% Na doped sulfur melts measured under ultrasonics irradiation (in the heating process) are shown in Figure 25. Experiments 1′, 2′, and 3′ were carried out using once heated, twice heated and four times heated samples respectively. Dissimilar to curve 4 for irradiated sulfur melt doped with 5 mol% Na doped sulfur (Figure 22), curves 1′ and 2′ of Figure 25 show a very sharp conductivity jump at 190°C. The jump width is so high that the conductivity increases from 10^{-6} to 10^{-2}–10^{-1} Ω^{-1} cm^{-1}. Curve 3′ also

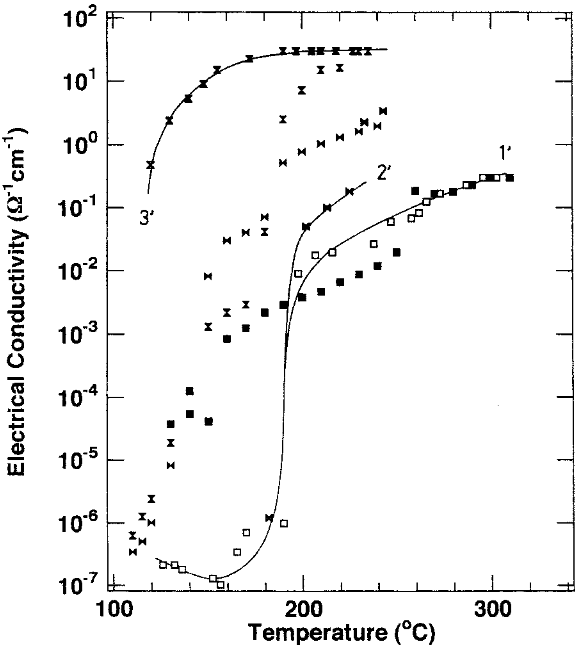

FIGURE 25 Electrical conductivity of 10 mol% Na doped sulfur as a function of temperature (ultrasonic irradiation). □, ■: Experiment 1′ using once heated sample; ⋈, ⧓: Experiment 2′ using twice heated sample; ⧖, ⧗: Experiment 3′ using four times heated sample. Open and filled marks show the hating and cooling processes respectively.

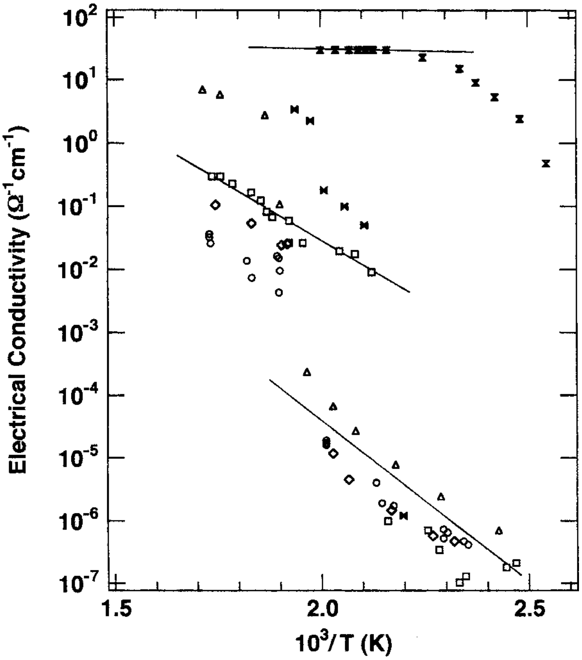

FIGURE 26 Logarithm of electrical conductivity plotted against 10^3/T for 10 mol% Na doped sulfur. ○: New sample without ultrasonic irradiation; ◇: Once heated sample without ultrasonic irradiation; △: Three times heated sample without ultrasonic irradiation; □: Once heated sample with ultrasonic irradiation; ⋈: Twice heated sample with ultrasonic irradiation; ⧗: Four times heated sample with ultrasonic irradiation.

shows the jump, but the jump point is shifted to a considerably lower temperature (∼120°C). Also, the κ values are much higher than those of curves 1′ and 2′. These results seem to be assocaited with the heating history of the sample; the jump temperature lowers with increasing number of heating times.

In Figure 26, the electrical conductivities are plotted against 10^3/T. In a low temperature region below ∼230°C, a high activation energy of 97.5 kJ/mol was obtained. Above ∼230°C, the activation energy was lowered to 74.2 kJ/mol. No significant change of the activation energy seemed to arise by the irradiation of ultrasonics. For the sample which had been heated four times before the experiment, however, a low activation energy of 3.1 kJ/mol was obtained above 190°C.

A number of electrical conductivity measurements of sodium polysulfides have been performed and discussions thereof have been made comparing in some cases with the physico-chemical properties of the other metal sulfides.[27,30–33] In the Na-S system, several kinds of sulfides of Na are known: They are Na_2S (Na 66.7 mol%), Na_2S_2 (50 mol%), Na_2S_3 (40 mol%), Na_2S_4 (33.3 mol%), $Na_2S_{4.7}$ (30 mol%), and Na_2S_5 (28.6 mol%) of which the melting points are reported to be 1170, 474 (meritectic point), 234 (eutectic point), 283, 237, and 258°C respectively.[32] Cleaver et al.[21] measured the electrical conductivity of sodium polysulfide melts with 28.2, 31.7, 34.6, and 37.4 mol% Na at temperatures 220, 260, 300, 340, 380, and 420°C. The electrical conductivity was observed to increase as the sodium proportion in the melt was increased. According to them, this trend can be ascribed to the increase of the ionic concentration of the polysulfide ions which is caused by the reduction of their size with the increase of the sodium proportion. The retrieved, values at 220°C are, for example, 0.032 and 0.09 $\Omega^{-1}cm^{-1}$ for 28.2 and 37.4 mol% Na respectively. At 420°C, these values were heightened to 0.63 and 0.99 Ω^{-1} cm^{-1}. The electrical conductivity was increased by a factor of 10–20 during the temperature rise from 220 to 420°C. Our κ values for unirradiated 10 mol% Na doped sulfur shown by curves 1, 2, and 3 in Figure 24 are in a range ~0.05–10 Ω^{-1} cm^{-1} at 300°C, which is comparable with 0.22 Ω^{-1} cm^{-1} for the reference 28.2 mol% Na doped sulfur at 300°C.[21] For lower temperatures, however, agreement is not good. Our κ values at 220°C are 10^{-5}–10^{-4} Ω^{-1} cm^{-1}, which are considerably lower than the conductivities reported by Cleaver et al.[21] This difference is due to the nonexistence of the conductivity jump in their κ values.[21] The κ values measured in the cooling processes of this work shown by the filled marks in Figure 24 are rather close to their conductivities below 245°C.

Note, however, that the above discussion does not take into account the concentration of sodium in the sulfur melts. The Na concentrations studied in this work are much lower than 28.2 mol% Na studied in Cleaver et al.[21] The electrical conductivity has also been measured by Wang and Newman[30] for the melts in a Na concentration range above 28 mol%, where the similar temperature dependence of electrical conductivity to that of Cleaver et al.[21] was obtained.

The phase diagrams published on the Na-S system are essentially consistent.[33–37] In the sulfur-rich region below 28.6 mol% Na (Na_2S_5), two kinds of liquids exist above 242°C.[36] Below that temperature, a liquid sulfur phase exists together with solid Na_2S_5 of which the solubility in the liquid sulfur has been estimated to be less than 1 mol% Na.[34] For the saturated solution with Na_2S_5, the κ values were reported to be lower than those of the sodium polysulfide melts by about six orders of magnitude (e.g. 3×10^{-8} and 10^{-7} Ω^{-1} cm^{-1} at 300 and 350°C respectively).[31]

The phase diagrams show that the melts having the sodium concentrations of this work (5 and 10 mol%) fall in the sulfur-rich region above mentioned, where the Na concentration in both the liquids added with 5 and 10 mol% Na should be the same as that in the reported melt.[31] However, the conductivities at 300°C for the sulfur melts containing 5 and 10 mol% Na in this study are in the ranges of 10^{-3}–10^{-2} (Figure 22) and 3×10^{-2}–10^{1} Ω^{-1} cm^{-1} (Figure 24) respectively. These κ values are much higher than 3×10^{-8} Ω^{-1} cm^{-1} given in Cleaver[31] It is almost unrealistic to assume that a certain impurity material, which can drastically enhance the electrical conductivity of sulfur melt, was in a small amount migrated in the present melts, sicne such a material has not been known. The above discrepancy is left unsettled. Another point to be considered is the experimental fact that the κ values for 5 mol% Na doped sulfur are fairly lower than those for 10 mol% Na melt at all temperatures measured in this work. According to the phase diagram, the Na concentration is the same in both the melts. Therefore, the higher electrical conductivities measured for 10 mol% Na melt suggest that the undissolved sodium polysulfide significantly contribute to the increase of the electrical conductivity. Wang and Newman[30] presented a macroscopic model as applicable to obtain the binary interaction coefficients quantifying the interaction between sodium cations and monosulfide cations in the sodium polysulfide melts of Na_2S_4 and Na_2S_5 from the electrical conductivity values. The high electrical conductivities observed in the present measurements may be related with the above interaction of sodium polysulfide ions which are sensitive to the molten state.

The jump temperature of 245°C in Figures 22 and 24 for unirradiated melts coincides with the melting point of Na_2S_5 (258°C,[32] 242°C[36]) in the liquid sulfur. From this result, it can be assumed that the jump is associated with the melting of Na_2S_5: The electrical conductivity of liquid Na_2S_5 would be much higher than that of the sulfur melt saturated with Na. The lower jump temperature of 180–190°C for irradiated melts doped with 5 mol% and 10 mol% Na could then be rationalized by assuming the microscopic temperature in the case of ultrasonics irradiation. Under the ultrasonic waves, the temperature of the cavities is estimated to be very high.[7,8] In the mechanism to transfer this energy to the sulfur moleculers of much larger amounts as vibrational energy, the temperature of such microscopic sulfur molecules containing sodium polysulfides (microscopic temperature) would markedly be lowered, but it is still higher than the measured temperature (macroscopic temperature) producing a transient thermal state. At 190°C, the sulfur molecules irradiated with ultrasonics are melted. In other words, the ultrasonic waves lower the jump temperature.

Effect of Dopant and Ultrasonic Irradiation

The electrical conductivities described in the previous two sections for each doping material are compared here to have a comprehensive insight into the effect of dopant and ultrasonic irradiation. Discussion is made in two subsections for unirradiated and irradiated melts.

Unirradiated Melts

The electrical conductivity and the activation energy of conduction for unirradiated melts are summarized in Table I. The doping of the materials described earlier (Na Doped Sulfur) does not enhance largely the electrical conductivity of the sulfur melt. Some materials have no siginficant effect. The conductivity will be compared in the temperature range between 200°C and 300°C, which increases without showing peak from 2×10^{-8}–7×10^{-7} Ω^{-1} cm^{-1} at 200°C to 1×10^{-7}–2×10^{-5}– Ω^{-1} cm^{-1} at 300°C for undoped sulfur. By the addition of LiF, NaF, or NaCl, the electrical conductivity of sufur does not change at all in the temperature range 200–300°C. A slight enhancement of the electrical conductivity by about half of one order of magnitude occurs by the addition of 5 mol% NaBr. In the cases of 5 mol% Se and 5 mol% Na_2SO_4, the electrical conductivity of doped sulfur is higher than that of undoped sulfur by more than one order of magnitude at 200°C, although the two conductivity curves approach giving virtually the same value at 300°C. This change is resulted from the shape of the curves of the sulfur melts doped with Se and Na_2SO_4 which depict a gentler conductivity increase with increasing temperature at higher temperatures. The similar shape of the Na_2SO_4 curve to the NaF and NaBr curves suggests that the effect of ${SO_4}^{2-}$ ions is not so apart from those of F^- and Br^- ions. The mixed dopant of 5 mol% NaBr + 5 mol% Se causes to increase the electrical conductivity with the magnitudes from more than one to one order at 200–300°C. The addition of 5 mol% KCl gives the electrical conductivity higher than that of undoped sulfur by more than two orders of magnitude at 200°C. By more than one order of magnitude at 300°C.

The heating history of sample does not effect to change the electrical conductivity for new and once heated samples of NaBr and Se. For NaBr + Se, however, the difference of the two curves for new and once heated sulfur becomes large below 200°C. The curve of new sample rather resembles to that of the sulfur melts doped with NaBr, whereas that of once heated sample to that of the sulfur melts doped with Se.

For LiF, NaF, and Na_2SO_4, a shallow minimum in the electrical conductivity has been observed at ∼160°C. Such conductivity minima have already been reported by Fehér et al.[22]

TABLE I Electrical Conductivity for Unirradiated Sulfur Melts (Heating Process)

Dopant	Concentration (mol%)	Electrical Conductivity (Ω^{-1} cm^{-1}) 150 (°C)	200 (°C)	250 (°C)	300 (°C)	340 (°C)	Activation Energy (kJ/mol)	Remarks
Undoped		2×10^{-8}–2×10^{-7}	2×10^{-8}–7×10^{-7}	7×10^{-8}–3×10^{-6}	1×10^{-7}–2×10^{-5}	2×10^{-7}–1×10^{-4}	98.9 (>ca.230°C, new or once heated samples) 20.3 (>ca.230°C, twice heated sample)	κ lowers with increasing heating time.
LiF	5	1×10^{-7}	3×10^{-7}	2×10^{-6}	1×10^{-5}	2×10^{-5}	75.0 (>200°C)	Shallow minimum at ca.160°C
NaF	5	2×10^{-7}	3×10^{-7}	1×10^{-6}	5×10^{-6}	8×10^{-6}	75.0 (>200°C)	Shallow minimum at ca.170°C
NaCl	13.4			3×10^{-7}	1×10^{-6}	4×10^{-6}	105.2 (>200°C)	
KCl	5		8×10^{-6}	4×10^{-5}	1×10^{-4}	3×10^{-4}	105.2 (>200°C)	
NaBr	5	3×10^{-7}	3×10^{-7}	1×10^{-6}–3×10^{-6}	$6 \times 10^{-6} - 3 \times 10^{-5}$		84.8 (>230°C)	
Se	5	1×10^{-6}–2×10^{-6}	3×10^{-6}	5×10^{-6}–6×10^{-6}	1×10^{-5}–3×10^{-5}		83.5 (<150°C), 15.2 (150–230°C), 83.5 (>230°C)	
NaBr+Se	5+5	5×10^{-7}–2×10^{-5}	3×10^{-6}–1×10^{-5}	2×10^{-5}	7×10^{-5}	1×10^{-4}	60.0 (>ca. 180°C)	New sample shows a big broad minimum at 200°C.
Na_2SO_4	5	1×10^{-7}	1×10^{-6}	6×10^{-6}	1×10^{-5}	2×10^{-5}	33.2 (>230°C)	Minimum at ca. 160°C
Na	5	4×10^{-7}	5×10^{-7}–1×10^{-6}	2×10^{-4}	1×10^{-3}–8×10^{-3}	3×10^{-3}–3×10^{-2}	127.5 (>260°C) 25.2 (<220°C)	κ jump at 245°C
Na	10	4×10^{-7}–1×10^{-6}	3×10^{-6}–1×10^{-5}	7×10^{-3}–$6{\times}10^{-2}$	4×10^{-2}–6×10^{0}	1×10^{-1}–1×10^{1}	97.5 (<ca.230°C) 74.2 (>ca.230°C)	κ jump at 245°C

They observed the small minima for undoped sulfur melt as well as sulfur melts doped with various organic compounds or bromine. In these cases and also in this work, the temperature which gives the minima is in agreement with the polymerization temperature, i.e., 159.4°C.[9] The above phenomenon is assumed to be related with the transformation of sulfur: On heating sulfur, the low temperature form α-S gradually changes to high temperature form β-S or γ-S with a decrease in the electrical conductivity. At the polymerization temperature of 160°C, the rapid change to $S_\propto$ causes to produce the conductivity minimum. Above that temperature, the conductivity increases with increasing temperature as a result of reluctant disruption of the sulfur polymers.

The behavior of the sulfur melts doped with Na metal is quite different. In these melts, the formed sodium polysulfides greatly increase the electrical conductivity at temperatures higher than the jump temperature. That is to say, these melts show a wide jump of electrical conductivity at 245°C in the heating process experiments, although the melts are not irradiated with ultrasonic waves. This temperature is the same for both the 5 mol% Na and 10 mol% Na doped melts. The jump is wider for the melts with higher Na concentrations, i.e., the width is 10^2 from 3×10^{-6} to $3 \times 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for 5 mol% Na melt, while the width attains 10^4 from 3×10^{-5} to $3 \times 10^{-1}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ for 10 mol% Na melt. The jump width also depends on the heating history of the sample. It becomes wider as the cycle of heating and cooling is repeated. At 300°C, the electrical conductivity for the sulfur melt doped with 5 mol% Na attains $1 \times 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ (new sample)—$8 \times 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ (twice hated sample). The conductivities for 10 mol% Na are $4 \times 10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ (new sample) and $6 \times 10^{0}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ (three times heated sample) at the same temperature.

On the other hand, the electrical conductivity is low for both the sulfur melts doped with 5 mol% Na and 10 mol% Na at lower temperature, e.g., 150°C. The κ value is of the same order of magnitude as undoped sulfur.

The obtained activation energies can be classified into three groups. (A) Low activation energy: (1) twice heated sample of undoped sulfur at $>\sim 230$ (20.3 kJ/mol), (2) new or once heated sample of Se doped sulfur in the medium temperature region 150–230°C (15.2 kJ/mol), (3) new sample of Na_2SO_4 doped sulfur at >230°C (33.2 kJ/mol), and (4) new or twice heated sample of 5 mol% Na doped sulfur at <220°C (25.2 kJ/mol), for which the corresponding temperatures are in the low temperature region. (B) Medium activation energy: (1) new samples of LiF and NaF doped sulfur at >200°C (75.0 kJ/mol), (2) new and once heated samples of NaBr doped sulfur at >230°C (84.8 kJ/mol), (3) new and once heated samples of Se doped sulfur at <150°C and >230°C

(83.5 kJ/mol), (4) once heated sample of NaBr + Se doped sulfur at $>\sim 180^\circ$C (60.0 kJ/mol), and (5) new and once heated samples of 10 mol% Na doped sulfur at $>\sim 230^\circ$C (74.2 kJ/mol), for which the activation energy does not change even if the ultrasonics irradiation was made. (C) High activation energy: (1) new and once heated samples of undoped sulfur at $>\sim 230^\circ$C (98.9 kJ/mol), (2) new samples of NaCl and KCl doped sulfur at $>200^\circ$C (105.2 kJ/mol), (3) new and twice heated samples of 5 mol% Na doped sulfur at $>260^\circ$C (127.5 kJ/mol), and (4) new, once heated and three times heated samples of 10 mol% Na doped sulfur below the jump temperature ($<230^\circ$C, 97.5 kJ/mol). Cleaver et al.[21] calculated the activation energy from their measured conductivity data on the sodium polysulfides with >28.2 mol% Na by the use of the Vogel-Tammann-Fucher equation.[38] Their values are 3.1–11.2 kJ/mol. Our low temperature energies are in fairly good agreement with the above energies.

Irradiated Melts

The electrical conductivity and the activation energy of conduction for irradiated melts are summarized in Table II. First, let us evaluate the effect of ultrasonic irradiation for each melt in a temperature range 200–300°C. This is made by comparing Tables I and II. No irradiation effect was observed for NaCl and KCl. For Se, NaBr + Se, and 5 mol% Na, irradiation raised the electrical conductivity by more than one order of magnitude at 200°C, but no effect was observed at 300°C. For LiF, no effect was observed at 200°C, but a small increase of electrical conductivity by about half of one order of magnitude was detected at 300°C. For Na_2SO_4 , the ultrasonic waves caused to heighten the electrical conductivity by less than one order of magnitude at 200–300°C. For undoped sulfur and NaBr, the effect increased to less than two orders of magnitude at 200–300°C. The effect still more increased to 2–3 orders of magnitude for NaF. For 10 mol% Na, the effect was as large as three-five orders of magnitude at 200°C, and it was one order of magnitude at 300°C.

Next, we evaluate the effect of dopant in the irradiated melts. From Table II, it is seen that the electrical conductivity is significantly increased only by doping 5 mol% Na or 10 mol% Na for irradiated melts. Compared with the electrical conductivity of undoped sulfur, which are 3×10^{-5}–1×10^{-4} and 8×10^{-6}–3×10^{-4} Ω^{-1} cm^{-1} at 200 and 300°C, respectively, the sulfur melt doped with 5 mol% Na gives 5×10^{-3} Ω^{-1} cm^{-1} at 300°C. The sulfur melt doped with 10 mol% Na shows much higher conductivities of 7×10^{-3}–3×10^{1} Ω^{-1} cm^{-1} and 3×10^{-1}–3×10^{1} at 200 and 300°C respectively.

TABLE II Electrical Conductivity for Ultrasonic Irradiated Sulfur Melts (Heating Process)

Dopant	Concentration (mol%)	Electrical Conductivity (Ω^{-1} cm^{-1})					Activation Energy (kJ/mol)	Remarks
		150 (°C)	200 (°C)	250 (°C)	300 (°C)	340 (°C)		
Undoped		5×10^{-7}–2×10^{-5}	3×10^{-5}–1×10^{-4}	3×10^{-6}–2×10^{-4}	8×10^{-6}–3×10^{-4}	2×10^{-5}–4×10^{-4}	3.6–28.1 (>230°C, new sample) 59.0 (>250°C, once heated sample)	κ lowers with increasing heating time. κ jump at 160°C (new samples) Jump at 220°C (once heated sample)
LiF	5		2×10^{-5}	5×10^{-5}	7×10^{-5}	9×10^{-5}	11.1 (>200°C)	κ jump at 190°C
NaF	5		2×10^{-4}	3×10^{-4}	4×10^{-4}	4×10^{-4}	11.1 (>200°C)	κ jump at 180–190°C
NaCl	13.4			3×10^{-7}	1×10^{-6}	4×10^{-6}	105.2 (>200°C)	
KCl	1	5×10^{-5}	3×10^{-6}	5×10^{-5}	2×10^{-4}	2×10^{-4}	105.2 (>200°C)	Broad κ maximum at 130°C Deep κ minimum at ca.180°C
KCl	5	4×10^{-4}	3×10^{-5}	1×10^{-4}	1×10^{-4}	1×10^{-4}	105.2 (>200°C)	Sharp κ minimum at 175°C
NaBr	5		6×10^{-5}	1×10^{-4}	2×10^{-4}	3×10^{-4}	84.8 (>250°C)	κ jump at 165°C (once heated sample)
Se	5	3×10^{-7}	1×10^{-5}	2×10^{-5}	3×10^{-5}	4×10^{-5}	15.2 (>170°C)	κ jump at 160°C
NaBr+Se	5+5	1×10^{-4}	1×10^{-4}	2×10^{-4}	2×10^{-4}	2×10^{-4}	6.0 (>160°C)	κ jump at 145°C
Na_2SO_4	5	2×10^{-7}	8×10^{-6}	3×10^{-5}	7×10^{-5}	1×10^{-4}	33.2 (>230°C)	κ jump at 180°C
Na	5		4×10^{-5}	8×10^{-4}	5×10^{-3}	2×10^{-2}	127.5 (>200°C)	Small κ jump near 200°C
Na	10	1×10^{-7}–1×10^{1}	7×10^{-3}–3×10^{1}	8×10^{-2}–3×10^{1}	3×10^{-1}–3×10^{1}		74.2 (>ca.230°C) 3.1 (>190°C, four times heated sample)	Sharp κ jump at 190°C κ jump at ca.120°C (four times heated sample)

A characteristic feature observed for the sulfur melts under ultrasonic irradiation is the jump of electrical conductivity excluding the case of sulfur melt doped with either NaCl or KCl, for which no such increase was detected in the conductivity curves. The undoped sulfur melts give rise to the jump at 160 (new sample) and 220°C (once heated sample). The use of the once heated sample may be the reason for the increase of jump temperature and the decrease of electrical conductivity in this case of undoped sulfur. The jump temperatures are 165, 160, and 145°C for NaBr (once heated sample), Se (twice heated sample), and NaBr + Se (twice heated sample) respectively. In the case of NaBr, the jump occurs at the same temperature also for twice heated sample. However, the jump width of this sample is small and the electrical conductivity rises with considerable rates with increasing temperature at temperatures higher than the jump temperature. The similar trend is seen also for Se and Na_2SO_4. On the other hand, if the jump takes place with a wide width, the electrical conductivity does not increase so largely at temperatures higher than the jump temperature. This trend is seen for LiF (once heated sample), NaF (once heated sample) and NaBr + Se. The jump temperatures are 190 and 180–190°C for LiF and NaF respectively. That of Na_2SO_4 (once heated sample) is 180°C.

The jump behavior of sulfur melts doped with Na much differs from that of the other melts studied in this work. For the sulfur melt doped with 5 mol% Na, a small unclear jump of electrical conductivity was observed at 190–200°C in the heating process experiment using once heated sample. For the melts doped with 10 mol% Na, on the other hand, the sharp and wide conductivity jump was observed for once heated and twice heated samples at 190°C. When the sample of four times heated one was used, the electrical conductivity was high and the jump temperature was as low as ~120°C. It seems likely for sodium doped sulfur that the jump temperature lowers and the electrical conductivity rises as the number of heating times is increased. The reason of this change has not been verified yet. But if we suppose that the repeated heating promotes the slow equilibration reaction of sodium polysulfides in sulfur, it becomes understandable.

The electrical conductivity of the new sample of 1 mol% KCl doped sulfur increases from 120°C with increasing temperature giving a maximum at 130°C. Then, it decreases as the temperature increases forming a minimum at 180°C. The once heated sample of 5 mol% KCl doped sulfur exhibits a discontinuous sharp minimum at 175°C. The anomalies of this type have also been reported for the unirradiated sulfur melts doped with various organic dopants.[22] Here, only for the irradiated KCl doped melt it was observed. These phenomena are assumed to be associated with the polimerization and/or transition of sulfur which are brought about near temperatures.

The low activation energies of conduction have been observed for the following melts: (1) new samples of undoped sulfur at >180°C (3.6–28.1 kJ/mol), (2) once heated samples of LiF and NaF doped sulfur at >200°C (11.1 kJ/mol), (3) twice heated sample of Se doped sulfur at >170°C (15.2 kJ.mol), (4) twice heated sample of NaBr + Se doped sulfur at >160°C (6.0 kJ/mol), and (5) four times heated sample of 10 mol% Na doped sulfur at >190°C (3.1 kJ/mol). For undoped sulfur, the once heated sample yields a higher activation energy of 59.0 kJ/mol (>250°C) than the new one. The twice heated sample of NaBr doped sulfur gave the higher energy than the once heated sample. In these cases, the activation energy increased with increasing heating times. The reverse was observed for the melts doped with 10 mol% Na, where the energy decreased with increasing times of heating.

Earlier (section 10 mol% Na Doped Sulfur), we found that the assumption of microscopic temperature for sulfur molecules could explain the lowering of the jump temperature of the sulfur melts doped with Na when the melts were subjected to irradiation of ultrasonic waves. The assumption claims that the microscopic sulfur molecules feel higher temperatures than the measured macroscopic temperature. If this microscopic temperature mechanism is also valid for the sulfur melts doped with other materials, it can be said that the ultrasonics irradiation is generally effective to realize the microscopically higher temperature phenomena of sulfur melts at lower measured temperatures.

SUMMARY AND CONCLUSION

The electrical conductivity was measured for undoped sulfur melts, doped sulfur melts with 5 mol% LiF, 5 mol% NaF, 13.4 mol% NaCl, 1 and 5 mol% KCl, 5 mol% NaBr, 5 mol% Se, 5mol% NaBr + 5 mol% Se, 5 mol% Na_2SO_4, 5 and 10 mol% Na in the temperature range from above 110°C to ca. 340°C. The doping effect of these materials on the electrical conductivity was studied. The above melts were irradiated with ultrasonic waves of 20 kHz, and the resultant change in the electrical conductivity was studied.

Unirradiated Melts

(1) The electrical conductivity of undoped sulfur in the heating process measurements increases from 10^{-8}–10^{-7} $\Omega^{-1}\,cm^{-1}$ at ~150°C to max. 10^{-4} Ω^{-1} cm^{-1} at 340°C.

(2) The electrical conductivity does not change by the addition of LiF, NaF, and NaCl at temperatures 200–300°C without ultrasonic irradiation.
(3) The electrical conductivity slightly increases by about half of one order of magnitude by the addition of NaBr.
(4) In the case of Se and Na_2SO_4, the electrical conductivity increased by more than one order of magnitude at 200°C, while it merged into virtually the same conductivity as undoped sulfur at 300°C.
(5) The electrical conductivity of sulfur with a mixed dopant NaBr + Se increases by more than one to one order of magnitude at 200–300°C.
(6) KCl caused to increase the electrical conductivity by more than two orders of magnitude at 200°C.
(7) For the sulfur melts doped with either 5 or 10 mol% Na, a wide jump of electrical conductivity takes place at 245°C on heating, of which the width increases with increasing number of heating times.
(8) The electrical conductivity of the above melts is exceedingly high at higher temperatures after the jump, viz. $4 \times 10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ (new sample) - $6 \times 10^{0}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ (three times heated sample) at 300°C for 10 mol% Na.
(9) The activation energy of electrical conduction can be classified into three groups, i.e., low, medium and high activation energies depending on the doping material, temperature and heating history of sulfur.
(10) The low activation energies of 15.2–33.2 kJ/mol were obtained for undoped sulfur, doped sulfur with Se, Na_2SO_4, and 5 mol% Na.
(11) The medium activation energies in a range 60.0–84.8 kJ/mol were obtained for doped sulfur melts with LiF, NaF, NaBr, Se, NaBr + Se, and 10 mol% Na.
(12) The high activation energies of 97.5–127.5 kJ/mol were obtained for undoped sulfur, doped sulfur melts with NaCl, KCl, 5 mol% Na, and 10 mol% Na.

Irradiated Melts

(1) The electrical conductivity of undoped sulfur (new sample) shows a jump of $<10^{2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ width on heating at 160°C. The κ values are 3×10^{-5}–$1 \times 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 200°C and 8×10^{-6}–$3 \times 10^{-4}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 300°C. The electrical conductivity was markedly lowered for once heated sample.
(2) Irradiation of ultrasonic waves causes an increase in the electrical conductivity of undoped sulfur when compared with the electrical

conductivity of unirradiated sulfur by about one order of magnitude in the temperature range 200–300°C.

(3) No increase of electrical conductivity by ultrasonics irradiation was observed for the sulfur melts doped with NaCl and KCl at 200–300°C.

(4) For Se, NaBr + Se, and 5 mol% Na, irradiation raised the electrical conductivity by more than one order of magnitude at 200°C, but no increase was observed at 300°C.

(5) For LiF and Na_2SO_4 , the electrical conductivity is increased by ultrasonics by less than one order of magnitude at 200–300°C.

(6) For NaBr, the irradiation effect increased to less than two orders of magnitude at 200–300°C. The effect still more increased to two-three orders of magnitude for NaF.

(7) For 10 mol% Na, the irradiation effect was as large as three-five orders of magnitude at 200°C after the jump at 190°C, although it was one order of magnitude at 300°C.

(8) The difference of the electrical conductivity and that of irradiated undoped sulfur gives the change of irradiation effect by dopant. The largest effect was found to be for 5 mol% and 10 mol% Na.

(9) Except for NaCl and KCl, the doped sulfur melts show the conductivity jump on heating under irradiation. For the sulfur melts doped with Na, the jump temperature is likely to be lowered from 190°C as the number of heating times is increased.

(10) The low activation energies ranging from 3.6 to 28.1 kJ/mol were obtained for undoped sulfur, doped sulfur melts with LiF, NaF, Se, NaBr + Se, and 10 mol% Na.

(11) The high activation energies of 105.2–127.5 kJ/mol were obtained for doped sulfur melts with NaCl, KCl and 5 mol% Na at temperatures above 200°C.

(12) The assumption of microscopic temperature was proposed for the present melts, which claims that the molten sulfur molecules irradiated with ultrasonic waves are microscopically in a state of equilibrium with a higher temperature, by absorbing ultrasonic energy nearly adiabatically, than the macroscopic (measured) temperature. That is to say, the phenomena of higher microscopic temperatures can be observed at lower temperatures by the irradiation of ultrasonic waves.

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