Original Paper

Ionic conductivity of $Li_2O-B_2O_3-Li_2SO_4$ glasses

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Electrical conductivity and Raman spectra were measured and glass-forming region was determined in the $Li_2O-B_2O_3-Li_2SO_4$ glass system. The relation between conductivity and composition was discussed on the basis of the glass structure. Conductivity rapidly increased with addition of Li_2SO_4 up to 20 mol%. Maximum conductivity was obtained in the metaborate compositions containing a larger amount of Li_2SO_4, and minimum activation energy at the composition of metaborate with a modest amount of Li_2SO_4. The glasses containing a large amount of Li_2O or Li_2SO_4 had higher activation energies. The activation energy change with Li_2O/B_2O_3 ratio may be explained from the viewpoint of borate structure. But the reason for the activation energy change with Li_2SO_4 addition in a metaborate composition has not yet been clarified.

Ionenleitfähigkeit von $Li_2O-B_2O_3-Li_2SO_4$-Gläsern

Im Glassystem $Li_2O-B_2O_3-Li_2SO_4$ wurden die elektrische Leitfähigkeit gemessen, die Raman-Spektren aufgenommen und der Glasbildungsbereich bestimmt. Die Beziehung zwischen Leitfähigkeit und Zusammensetzung wird aus struktureller Sicht diskutiert. Die Leitfähigkeit stieg bei Zugabe von weniger als 20 % (Stoffmengengehalt) Li_2SO_4 rasch an. In Metaboratzusammensetzungen trat bei hohen Li_2SO_4-Gehalten die höchste Leitfähigkeit und bei niedrigen Li_2SO_4-Gehalten die geringste Aktivierungsenergie auf. Die Gläser mit großen Anteilen an Li_2O oder Li_2SO_4 hatten die höheren Aktivierungsenergien. Die Änderung der Aktivierungsenergie mit dem Li_2O/B_2O_3-Verhältnis kann mit Hilfe der Boratstruktur erklärt werden; dagegen konnte bisher noch keine Erkärung gefunden werden für die Änderung der Aktivierungsenergie mit dem Li_2SO_4-Gehalt in Metaboratzusammensetzungen.

1. Introduction

Recently, lithium ion-conducting glasses have attracted a great deal of attention as a possible solid electrolyte material. Among this group of glasses, the borate glass systems exhibit a considerably higher ionic conductivity because of the larger quantities of dissolved lithium ions [1 and 2]. The addition of lithium salts, such as LiCl and Li_2SO_4, to the borate glasses may broaden the glass-forming region owing to the multiplication effect of glass components. It is known that Li_2SO_4 is a good lithium ion conductor at high temperature [3] and less hygroscopic than LiCl. The addition of it is therefore favorable to produce the fast lithium ion-conducting glasses. The Li_2SO_4-containing borate glass system was previously investigated by Levasseur et al. [2], but the glass-forming region was limited to a rather small lithium content and the relation between composition and conductivity was not discussed in detail. It was pointed out, however, in [2] that SO_4^{2-} was not incorporated in the borate structure like Cl^- in the $LiCl-Li_2O-B_2O_3$ system.

In this study, the Li_2SO_4-containing borate glasses were prepared in a broad composition range and on the relations between composition and conductivity were investigated by means of the complex impedance method and Raman spectroscopy. It was examined whether the incompatibility between Li_2SO_4 and borate glass proposed by Levasseur et al. [2] exists in such a high lithium content region.

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2. Experimental

The starting materials were commercial reagent grade Li_2CO_3 or Li_2O, H_3BO_3, and $Li_2SO_4 \cdot H_2O$. The raw materials were mixed thoroughly and melted in a Pt-crucible at 900 to 1000 °C for 30 min, then quenched by pressing the poured melt using brass plates. The glass blocks were annealed near the glass transformation temperature, T_g, for 4 h. The exact T_g values of these glasses were measured by DTA, and the density by the Archimedean method in CCl_4. Since the glass specimens were fairly hygroscopic, they were kept in a vacuum desiccator.

For the electrical measurement, a gold blocking electrode with guard ring was deposited by sputtering. The typical sample size was 12 mm in diameter and 0.7 mm in thickness. The electrode was 5.7 mm in diameter and 1 mm in guard gap width, the effective electrode area was about 0.35 cm^2. The samples were kept at constant temperature with thermocontroller in argon. The electrical conductivity was measured by the complex impedance method with the impedance analyzer (Hewlett Packard, 4192A) from room temperature to T_g in the frequency range 5 Hz to 1 MHz. By this method, the

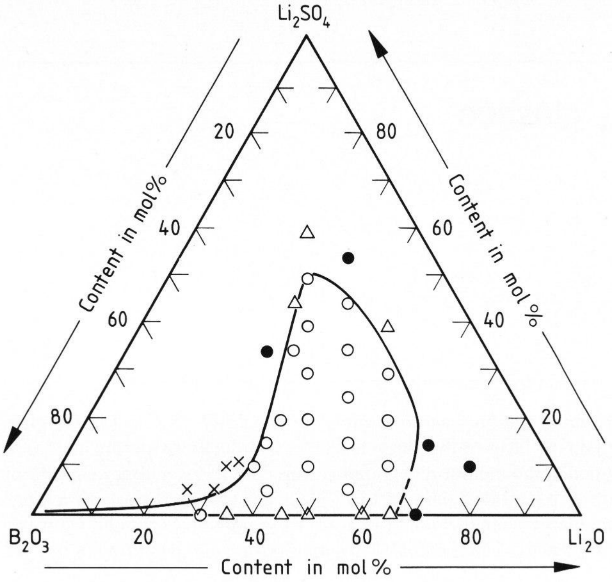

Figure 1. Glass-forming region in the $Li_2O-B_2O_3-Li_2SO_4$ system. ○: glass, △: partially crystalline phase, ●: crystalline phase, ×: liquid-liquid immiscibility.

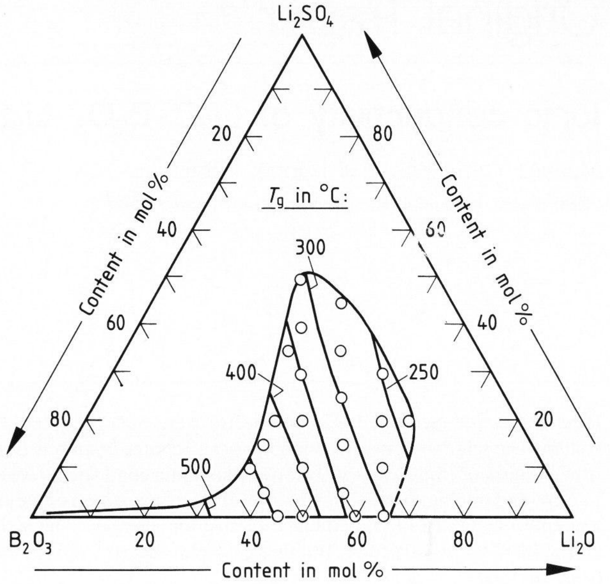

Figure 2. Glass transformation temperature, T_g, of the $Li_2O-B_2O_3-Li_2SO_4$ system.

Table 1. Nominal and analytical compositions for some glass samples

glass sample	nominal composition in mol%			composition calculated from chemical analysis in mol%		
	Li_2O	B_2O_3	Li_2SO_4	Li_2O	B_2O_3	Li_2SO_4
a	50	50		50.24	49.76	
b	65	35		64.51	35.49	
c	40	55	5	40.41	54.49	5.10
d	40	40	20	40.41	39.19	20.39
e	55	25	20	55.62	24.16	20.22
f	60	20	20	54.99	21.71	23.30
g	30	40	30	30.32	39.06	30.62
h	25	25	50	25.51	23.88	50.61

value of the bulk resistance could be determined with an accuracy of 2 %.

Because of the small sample size, the conductivity may be systematically deviated within ± 0.1 in logarithmic scale. But the deviation must not have affected the value of activation energy of conductivity.

The Raman spectra of these glass specimens were measured using the Raman spectrometer (JEOL, JRS-400D) with argon laser (λ = 514.5 nm).

3. Results

Figure 1 shows the glass-forming region in the system $Li_2O-B_2O_3-Li_2SO_4$. This region deviates slightly from the previous data by Levasseur et al. [2]. In the B_2O_3-rich region in figure 1, phase separation appeared in the melt with small additions of Li_2SO_4, and no uniform glass could be formed. Button et al. [4] pointed out the similar liquid-liquid immiscibility in the system $Li_2O-B_2O_3-LiCl$. Judging from the glass-formating region in figure 1 and Button's data,

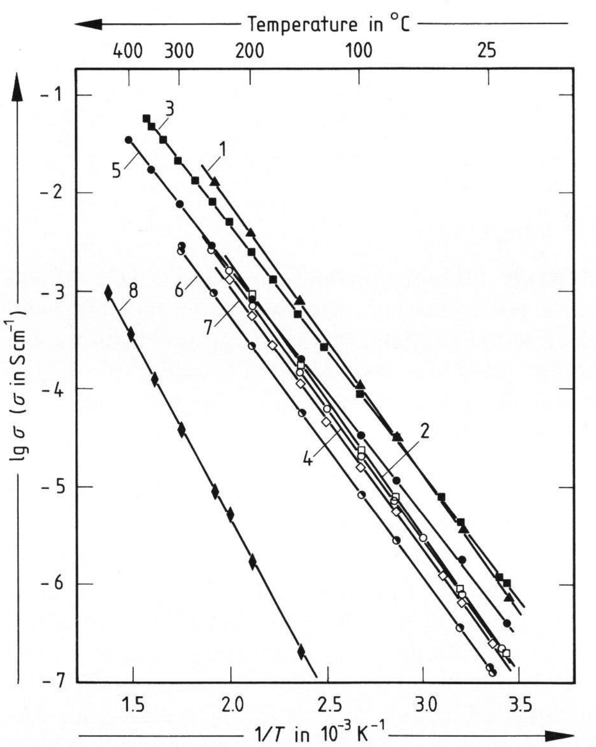

Figure 3. Typical Arrhenius plots of conductivity for various glass compositions.
1: $0.25\ Li_2O \cdot 0.25\ B_2O_3 \cdot 0.5\ Li_2SO_4$,
2: $0.5\ Li_2O \cdot 0.2\ B_2O_3 \cdot 0.3\ Li_2SO_4$,
3: $0.35\ Li_2O \cdot 0.35\ B_2O_3 \cdot 0.3\ Li_2SO_4$,
4: $0.55\ Li_2O \cdot 0.25\ B_2O_3 \cdot 0.2\ Li_2SO_4$,
5: $0.45\ Li_2O \cdot 0.45\ B_2O_3 \cdot 0.1\ Li_2SO_4$,
6: $0.35\ Li_2O \cdot 0.55\ B_2O_3 \cdot 0.1\ Li_2SO_4$,
7: $0.65\ Li_2O \cdot 0.35\ B_2O_3$,
8: $0.3\ Li_2O \cdot 0.7\ B_2O_3$.

Li_2SO_4 was less soluble in borate melts than LiCl at a Li_2O content of less than 40 mol%. It seems that the alkali salts, such as LiCl and Li_2SO_4, are less soluble

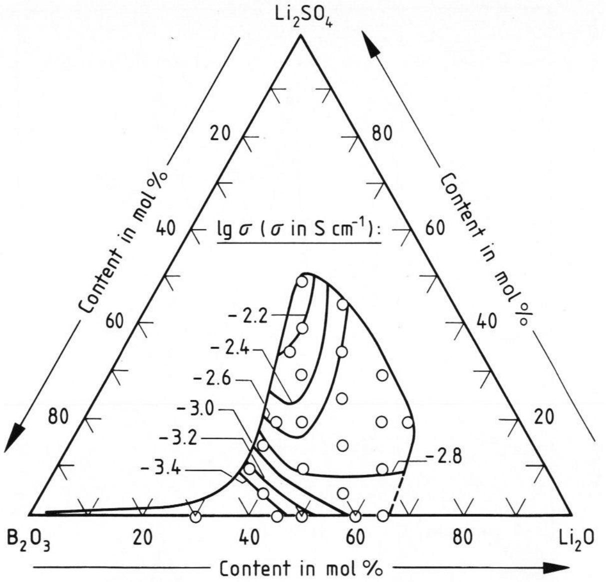

Figure 4. Ionic conductivity at 500 K in the $Li_2O-B_2O_3-Li_2SO_4$ system.

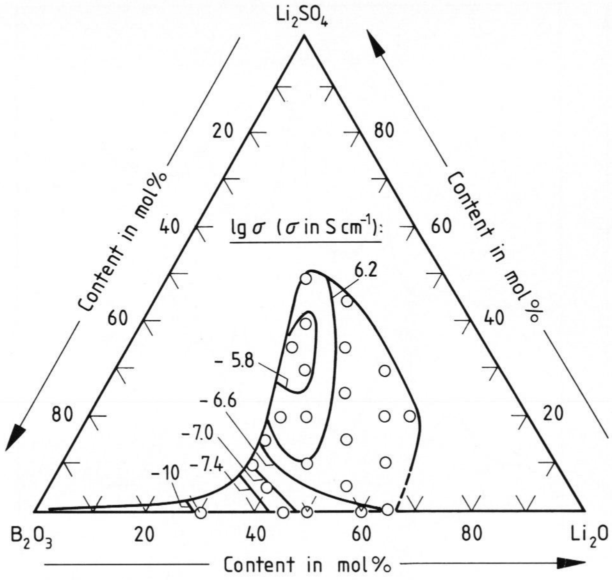

Figure 5. Ionic conductivity at 298 K in the $Li_2O-B_2O_3-Li_2SO_4$ system.

in borate glass at a O/B ratio <1.8 (except for oxygen contained in SO_4), where boroxol rings and triborates etc. exist without non-bridging oxygen [5]. At high lithium contents, more rapid quenching was required to prevent crystallization in molten glasses, and the glass-forming region was limited by the quenching rate. In the lithium-rich region where the Li_2O content was more than 55 mol%, Li_2O was used as starting material instead of Li_2CO_3 since a residue of CO_3^{2-} ion in the glass was observed by Raman spectra at 1100 cm^{-1} [6] in the sample produced with Li_2CO_3. In the $Li_2O-B_2O_3$ binary system, the glass-forming region was rather narrow [7] and thus the mixtures of glass/crystal were obtained (see figure 1). The glassy parts of these specimens were used as samples. Table 1 shows the analyzed compositions of some glasses. A little volatilization loss occurred in all samples of borates, but the deviation of the compositions was not so large except for the no. 5 glass samples.

In order to examine the influence of water, $0.35\,Li_2O \cdot 0.35\,B_2O_3 \cdot 0.3\,Li_2SO_4$ glass was melted in an argon-filled glove box using Li_2O, B_2O_3 and dehydrated Li_2SO_4 as starting materials. The water content in this glass estimated from IR spectrum was less than in the sample melted in air, and no detectable change was observed in conductivity. It seemed, hence, that the water in this system had little influence on the conductivity.

Figure 2 indicates the transformation temperatures of these glasses, which decrease from B_2O_3-rich to Li_2O-rich glass.

The relation between ionic conductivity and temperature was processed by the Arrhenius type equation:

$$\sigma = \sigma_0 \exp (E_a / k\, T)$$

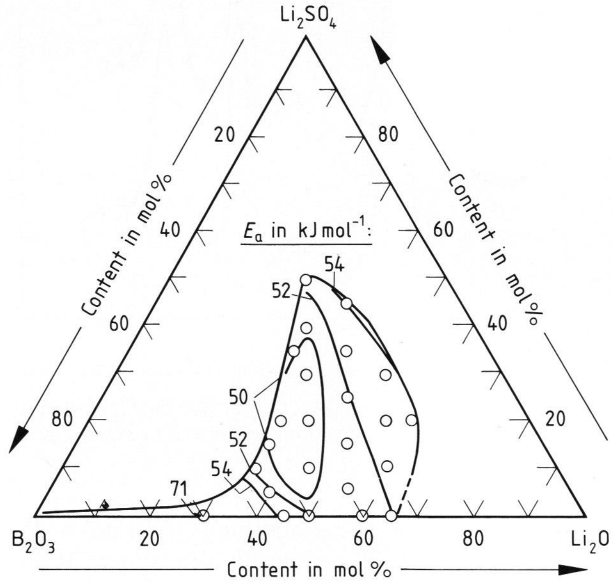

Figure 6. Activation energy E_a of the conductivity in the $Li_2O-B_2O_3-Li_2SO_4$ system.

where E_a is the activation energy and σ_0 the pre-exponential factor. Figure 3 shows an example of the Arrhenius plot. It was found that the data points almost fitted in with straight lines. The crystallization rate of the glasses increased with an increase in temperature above T_g and the conductivity rapidly decreased by crystallization.

Figures 4 to 6 show the logarithm of conductivity at 500 K and 298 K, and E_a. The minimum value of E_a was at the metaborate (BO_2) composition. At less than 10 mol% of Li_2SO_4 content, the conductivity increased with increasing Li_2O or Li_2SO_4 content. But in a region with higher Li_2SO_4 contents, the conductivity no longer increased with Li_2O content,

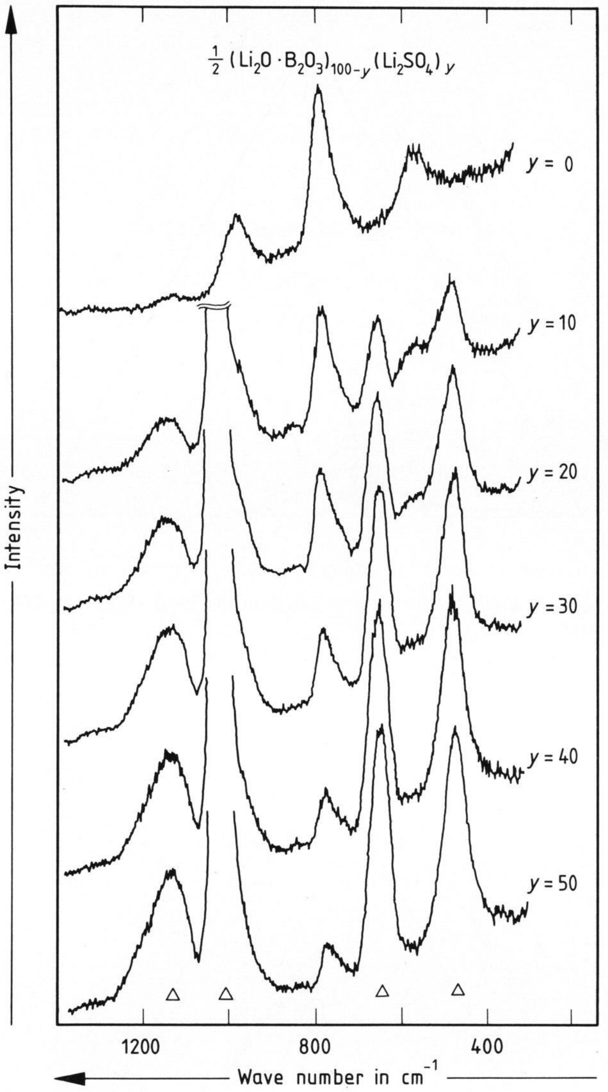

Figure 7. Raman spectra in the $Li_2O-B_2O_3-Li_2SO_4$ system at metaborate composition with various amounts of Li_2SO_4. △: peak of the SO_4^{2-} ion.

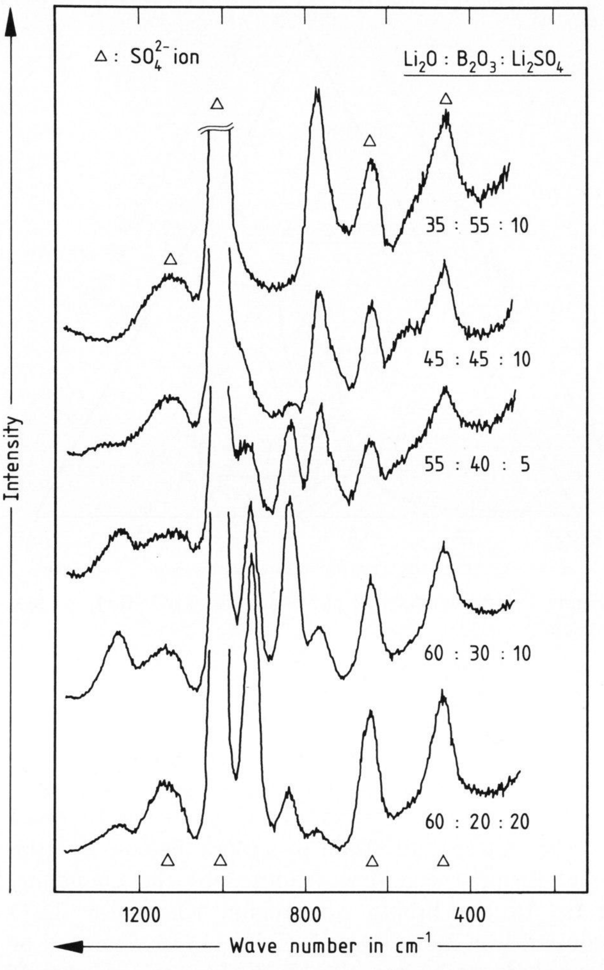

Figure 8. Raman spectra in the $Li_2O-B_2O_3-Li_2SO_4$ system for different O/B ratios. △: peak of the SO_4^{2-} ion.

showing a maximum at metaborate (O/B ratio = 2). The conductivity at 500 K showed its maximum at the highest Li_2SO_4 content, but at room temperature, the maximum conductivity was in the composition region of minimum values of E_a as shown in figure 5.

The peaks of the borate structure and the SO_4^{2-} ion in the Raman spectra are shown in figures 7 and 8. The peak at 770 cm^{-1} is assigned to a borate ring containing 4-coordinated boron, at 725 cm^{-1} to chain-type metaborate, at 825 cm^{-1} to pyroborate, at 930 cm^{-1} to orthoborate [8]. Peaks at 1008, 550, 450 and 1200 cm^{-1} are assigned to SO_4^{2-} ion [2]. Figure 7 shows a change of Raman spectra with the addition of Li_2SO_4 at metaborate composition. In these spectra, there were little changes in the peak ratio of the borate structures and only the SO_4^{2-} peak was increased with SO_4^{2-} contents. According to Levasseur et al. [2], the addition of lithium salts, such as LiCl and Li_2SO_4, did not change the borate structure. This can be explained by the fact that lithium salts are located in the space of the borate network and do not bond with the borate skeleton. In this experiment, the same phenomena were observed at any O/B ratio, although it did not so clearly originate from the influence of the SO_4^{2-} peak. Figure 8 shows a change in spectra with Li_2O content. The peak shoulder around 960 cm^{-1} shown in figure 7 could not be assigned to any borate structure [9]. As the Li_2O content increases, pyroborate and orthoborate increase instead of the formation of a borate ring with 4-coordinated boron.

4. Discussion

The lithium concentration which was calculated from density increased with increasing Li_2O and Li_2SO_4 contents as shown in figure 9. In the $Li_2O-B_2O_3$ system, the conductivity increases with the lithium concentration. For the addition of Li_2SO_4, however, a distinct relation between conductivity or activation energy and lithium concentration was not observed, but the conductivity decreased at higher lithium concentration. The similar phenomena of the conductivity maximum or E_a minimum at O/B ratio = 2

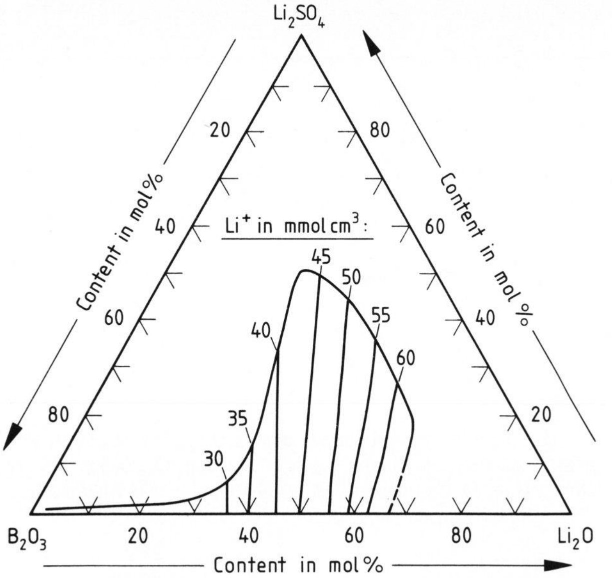

Figure 9. Lithium concentrations of the Li_2O–B_2O_3–Li_2SO_4 system calculated from composition and density.

(see figure 5) occur in other borate systems [10 and 11]. The lowering of E_a with increasing alkali contents for low-alkali glass can be explained by a decreasing jump distance [10]. However, the increasing of E_a at O/B ratio above 2 can not be explained by the same reason. This behavior was independent of Li_2SO_4 content, so that the cause of E_a minimum must be considered to relate to the borate structure. It was found (figure 8) that many 4-coordinated boron units exist at a O/B ratio = 2, while non-bridging oxygens contained in pyroborate or orthoborate increase instead of 4-coordinated borons with increasing O/B ratio. It can be inferred that the negative charge in 4-coordinated boron extends around the boron atom so that the lithium ion is weakly bonded with this borate and has a larger mobility. On the contrary, the negative charge on pyroborate or orthoborate is located at non-bridging oxygen ($-O^-$) so that the lithium ion bonds strongly with $-O^-$ and can not easily move. The reason may be that the composition of O/B ratio = 2 gives the lower E_a value (see [10]).

In the case of addition of Li_2SO_4, the increase of the number of carriers brings about the increase of conductivity. And if a similar negative charge dispersion exists around the SO_4 molecule, the lithium can weakly bond to them, and easily move to some extent. But this explanation does not apply to the case of larger amounts of Li_2SO_4. The activation energies shown in figure 5 decrease at lower Li_2SO_4 content, and then increase at more than 40 mol% of Li_2SO_4 content. This rising of E_a at a larger SO_4 content can not be explained by the above-mentioned reason.

One possible explanation is based on the mixed anion effect proposed by Tatsumisago et al. [12]. According to them, a measure of "frozen" structure, $(T_l - T_g)/T_l$, relates to the degree of conductivity enhancement. In this experiment, however, the value $(T_l - T_g)/T_l$ calculated from figure 2 and the phase diagram in [13] increased monotonically, and there was no clear relation between this value and the conductivity maximum or E_a minimum in this system.

The phenomena of the conductivity maximum also occur in other systems [14], and further investigations are needed for an exact explanation of such a lithium ion behavior.

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