

Application of Space-Charge Model in Describing the Ionic Conductivity of Lithium-Borate Thin Films

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Abstract

Ionic conduction of lithium-borate thin films shows a nontrivial increase when the layer thickness is less than 120 nanometers. In this research, the space-charge model is used to describe high conductivity in lithium-borate thin films. Regarding the amorphous structure of these layers, similar to the crystalline structure, we assume the Li⁺ ions and their counterparts as defects and the regions adjacent to electrode-electrolyte interfaces as space-charge regions. The electrochemical potential of defects arising from these regions leads to the well-known Poisson-Boltzmann equation. To solve this equation numerically, the fourth-order Rung-Kutta integration, together with a shooting method for two-point boundary value problems, is used. Since these two boundary conditions are at two different points, the shooting method is used to solve this problem. Finally, the calculated ionic conductivity is compared to the experimental one. A free parameter that is related to the size of the space-charge region is used to fit space-charge model data to the experimental results. Although the space charge model is used in this research to describe the ionic conductivity of lithium borate, it is expected that this model can be used for other ionic conductors by changing the model parameters.

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1. Introduction

The effects of a conductivity enhancement with decreasing layer thickness have already been reported for different crystalline ion conductors [1-4]. Sata et al. [4] observed the conductivity enhancement for hetero layered films composed of CaF₂ and BaF₂ prepared by molecular-beam epitaxis. They observed a conductivity enhancement of about twenty-fold.

This conductivity enhancement of the crystalline thin film ion conductors can be explained by the space-charge model [1, 5]. This model is based on the increase of defect concentration in the boundary regions of heterogeneous

systems. The increase of the defect concentration causes a redistribution of the ions in such a way that the electrochemical potential gradient of the defects vanishes.

Although in a stochastic structure, there is no direct analogy with lattice defects, in this paper, we will tend to the concept of defects to use this model for amorphous materials.

Studies on the ionic conductivity of lithium-borate ($y \text{Li}_2\text{O} \cdot (1-y) \text{B}_2\text{O}_3$) layers with amorphous structure in terms of thickness show significant changes in the conductivity of the layer at small thicknesses of a few nanometers [6, 7]. From the structural point of view, interfaces between the lithium-borate glass films and the metallic electrodes differ substantially from the volume of the glass films. Consequently, the structure of the glass film is affected by the interface in a zone of a few nanometers adjacent to the interface. This structural difference, together with the presence of Al Li electrodes, causes a redistribution of mobile charge carriers in this region. The Al Li electrodes and the glass layer of Lithium-borate are illustrated in (Figure 1).

In lithium-borate glasses ($y \text{Li}_2\text{O} \cdot (1-y) \text{B}_2\text{O}_3$), the network consists of BO_3 and BO_4^- units. Lithium ions can move within this network. With a Li_2O concentration below $y=25$ atom%, negatively charged units BO_4^- represent the dominating electrical counterparts to the Li^+ ions [8, 9]. Because of electrostatic interaction, Li^+ ions are bounded in the neighborhood of the units, but they can overcome this bounding by thermal excitation. The bounded Li^+ ions and the units may be considered electrically neutral defect pairs.

It is supposed that the difference in the electrochemical potential of oxygen in the glass layer and at the interface causes segregation of the units towards the interface. Consequently, a very thin negatively charged layer on the glass surfaces is formed. Charge neutrality causes the presence of more Li^+ ions in the vicinity of this region, and hence the region close to the interfaces has a higher conductivity. This region will be considered the space-charge region.

The conductivity contribution of the space-charge regions to the overall conductivity of the layer depends on the layer thickness. For thick layers, this contribution is negligible, and for this reason, their conductivity remains independent of the layer thickness, while in the case of the thin films, this contribution becomes significant. For layers with a thickness comparable to the thickness of the space-charge regions, an appreciable higher conductivity is expected.

2. Materials and Methods

2.1 Space-charge model

Generally, the space-charge region is the zone where the ionic and electronic point defects are redistributed. These regions are being formed adjacent to the interfaces between two different phases. Redistribution of the charged particles is carried out so that in thermal equilibrium, the gradient of the electrochemical potential of defects vanishes.

In order to use this model for the lithium-borate glass films, we consider the mobile Li^+ ions and their counterparts BO_4^- as defects. The electrochemical potential of the defects can be described by two chemical and electrical terms

$$\eta_j(x) = \mu_j(x) + ez_j\phi(x), \quad (2.1)$$

Where η_j is the electrochemical potential of the defects type (j). The two defect types here will be indicated by (+) and (-) indices. Moreover, μ_j is the chemical potential of defects, e is the elemental charge, z is the charge

number of defect species (here ± 1), and $\phi(x)$ is the electrical potential. The space coordinate x regarding to the setup of a sample with thickness of t is illustrated in (Figure 1).

We assume that the number of defects (Li^+ mobile ions) is small compared to the lattice molecules (molecules of the lithium-borate network or in other words number of all possible places for Li^+ ions in the network). Under this condition, it is possible to relate the chemical potential linearly to the logarithm of the defect concentration c_j [10] and Equation (2.1) can be rewritten in the following form:

$$\eta_j(x) = \mu_j^0 + k_B T \cdot \ln c_j(x) + ez_j \phi(x). \quad (2.2)$$

Here k_B is the Boltzmann constant, T is the absolute temperature, and μ_j^0 is the standard value for chemical potential, which is independent of x . This standard value can be considered as the chemical potential of defects far from the space-charge regions, for thick layers at $x=0$ (see Figure 1).

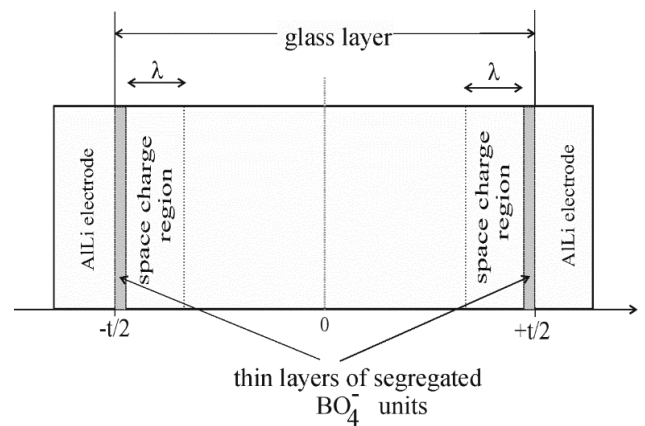


Figure 1. Space-charge region for a sample with a thickness of t .

The equilibrium condition for a pure transport of a defect type j from x to $x + \Delta x$ [5, 10] is

$$\nabla_x \eta_j(x) = 0. \quad (2.3)$$

Applying the equilibrium condition, on the electrochemical potential Equation (2.2) at two different points, $x=0$ and an arbitrary x yields

$$\frac{c_j(x)}{c_{0j}} = \exp\left(-\frac{ez_j(\phi(x) - \phi(0))}{k_B T}\right), \quad (2.4)$$

where c_{0j} is the standard value of the defect concentration type j at $x=0$. Equation (2.4) shows that for $\phi(x) > \phi(0)$, the concentration of negative defects rises by the exponential factor on the right-hand side of the equation, while that of the positive defects reduces by the same factor.

Poisson equation relates the electrical potential $\phi(x)$ to the defect charge density $\rho(x)$ as

$$\nabla^2 \phi(x) = \frac{1}{\epsilon_0 \epsilon_r} \rho(x), \quad (2.5)$$

where ϵ_0 is the permittivity of free space and ϵ_r is the relative dielectric constant. The charge density $\rho(x)$ in terms of the concentrations of the positive and negative defects c_+ and c_- can be written as

$$\rho(x) = e \cdot (c_+(x) - c_-(x)). \quad (2.6)$$

Substitution of the defect concentrations from Equation (2.4) yields

$$\rho(x) = e \cdot c_0 \cdot \left\{ \exp\left(-\frac{e \cdot (\phi(x) - \phi(0))}{k_B T}\right) - \exp\left(\frac{e \cdot (\phi(x) - \phi(0))}{k_B T}\right) \right\}. \quad (2.7)$$

Here it is assumed that the two defect types of (+) and (-) have the same standard concentration c_0 , which is neutrality at middle of a thick layer for the case of $z_+ = z_-$. Since $\nabla^2 \phi(0) = 0$, by use of $\phi'(x) = \phi(x) - \phi(0)$ and the substitution of $\rho(x)$ in the Poisson equation, we obtain

$$\frac{d^2 \phi'(x)}{dx^2} = \frac{e \cdot c_0}{\epsilon_0 \epsilon_r} \left\{ \exp\left(-\frac{e \cdot \phi'(x)}{k_B T}\right) - \exp\left(\frac{e \cdot \phi'(x)}{k_B T}\right) \right\}. \quad (2.8)$$

Substitution of $U(x) = -\frac{e \cdot \phi'(x)}{k_B T}$ as reduced electric potential yields

$$\frac{d^2 U(x)}{dx^2} = \left(\frac{2e^2 c_0}{\epsilon_0 \epsilon_r k_B T} \right) \cdot \sinh U(x). \quad (2.9)$$

Normalized distance is defined as $\xi = x/\lambda$ with

$$\lambda = \sqrt{\frac{\epsilon_0 \epsilon_r k_B T}{2e^2 c_0}}, \quad (2.10)$$

where λ is known as Debye length. Using the variable ξ instead of x in Equation (2.9) results in

$$\frac{d^2 U(\xi)}{d\xi^2} = \sinh U(\xi). \quad (2.11)$$

Equation (2.11) is the well-known Poisson-Boltzmann equation. The desired analytical solution of this equation cannot be explicitly given except for special boundary conditions [1]. The following section treats a numerical solution of this equation, which allows us to find the conductivity of the lithium-borate glass films as a function of their thickness.

2.2 Numerical solution of the Poisson-Boltzmann equation

To solve Equation (2.11) numerically, the fourth-order Rung-Kutta integration, together with a shooting method for two-point boundary value problems [11], is used. For this solution, the following boundary conditions are considered:

a) The conductivity and hence the ion concentration rises approaching to the interfaces from the middle of the layer; regarding the symmetry, it is expected that $\left. \frac{dU(\xi)}{d\xi} \right|_{\xi=0} = 0$. In other words, the value of U at middle of the layer remains constant.

b) The second boundary condition is the maximum value of $U(\xi)$ on the layer surfaces with $\xi = \pm \frac{t}{2\lambda}$. This value must be selected in such a way that the desired value of the maximum conductivity (for extremely thin films) is obtained.

Since these two boundary conditions are at two different points of ξ , the shooting method must be used to solve this problem.

Figures 2 and 3 represent the results of the numerical solution of the function $U(\xi)$ for $\lambda = 20$ nm and $U_{\max} = 8$. This function is also related to the defect concentrations by

$$c_+(x) = c_0 \exp[U(x)] \quad (2.12)$$

and

$$c_-(x) = c_0 \exp[-U(x)]. \quad (2.13)$$

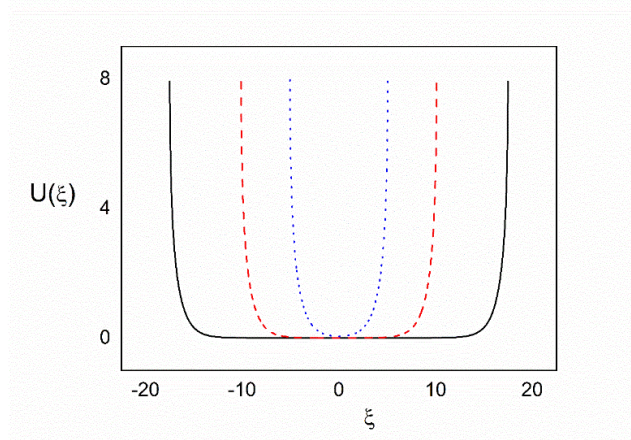


Figure 2. Reduced electric potential U versus normalized distance ξ resulting from the numerical solution of Poisson-Boltzmann equation with $\lambda = 20$ nm, and $U_{\max} = 8$ for thick layers, 700 nm (black line) 400 nm (red dashed line), and 200 nm (blue dotted line).

For thick films (Figure 2), the defect concentration of positive charges increases dramatically at the layer surfaces, while in the centre of the layer it is approximately constant and equal to c_0 . For thin films (Figure 3), the minimum values of $U(\xi) = U(0)$ are larger than zero. Therefore, the concentration of the positive defects is larger than c_0 even in the centre of the layer. This leads to an increase of the overall conductivity of the thin films.

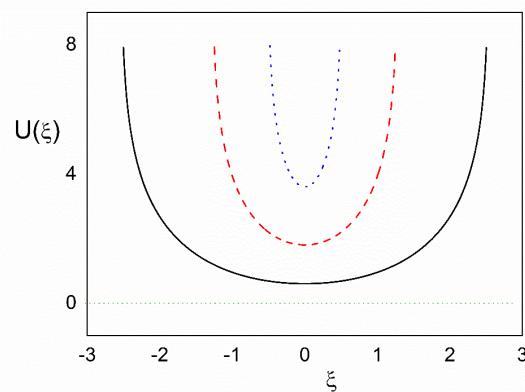


Figure 3. Reduced electric potential U versus normalized distance ξ resulting from the numerical solution of Poisson-Boltzmann equation with $\lambda = 20$, and $U_{\max} = 8$ for thin layers, 100 nm (black line), 50 nm (red dashed line) and 20 nm (blue dotted line).

In general, conductivity depends linearly on the charge concentration

$$\sigma = m \cdot e \cdot c, \quad (2.14)$$

where m is the mobility of the charge carriers and e is the elemental charge. The conductivity of the layers is a function of ξ and hence a function of x . It is assumed that only a fraction of the Li^+ ions is mobile. This fraction is a function of x , and all of the mobile ions have a constant mobility. This assumption is compatible to the defect approach of the space-charge model. Therefore, the conductivity of the lithium-borate glass films can be written as

$$\sigma(x) = m \cdot e \cdot c_+(x). \quad (2.15)$$

3. Results and Discussion

3.1 Comparing the results of space-charge model to experimental data

The ionic conductivity obtained from the space-charge model is a function of x in the layer. That is, different points of the layer may have different conductivities. The average conductivity of a layer is considered to compare the measured values to the results obtained from the space-charge model. The resistance of a layer with thickness t and area S is equal to the sum of the resistances of the infinitesimal thin layers with thickness dx from $x = -t/2$ to $x = t/2$

$$R_{layer}(t) = \frac{1}{S} \cdot \int_{x=-t/2}^{t/2} \frac{dx}{\sigma(x)}, \quad (3.1)$$

and the substitution of the conductivity from Equations (2.12) and (2.15) results

$$R_{layer}(t) = \frac{1}{Sm \cdot ec_0} \cdot \int_{x=-t/2}^{t/2} e^{-U(x)} \cdot dx. \quad (3.2)$$

The average conductivity of the layer becomes

$$\sigma_{layer}(t) = \frac{t}{R_{layer}(t)S}, \quad (3.3)$$

and placing of $R_{layer}(t)$ from Equation (3.2) yields

$$\sigma_{layer}(t) = md \cdot ec_0 \cdot \frac{1}{\int_{x=-t/2}^{t/2} e^{-U(x)} \cdot dx}. \quad (3.4)$$

The experimental data used in this research have already been measured by the author [6, 7]. Experimental values of conductivity in terms of layer thickness for three different concentrations of Li_2O are shown in Figure 4. To calculate the layer conductivity from Equation (3.4), the value of the constant factor $C^* = m \cdot ec_0$ is required. To determine this factor, the experimental conductivity of the glass film with thickness of 700 nm is used. It is assumed that this value is constant for all layers with the same concentration of Li_2O . This is the minimum value of conductivity for a given concentration. Therefore, C^* can be expressed by

$$C^* = \frac{\sigma_{layer}(700nm)}{700nm} \cdot \int_{-350nm}^{350nm} e^{-U(x)} \cdot dx. \quad (3.5)$$

Moreover, C^* is not a completely independent parameter, rather it depends on the Debye length λ through c_0 ; see Equation (2.10), and its calculation by Equation (3.5) shows the dependency on λ through $U(x)$. An independent parameter in C^* is the base conductivity of the layer or the conductivity of the thick layers.

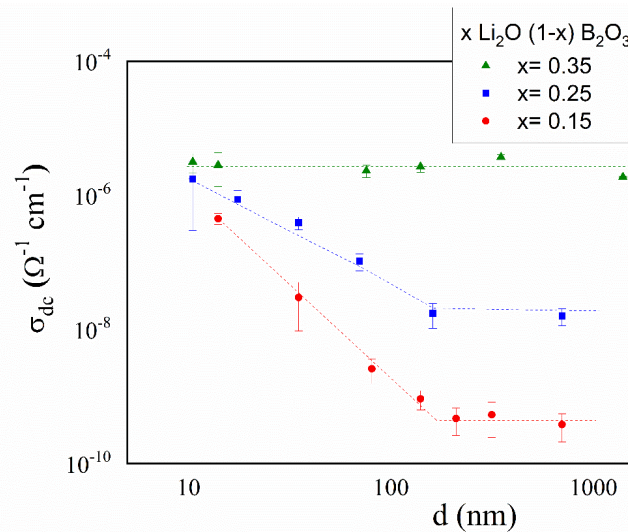


Figure 4. Experimental results for ionic conductivity of lithium-borate with three different concentrations of Li_2O . The dashed Lines are a guide for eyes.

A common maximum conductivity is considered for all glass films with different concentration of Li_2O . This value amounts $\sigma_{\max} = 2.6 \cdot 10^{-6} \text{ (}\Omega^{-1} \text{ cm}^{-1}\text{)}$ and it is the conductivity of the layers with concentration of 0.35 $\text{Li}_2\text{O} \cdot 0.65 \text{ B}_2\text{O}_3$.

Also, U_{\max} is the maximum value of $U(\xi)$ and it is related to σ_{\max} as well as to the base conductivity, σ_{\min} . According to Equation (3.10), we will show that $U_{\max} = \ln\left(\frac{\sigma_{\max}}{\sigma_{\min}}\right)$. The value of U_{\max} , which fulfils the two boundary values of the conductivities, may be derived as follows. The conductivity of a layer with thickness t is given by Equation (3.4). The maximum value of the conductivity is obtained when $t \rightarrow 0$. This can be written as

$$\sigma_{\max} = \lim_{d \rightarrow 0} \sigma_{\text{layer}}(t) = \lim_{d \rightarrow 0} \left(\frac{C^* t}{2} \right) \cdot \frac{1}{\int_{x=0}^{t/2} e^{-U(x)} \cdot dx} \quad (3.6)$$

Figure 3 shows that by reduction of the film thickness, the difference between U_{\max} and U_{\min} decreases. For extremely thin films it can be concluded that $U_{\min} \rightarrow U_{\max}$ and hence the value of U is approximately constant for different values of x . Under this assumption, the integral in Equation (3.6) becomes

$$\lim_{t \rightarrow 0} \int_{x=0}^{t/2} e^{-U(x)} \cdot dx = \frac{t}{2} \cdot \exp(-U_{\max}), \quad (3.7)$$

and Equation (3.6) yields

$$\sigma_{\max} = C^* \cdot \exp(U_{\max}). \quad (3.8)$$

Equation (3.5) gives the value of C^* . Under assumption of $U(x) \approx U_{\min} \approx 0$ for thick layers (see Figure 2), we obtain

$$C^* = \sigma_{layer}(700nm) = \sigma_{min}, \quad (3.9)$$

and

$$U_{max} = \ln\left(\frac{\sigma_{max}}{\sigma_{min}}\right). \quad (3.10)$$

The required parameters to determine the dependency of the conductivity on the layer thicknesses according to the space-charge model can be summarized as follows:

- λ , which is related to the size of the space-charge region.
- $\sigma_{min} = \sigma_{layer}$ (thick films), the base conductivity of the layers.
- σ_{max} , the maximum conductivity of glass films.
- U_{max} , which depends on the maximum conductivity of the layers (for extremely thin films) and σ_{min} according to Equation (3.10).

If we set the base conductivity and U_{max} according to the experimental values of the conductivities, only one free parameter, namely λ , remains to fit the model data to the experimental thickness dependent conductivity.

Now we set U_{max} according to Equation (3.10) for different compositions of the lithium-borate glass films. The resulting parameters are represented in Table 1. The parameter λ is obtained by fitting the experimental conductivities to the space-charge model data, which are shown in Figures 5-8.

Table 1. Base conductivity, common maximum conductivity, and Debye lengths of different lithium-borate glass films obtained from the space-charge model.

concentration of Li ₂ O	$\sigma_{max}(\Omega^{-1} \text{ cm}^{-1})$	$\sigma_{min}(\Omega^{-1} \text{ cm}^{-1})$	U_{max}	$\lambda(\text{nm})$
0.15	$2.6 \cdot 10^{-6}$	$3.8 \cdot 10^{-10}$	8.8	30
0.25	$2.6 \cdot 10^{-6}$	$1.3 \cdot 10^{-8}$	5.3	25
0.35	$2.6 \cdot 10^{-6}$	$2.6 \cdot 10^{-6}$	0	Uncertain

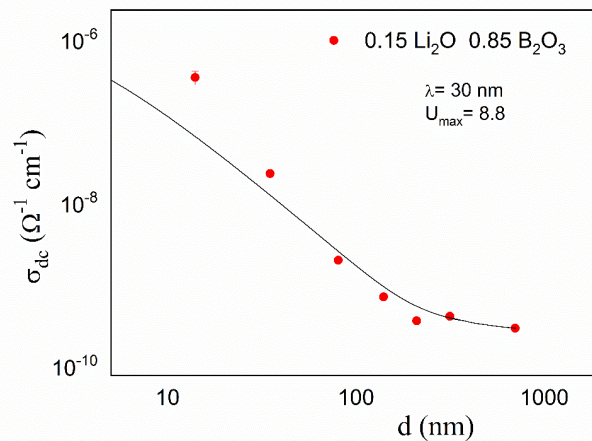


Figure 5. Space-charge model fit to the experimental data for (0.15 Li₂O · 0.85 B₂O₃) glass films at 120 °C with $U_{max} = 8.8$ and $\lambda = 30$ nm.

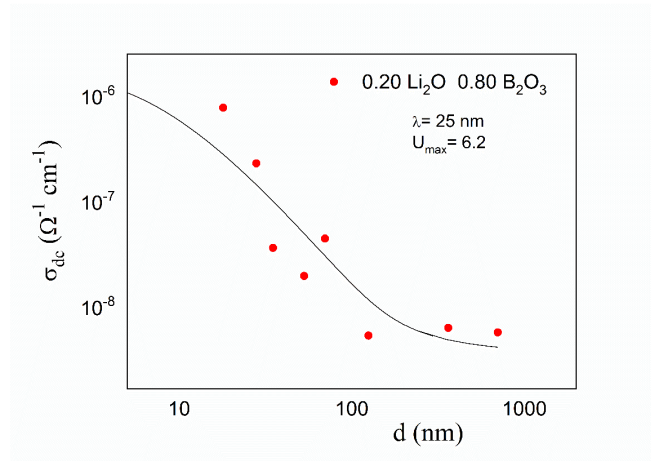


Figure 6. Space-charge model fit to the experimental data for (0.20 Li₂O · 0.80 B₂O₃) glass films at 120 °C with $U_{\max}=6.2$ and $\lambda=25$ nm.

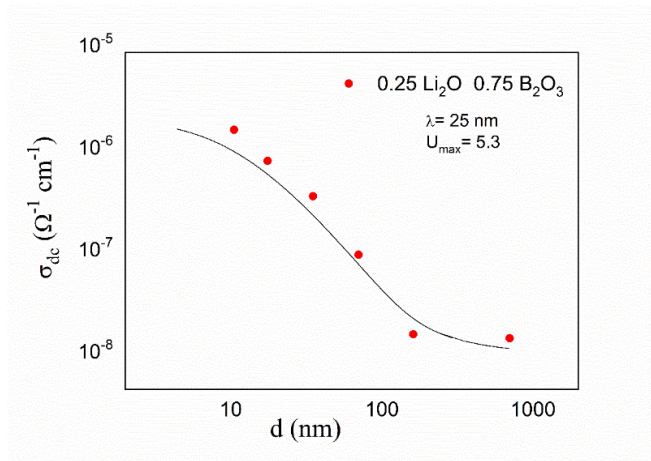


Figure 7. Space-charge model fit to the experimental data for (0.25 Li₂O · 0.75 B₂O₃) glass films at 120 °C with $U_{\max}=5.3$ and $\lambda=25$ nm.

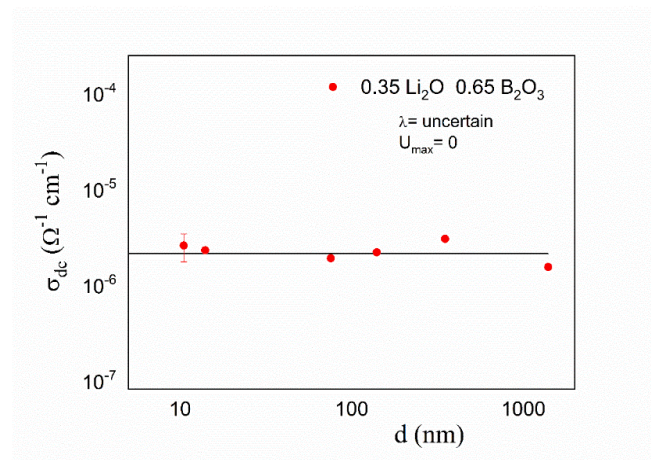


Figure 8. Space-charge model fit to the experimental data for (0.35 Li₂O · 0.65 B₂O₃) glass films at 120 °C with $U_{\max}=0$. The conductivity of these layers is selected as the common maximum conductivity.

Comparison of Figures 5-8 shows a decrease of the Debye length when increasing the Li₂O concentration from 0.15 to 0.20. However, an observable change in Debye length by increasing the Li₂O concentration from 0.20 to 0.25 is not seen. For the glass layers with concentration of 0.35 Li₂O, U_{max} becomes zero and it is not possible to determine the Debye length for these layers. This is because the conductivity of these layers is selected as the common maximum conductivity.

4. Conclusions

Assuming the existence of space-charge regions in lithium-borate thin films and considering Li⁺ and BO₄⁻ ions as structural defects similar to crystal structures, we tried to describe the ionic conductivity in these films. As can be seen from the results of fitting the experimental data with the space-charge model, this model describes the overall shape of the thickness dependence conductivity, and it is in good agreement with experimental data. An advantage of this research is the use of only one free parameter, the Debye length, to simulate this model. Other simulation parameters are selected based on experimental data.

Conflicts of Interest

The author declares that there are no conflicts of interest regarding this article.

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