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Polycrystalline and glassy $LiAlSi_2O_6$ are studied by dielectric relaxation measurements for the purpose of characterizing the nearly frequency independent contribution to the dielectric loss (near constant loss), which is commonly found in glassy ionic conductors independent of the chemical and physical structures. The data show the near constant loss is present in both the polycrystalline and glassy states of $LiAlSi_2O_6$. Further, its magnitude and temperature dependence is comparable in both forms of the same substance. The implications of these findings on the mechanism that gives rise to the near constant loss are discussed. © *2001 American Institute of Physics.*
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I. INTRODUCTION

Mobile ions in glassy and molten ionic conductors give rise to a complex conductivity $\sigma^*(\omega)=\sigma'(\omega)+i\sigma''(\omega)$ well-described by the empirical relation[1]

$$\sigma'(\omega)=\sigma_{\rm dc}+C\omega^s, \tag{1a}$$

$$\sigma''(\omega)=\epsilon_0\epsilon_\infty\omega+C\omega^s\tan(s\pi/2). \tag{1b}$$

Here ϵ_0 is the permittivity of free space, ϵ_∞ the high frequency dielectric constant, $\sigma_{\rm dc}$ the dc conductivity, C a constant, and s is a positive fraction of unity. Another equally well-described representation is given from the Maxwell relation $\sigma^*(\omega)=i\omega\epsilon_0\epsilon^*(\omega)$ with the reciprocal of the complex dielectric permittivity $\epsilon^*(\omega)=\epsilon'(\omega)-i\epsilon''(\omega)$, also known as the electric modulus,[2–4] calculated from the Laplace transform

$$1/\epsilon^*(\omega)=(1/\epsilon_\infty)\left[1-\int_0^\infty dt \times\exp(-i\omega t)(-d\exp[-(t/\tau)^\beta]/dt)\right]. \tag{2}$$

Here β is another positive fraction of unity. At high frequencies, both empirical representations give a fractional power frequency dependence for $\sigma'(\omega)$, which is ω^s from Eq. (1a) and ω^β from Eq. (2). However, at sufficiently low temperatures and high frequencies the experimental data invariably vary more strongly and assume the $\sigma'(\omega)=A\omega^n$ dependence with n nearly equal to one.[2–20] The corresponding dielectric loss, $\epsilon''(\omega)=(A/\epsilon_0)\omega^{n-1}$, becomes nearly independent of frequency and is appropriately called the constant loss (CL) or the near constant loss[10] (NCL). There are a number of indications[21] that the NCL is distinctly different in physical origin from the ac conductivity due to the long-range motions of mobile ions. For example,[21] the temperature dependence of the NCL or A is very weak compared to the Arrhenius temperature dependences of $\sigma_{\rm dc}$ and C in Eq. (1a) and τ in Eq. (2). In alkali oxide glasses, change in the alkali concentration or replacement by another alkali[13,21] has a much weaker effect on A than on $\sigma_{\rm dc}$, C, and τ. Different thermal histories of a glass[2] can change $\sigma_{\rm dc}$ by nearly half an order-of-magnitude but have nearly no effect on the value of A. Other authors have arrived at the same conclusion that Eq. (1a) and the NCL are due to separate mechanisms by showing that they superimpose.[10]

In spite of the NCL being ubiquitous, its physical origin remains unexplained.[21] More experimental work would help our understanding. In this study we investigate the NCL in the glassy and polycrystalline states of $LiAlSi_2O_6$. Several experiments have shown the presence of NCL in many glassy ionic conductors. Hence, the existence of NCL is certainly expected in glassy $LiAlSi_2O_6$. On the other hand, the study of crystalline ionic conductors without added impurities is rare. Our objective is find out whether the NCL exists also in the polycrystalline state of the same substance $LiAlSi_2O_6$ (polycrystals of β-spodumene), and if so, how its magnitude and temperature variation compare with that in the glassy state.

II. EXPERIMENTAL DETAILS

Samples of both glassy and polycrystalline $LiAlSi_2O_6$ in the current studies are prepared in exactly the same way as reported in the work by Munro *et al.*[22] Specimens of disc shape were prepared for dielectric relaxation measurements. Measurements of the complex dielectric function have been

made with a Novocontrol BDC-S system composed of a frequency response analyzer (Solartron Schlumberger FRA 1260) and a broad band dielectric converter with an active sample cell. The latter contains six reference capacitors in the range from 25 to 1000 pF. Measurements were made in the frequency range from 10^2 to 10^6 Hz using a combination of three capacitors in the active sample cell. The samples were confined between two 20 mm diameter gold-plated stainless steel plates separated by 1 mm. The sample cell was placed in the cryostat. The sample temperature was controlled between 160 and 373 K and measured with a PT100 sensor in the lower plate of the sample capacitor with an accuracy of ± 0.1 K.

III. RESULTS

Electrical conductivity relaxation measurements in glassy $LiAlSi_2O_6$ and polycrystalline $LiAlSi_2O_6$ or β-spodumene were first made by Munro *et al.*[22] These authors were interested mainly in the contributions from long-range motion of the mobile Li ions empirically described by Eqs. (1) and (2), and their measurements performed in the frequency range $1<f<10^7$ Hz at temperatures above 298 K do not reveal the NCL in either forms of $LiAlSi_2O_6$. To find the NCL in the glass, we have to make measurements at lower temperatures in a similar frequency range of $0.05 \leqslant f \leqslant 10^6$ Hz. The results are shown in Figs. 1(a) and 1(b) for $\sigma'(f)$, and $\epsilon''(f)$, respectively, at five temperatures. At the lower temperatures, the NCL can be clearly seen directly from the loss ϵ'', being almost independent of frequency, or alternatively from the rise of the ac conductivity linearly with frequency over more than six decades.

Böhmer *et al.*[23] reported conductivity relaxation of polycrystalline $LiAlSi_2O_6$ over wide frequency and temperature ranges. At low temperatures or very high frequencies, they found dielectric loss due to the freezing of the Li ions in the interstitial double-well potentials, inherent in the structure of β-spodumene to become an orientational glass. This interesting observation of the resemblance to an orientational glass transition is the major emphasis in the report by Böhmer *et al.*[23] At high temperatures, conductivity relaxation contributed by diffusing Li ions dominates. Thus the NCL can only be observed at some intermediate temperature range. Figures 2(a) and 2(b) show our measurements of $\sigma'(f)$ and $\epsilon''(f)$ on polycrystalline $LiAlSi_2O_6$ in the intermediate temperature region, $163 \leqslant T \leqslant 238$ K. As temperature is decreased the absolute value of the slope in the $\log \epsilon''(f)$ vs $\log f$ plot decreases and reaches the small value of 0.08 at 163 K. Therefore, the data at 163 K and vicinity show the existence of the NCL also in polycrystalline $LiAlSi_2O_6$. We do not make measurement below 163 K. The published data of Böhmer *et al.* indicates dielectric loss from dipoles formed by freezing of the Li ions in interstitials, which will make its presence in our experimental frequency window at temperatures somewhat below 163 K, rendering the result ambiguous to interpret.

IV. DISCUSSION

The electrical conductivity relaxation results of Figs. 1 and 2 show that the NCL exists not only in glassy $LiAlSi_2O_6$ but also in polycrystalline $LiAlSi_2O_6$. This is not a total surprise because NCL has been found in ionically conducting crystalline materials including Na β-alumina[24] and $Li_xLa_{1-x}TiO_3$ (LLTO).[17] At the same temperature, say 163 K, the exponent n governing the frequency dependences of $\sigma'(\omega)=A\omega^n$ and $\epsilon''(\omega)=(A/\epsilon_0)\omega^{n-1}$ is closer to 1.0 for the glass than for the polycrystals with $n=0.92$. The magnitude of the NCL at the same temperature and frequency or the quantity A is larger for the glass than for the polycrystals. However, the difference is not large. For example, at 163 K and $f=1$ kHz, the NCL of the glass is only approximately a factor of two larger than the polycrystals. The temperature dependences of the NCL or A in both forms of $LiAlSi_2O_6$ are also comparable and both are best described by either a power law T^α or $\exp(T/T_a)$, like that found in other glassy and nonglassy ionic conductors.[21] The fits of $\exp(T/T_a)$ to the temperature dependence of the NCL at 6×10^5 Hz of glassy and polycrystalline $LiAlSi_2O_6$ are shown by straight lines in

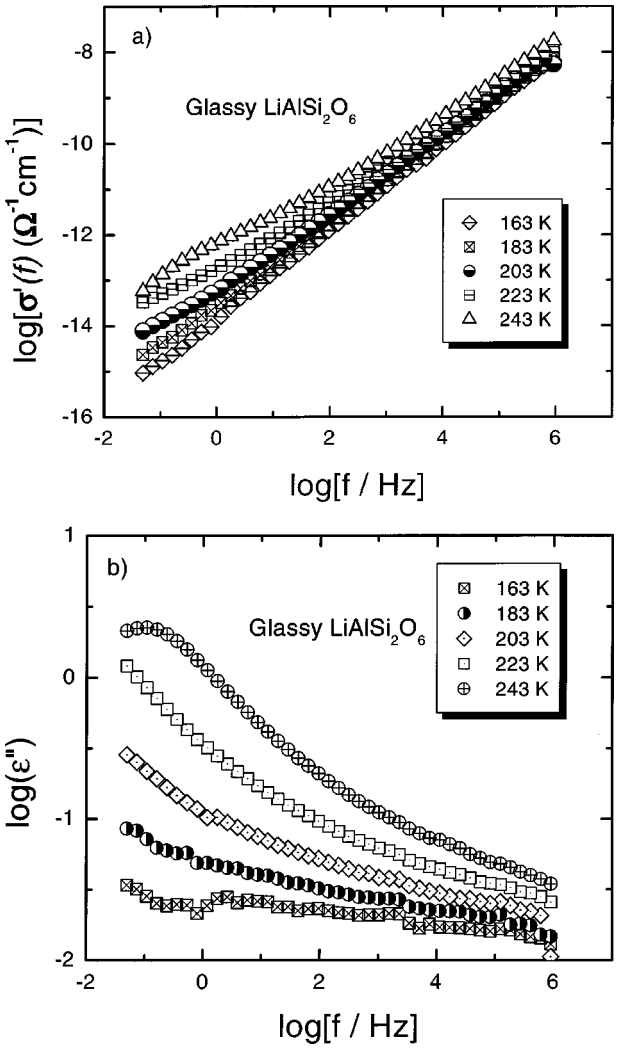

FIG. 1. (a) Isothermal electrical relaxation data of glassy $LiAlSi_2O_6$ shown as plots of $\log[\sigma'(f)]$ vs $\log f$ at 163, 183, 203, 223, and 243 K. The data at the lower temperatures has the Af^n dependence with n nearly equal to 1.0. (b) Isothermal electrical relaxation data of glassy $LiAlSi_2O_6$ shown as plots of $\log[\epsilon''(f)]$ vs $\log f$ at 163, 183, 203, 223, and 243 K. The data at the lower temperatures has the $(A/\epsilon_0)f^{n-1}$ dependence with n nearly equal to 1.0.

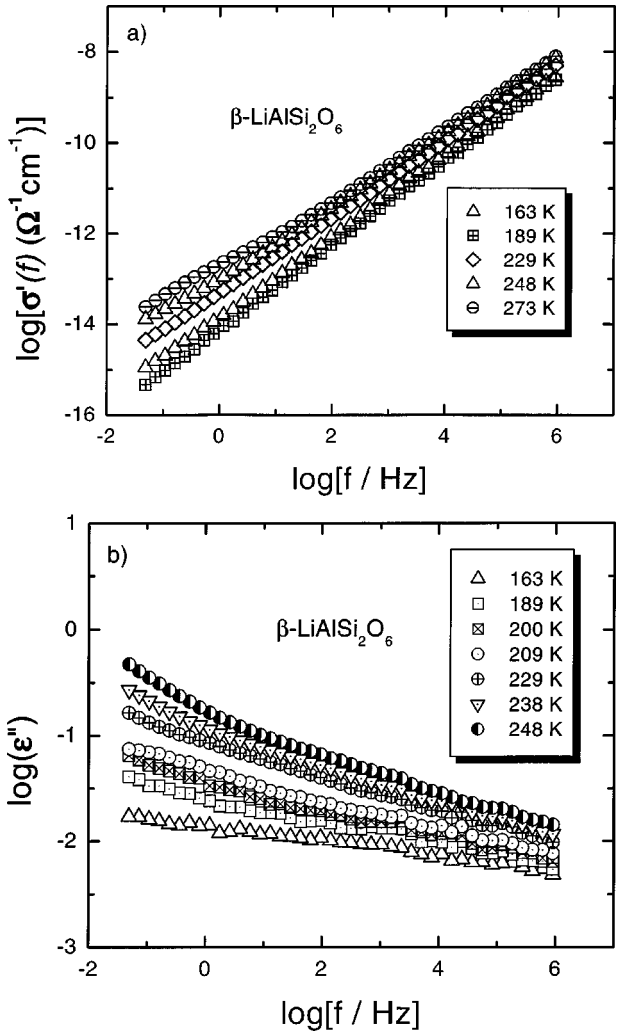

FIG. 2. (a) Isothermal electrical relaxation data of polycrystalline $LiAlSi_2O_6$ shown as plots of $\log[\sigma'(f)]$ vs log at 163, 189, 209, 248, and 273 K. The data at the lowest temperatures has the Af^n dependence with n nearly equal to 0.92. (b) Isothermal electrical relaxation data of polycrystalline $LiAlSi_2O_6$ shown as plots of $\log[\epsilon''(f)]$ vs log f at 163, 189, 200, 209, 229, 238, and 248 K. The data at the lowest temperatures has the $(A/\epsilon_0)f^{n-1}$ dependence, with n equal to 0.92, of the near constant loss.

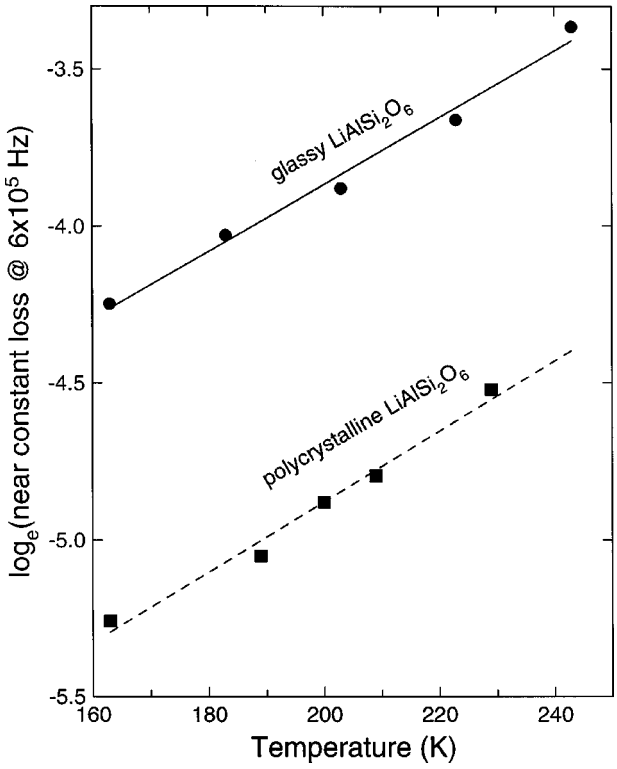

FIG. 3. Temperature dependence of the near constant loss at 6×10^5 Hz in glassy and polycrystalline $LiAlSi_2O_6$. The least-square fits to the data in this semilogarithmic plot indicate the temperature dependences in both forms of the ionic conductor are well-described by $\exp(T/T_a)$, where T_a is equal to 94 and 89 K for glassy and polycrystalline $LiAlSi_2O_6$, respectively. This figure serves also to show that the NCL in both forms of $LiAlSi_2O_6$ have similar temperature dependences and, at the same temperature, their magnitudes differ by a factor of about 2.7.

Fig. 3. For the glassy and polycrystalline $LiAlSi_2O_6$, T_a is equal to 94 and 89 K, respectively. Forced fits of the NCL to an Arrhenius temperature dependences have also been performed, but they lead to a very low and probably unphysical activation energy that is equal to 415 and 406 K for glassy and polycrystalline $LiAlSi_2O_6$, respectively. Such a weak temperature dependence of the NCL indicates that the NCL in glassy and polycrystalline $LiAlSi_2O_6$ does not originate from a thermally activated process.

The presence of NCL in polycrystalline $LiAlSi_2O_6$, comparable in order-of-magnitude and similar temperature dependence to the NCL in glassy $LiAlSi_2O_6$ (see Fig. 3), is the most interesting result of this work. These properties can be useful for understanding the mechanism that gives rise to the NCL because although they differ in physical structure, the chemical compositions of the two forms of $LiAlSi_2O_6$ are identical. For example, these properties suggest that structural disorder is not a prerequisite requirement for the mechanism that generates the NCL. Albeit it is conceivable that structural disorder can enhance the intensity of the NCL. Local hopping of the Li ion between the paired interstitial sites is unlikely to be the cause of the NCL because it is inconceivable that the dispersion of this local hopping process in polycrystalline $LiAlSi_2O_6$ can be so broad to explain the frequency dependence of the NCL. Further, NCL occurs in other glasses and crystalline $Li_xLa_{1-x}TiO_3$ in which there are no paired interstitial sites. In ionically conducting glasses and highly defective ceramics,[25] the NCL has been suggested to originate from relaxation of asymmetric double-well potentials (ADWP) having a broad distribution of relaxation times.[26] Real experimental evidence of ADWP has been seen in some ionic glasses, however the well-defined ones show up as peaks in the dielectric loss and not as the NCL.[26] No one has been able to describe the ADWP at an atomic level in glassy ionic conductors. Its extension to polycrystalline $LiAlSi_2O_6$ to explain the NCL makes the concept uncertain.

Having ruled out several possible origins of the NCL by the data of glassy and polycrystalline $LiAlSi_2O_6$, very few plausible choices remain. Before a mobile ion can hop by thermal activation, it is confined within the cage formed by the other ions and defined by an anharmonic potential. A previous work[21] has shown similar temperature dependence of NCL and the mean-square displacement of ion vibration below and above the glass transition temperature T_g. The

similarity suggests that a plausible mechanism that gives rise to the NCL is relaxation or difusion of the ion within the cage formed by the other ions at times before the ion hops out of the cage to contribute to conductivity. At higher temperatures, anharmonicity of the potential becomes more important and a possible cause of the increase of the NCL with temperature. More evidence of this link were found from the high frequency dielectric[19,20] and light scattering relaxation spectra[27,28] of the ionically conducting molten salt 0.4 $Ca(NO_3)\cdot 0.6\ KNO_3$ (CKN) above T_g. These relaxation spectra can be well-accounted for by the presence of the NCL. At these high temperatures, the NCL is much larger than in the glassy state, likely due to the effect of enhanced anharmonicity on the mean-square displacement of the ion within its cage. Caging of an ion is present also in the crystalline analogue of a glassy ionic conductor and the ion is also subjected to comparable anharmonic potential. Thus it is not surprising to have the NCL of comparable magnitude in both the crystalline and glassy states of the same ionically conducting substance as in the present case of $LiAlSi_2O_6$. In spite of the many evidences pointing to relaxation of an ion within the cage as the cause of the NCL, the mechanism that gives rise to many decades of nearly frequency independent loss is still unclear. The results of the present work should be useful as guidance to arrive at a satisfactory explanation of the microscopic origin of the NCL.

V. CONCLUSION

From our electrical conductivity measurements on polycrystalline $LiAlSi_2O_6$ and glassy $LiAlSi_2O_6$ that were made to study mainly the NCL, we can make the following conclusions.

(1) The NCL exists not only in glassy $LiAlS_2O_6$, but also in polycrystalline $LiAlSi_2O_6$.

(2) The magnitude of the NCL in polycrystalline $LiAlSi_2O_6$ is only about a factor between 2 and 3 times smaller than that in the glassy $LiAlSi_2O_6$ at the same temperature.

(3) It is not necessary to have structural disorder such as in a glass to generate the NCL. Although it may not be impossible, it is difficult to reconcile the proposed mechanisms of relaxation of ADWP or percolation of ions in a disordered medium for the NCL, with the observation of NCL of comparable magnitude and temperature dependence in polycrystalline and glassy $LiAlSi_2O_6$.

(4) The comparable magnitudes of the NCL in polycrystalline and glassy $LiAlSi_2O_6$ suggest that the mechanism that gives rise to the NCL is somehow related to the local motion (or vibrational relaxation) of the ion within the cage formed by the other ions. The cage defined by the anharmonic potential confining the ion is likely the only characteristic shared by both forms of $LiAlSi_2O_6$ as far as the NCL is concerned. Anharmonicity as well as mean-square displacement of the ion is expected to be larger in the glassy state than in the polycrystals, and this may explain the larger NCL observed in the former rather than in the latter.

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