

## Relaxation Model of Lithium Ions in the Garnet-like $\text{Li}_5\text{La}_3\text{Bi}_2\text{O}_{12}$ Lithium-Ion Conductor

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**Keywords:** Lithium Ion Conductor;  $\text{Li}_5\text{La}_3\text{Bi}_2\text{O}_{12}$ ; Internal Friction; Lithium Ion Diffusion.

**Abstract.** The relaxation mechanism of lithium ions in  $\text{Li}_5\text{La}_3\text{Bi}_2\text{O}_{12}$  electrolyte was investigated by internal friction (IF) method. A prominent relaxation-type IF peak was observed. From the shift of peak position with frequency, the activation energy of  $E=1.0-1.1$  eV and the pre-exponential factor of relaxation time in the order of  $\tau_0=10^{-25} \sim 10^{-18}$  s were obtained if one assumes a distributed Debye relaxation process. These values of relaxation parameters strongly suggest the existence of interaction between the relaxation species (here lithium ions or vacancies). Basing on the coupling model, the values of  $E$  and  $\tau_0$  were determined as 0.5-0.6 eV and  $10^{-17} \sim 10^{-15}$  s, which still deviated from the typical values for point defect relaxation. A new phenomenological model was used to describe the relaxation process, and the values of  $E$  and  $\tau_0$  were determined as 0.46 eV and  $3.6 \times 10^{-14}$  s, which is in agreement with the typical values for point defect relaxation.

### Introduction

Solid-state lithium electrolytes showing high ionic conduction at room temperature have been attracting great interest owing to their potential electrochemical applications in all-solid-state rechargeable lithium ion batteries, sensors, and other ionic devices [1]. The garnet-like  $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$  ( $M=\text{Nb}, \text{Ta}, \text{Bi}$ ) compounds [2-5] were found to have excellent pure lithium ionic conductivity as well as high decomposition voltages ( $>6\text{V}/\text{Li}$ ) at room temperature, making them promising for application as electrolyte in all solid state lithium rechargeable batteries. It is noted that the diffusion ability of lithium ions via vacancies plays a crucial role in lithium ionic conduction. So it is important to understand the key factors that control the lithium ion diffusion and to investigate the relaxation mechanism of lithium ions or vacancies because the long distance diffusion of lithium ions is realized through a series of jumps (or relaxation) of ions between the neighboring equilibrium sites.

In a previous study, two prominent internal friction (IF) peaks of relaxation type were observed in the aged pure  $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$  compounds [6], which are associated with the short-distance jump processes of lithium ions. However, the measured activation energy in the range of 0.8-0.9 eV for these two peaks is much larger than the values ( $\sim 0.5$  eV) deduced from the ionic conduction measurement. In a later investigation [7] it was revealed that in the aging process the proton doping was introduced through the reaction between  $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$  compounds and water vapors in the humid environment. Later on, we have carried out the IF study on the  $\text{Li}_7\text{La}_3\text{Ta}_2\text{O}_{13}$  compounds [8], and found that the larger activation energy and the smaller pre-exponential factor of relaxation time can be ascribed to the interaction between the relaxation species (lithium ions or vacancies) that can be appropriately described by the coupling model.

In this paper, the IF technique was exploited to investigate the microscopic transport properties of lithium ions in the  $\text{Li}_5\text{La}_3\text{Bi}_2\text{O}_{12}$  compound and the IF data were analyzed using the Debye model, the coupling model, and a new phenomenological model, respectively, in order to obtain the real dynamic parameters of the lithium ion diffusion.

## Experimental

The polycrystalline  $\text{Li}_5\text{La}_3\text{Bi}_2\text{O}_{12}$  samples (designated as sample LLBO) used in our experiments were synthesized with similar preparation route described in Ref. [9]. The measurements of low frequency internal friction (IF) were carried out on a computer controlled inverted torsion pendulum in the mode of forced vibration with a heating rate of 1 K/min and a maximum shear strain amplitude of  $1 \times 10^{-5}$ . The size of the strip samples is about  $50\text{mm} \times 4\text{mm} \times 1\text{mm}$ .

## Theoretical models

**Debye model.** In a system where the mutual interaction between the relaxation species is small enough to be neglected, the IF peak resulted from the jumps of the species among the neighboring equilibrium states can be well described by the Debye model:

$$Q^{-1} = \Delta \frac{\omega\tau}{1 + \omega^2\tau^2} \quad (1)$$

where  $\Delta$  is the relaxation strength,  $\omega = 2\pi f$  and  $f$  is the measurement frequency, and  $\tau = \tau_0 \exp(E/K_B T)$  is the relaxation time with the  $\tau_0$  being the pre-exponential factor and  $E$  the activation energy. If the IF was plotted as a function of  $\ln(\omega\tau)$ , a symmetric peak would appear at  $\omega\tau = 1$  with a width at half maximum being 2.634. In most cases however, there are distributions in both  $\Delta$  and  $\tau$ , and the peak will be broadened accordingly.

**Coupling model.** In the cases of strong mutual interaction between the relaxation species, the Debye model is not applicable, while the coupling model [10-13] is expected to be appropriate for describing this kind of mutual interaction. According to this model, the relaxation function  $C(t)$  is different in two regions separated by a crossover time  $t_c$ , that is,

$$C(t) = \exp(-t/\tau), \quad t \leq t_c \quad (2)$$

$$C(t) = \exp[-(t/\tau^*)^\beta], \quad t > t_c \quad (3)$$

where  $\tau$  and  $\tau^*$  are the decoupled (i.e., independent) and the coupled (or correlated) relaxation time, respectively, and  $\beta$  is the coupling parameter with the value of  $(0 < \beta \leq 1)$ , which decreases as the coupling strength increases. The existence of  $t_c$  is based on theoretical considerations, and confirmed by neutron-scattering experiments and molecular-dynamics simulations. The magnitude of  $t_c$  is of the order of  $10^{-11}$ - $10^{-12}$  s for amorphous polymers, and  $10^{-12}$ - $10^{-13}$  s for metals and ionic conductors.

From the condition of continuity of relaxation functions (2) and (3) at  $t = t_c$ , we have

$$\tau = t_c^{1-\beta} (\tau^*)^\beta \quad (4)$$

Considering the temperature dependence of relaxation time (Arrhenius law,  $\tau = \tau_0 \exp(E/K_B T)$  and  $\tau^* = \tau^*_0 \exp(E^*/K_B T)$ , respectively), we have

$$E = \beta E^* \quad (5)$$

$$\ln(\tau_0) = \beta \ln(\tau^*_0) + (1-\beta) \ln(t_c) \quad (6)$$

Where  $E$  and  $E^*$  are the decoupled and coupled activation energies,  $\tau_0$  and  $\tau^*_0$  are the pre-exponential factors of decoupled and coupled relaxation times, respectively. The IF peak corresponding to this coupling relaxation process can be obtained from the Fourier transformation of Eqs. (2) and (3), as done in Ref. [14], which is asymmetric in the plot of IF as a function of  $\ln(\omega\tau^*)$  if  $\beta \neq 1$ .

**The improved Jonscher's model.** In 1975 Jonscher [15] suggested a universal model to describe the dielectric relaxation in polymers where strong mutual interaction between the relaxation species plays crucial roles. Here we exploit it to describe the IF peak:

$$Q^{-1} = \Delta \frac{1}{(\omega\tau^*)^{-m} + (\omega\tau^*)^n} \quad (7)$$

where  $m$  and  $n$  fall in the range of  $(0 < m, n \leq 1)$  and may be temperature dependent in general. The case of  $m=n=1$  corresponds to the Debye model. Otherwise, the IF peak described by Eq. (7) appears at  $\ln(\omega\tau^*) = \ln(m/n)/(m+n)$  and is asymmetric in the plot of IF as a function of  $\ln(\omega\tau^*)$  if  $m \neq n$ , as shown in Fig.1 where the relaxation strength  $\Delta$  was set to be 0.5.

Similar to the coupling model, one can assume that at frequencies higher than  $\omega_c$  ( $\omega_c = \tau_c^{-1}$ ), the species relax independently, which can be described by Debye model, i.e. Eq. (1). From the continuity of relaxation functions (1) and (7) at  $\omega = \omega_c$  and considering  $\omega_c\tau^* \gg 1$ , we have

$$\tau = \tau_c^{1-n} (\tau^*)^n. \quad (8)$$

Again, assuming the Arrhenius law, we have

$$E = n E^*. \quad (9)$$

$$\ln(\tau_0) = n \ln(\tau_0^*) + (1-n) \ln(\tau_c). \quad (10)$$

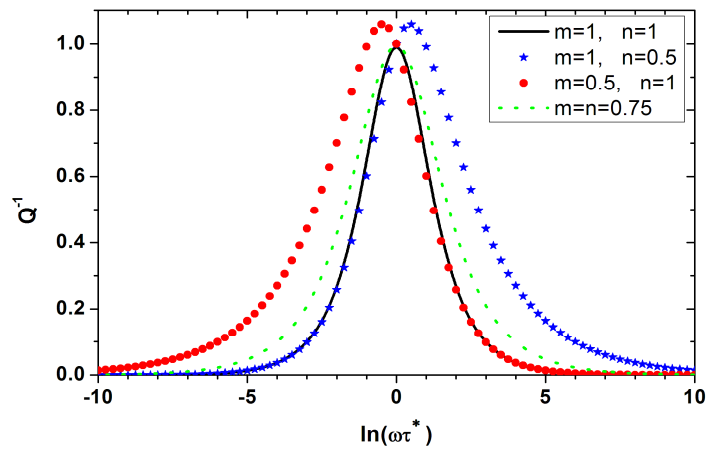


Fig. 1. Normalized IF versus  $\log_{10}(\omega\tau^*)$  for the improved Jonscher's model.

### Analysis of the experimental data by the models

Fig.2 shows the internal friction (IF) ( $Q^{-1}$ ) and the relative modulus ( $M$ ) versus the reciprocal of temperature at 0.5, 1, 2, and 4 Hz for LLBO samples. A prominent and wide IF peak was observed around 285K at 1Hz accompanied by a corresponding decrease in the modulus. The peak position shifts obviously toward higher temperature with the increase of frequency, which demonstrates that this peak is associated with a thermally activated relaxation process. As suggested in references [6, 8], this peak was associated with the short-distance jump processes of lithium ions.

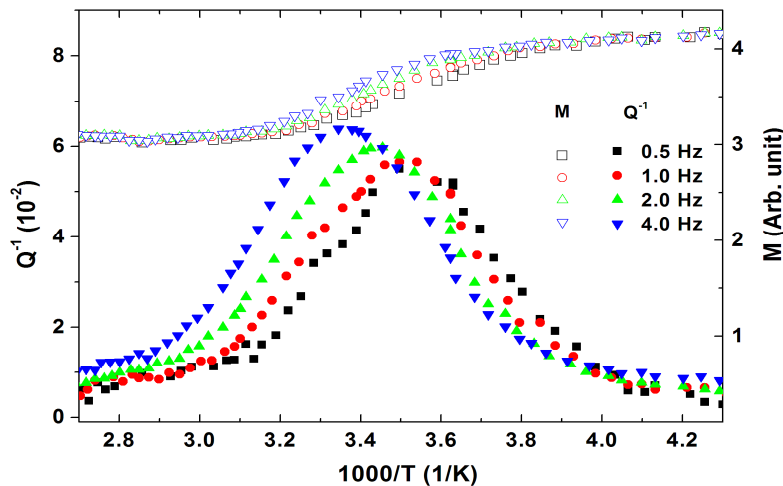


Fig. 2. The IF ( $Q^{-1}$ ) and the relative modulus ( $M$ ) versus  $1000/T$  for LLBO samples.

Accordingly, after carefully analyzing the data of the IF peak with the Debye model using a non-linear fitting method [16], the broad relaxation peak in LLBO compound can be fitted well by a Debye peak with distribution in relaxation time ( $\beta=2.8$ ) after subtraction of background. The relaxation parameters were obtained from the peak shift with frequency as  $E=1.1$  eV,  $\tau_0=2.4\times 10^{-20}$  s, as listed in Table 1. The activation energy is much higher than that deduced from lithium ionic conduction measurement (0.4 eV [9]). Furthermore, the  $\tau_0$  in the range of  $10^{-20}$  s is too small to have any physical meaning for a relaxation peak. Fitting the data with two or more Debye sub-peaks can not improve the issue. These results indicate the occurrence of mutual interaction between the relaxation species (here lithium ions or vacancies) that was further confirmed by the strong dipolar coupling of the lithium ions at low temperature deduced from the NMR results [17, 18], as well as by the IF study in  $\text{Li}_7\text{La}_3\text{Ta}_2\text{O}_{13}$  compounds [8], where the coupling model was exploited to describe the mutual interaction of the lithium ions.

However, one has to assume at least two sub-peaks when fitting the IF data of LLBO compounds by the coupling model, because the peak described by this model was skew. The fitting results were shown in Fig.3 for data at 1 and 4 Hz. The coupling parameter can be obtained as about 0.52 for both  $P_1$  and  $P_2$  peaks and the apparent (coupled) activation parameters were also unusual, as listed in Table 1. According to equations (5) and (6) and adopting  $t_c$  as  $10^{-12}$  s, one can obtain the decoupled activation energy and the pre-exponential factors of relaxation time as  $E_1=0.59$  eV,  $\tau_{01}=2.4\times 10^{-17}$  s for peak  $P_1$ , and  $E_2=0.52$  eV,  $\tau_{02}=1.3\times 10^{-15}$  s for peak  $P_2$ , respectively, as listed in Table 1. Although the decoupled  $\tau_0$  for peak  $P_2$  in the order of  $10^{-15}$  s falls in the range of typical values for processes of point defect relaxation, the decoupled activation energy of both peaks in the range of 0.5-0.6 eV is a little larger than the value deduced from the measurement of electrical conductivity in  $\text{Li}_5\text{La}_3\text{Bi}_2\text{O}_{12}$  compounds (0.40-0.49 eV [5, 9]) and the decoupled  $\tau_0$  for peak  $P_1$  is still too small. This means that the coupling model is not suitable to describe the relaxation process in the  $\text{Li}_5\text{La}_3\text{Bi}_2\text{O}_{12}$  compounds even though two sub-peaks were assumed.

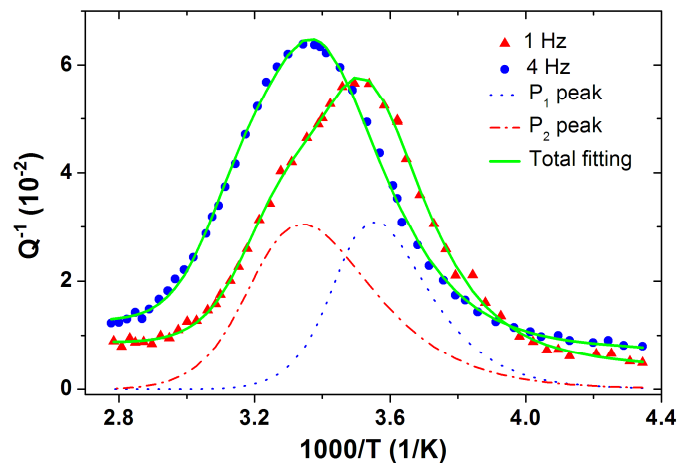


Fig. 3. The fitting results of experimental data at 1 and 4 Hz fitted by the coupling model.

Therefore, we have fitted the IF data by the temperature independent background and one peak according to the improved Jonscher's model and the fitting results were shown in Fig.4 for data at 1 and 4 Hz. The coupling parameters can be obtained as  $m=0.63$  and  $n=0.58$  and the apparent (coupled) activation parameters were more meaningful than those deduced from both Debye model and coupling model, as listed in Table 1. According to equations (9) and (10) and adopting  $t_c$  as  $10^{-12}$  s, one can obtain the decoupled activation energy and the pre-exponential factor of relaxation time as  $E=0.46$  eV,  $\tau_0=3.6\times 10^{-14}$  s, as listed in Table 1, which are in agreement with the typical values for point defect relaxation. More interestingly, the decoupled activation energy of 0.46 eV is very close to the value of 0.40-0.49 eV for electrical conductivity in  $\text{Li}_5\text{La}_3\text{Bi}_2\text{O}_{12}$  compounds [5, 9]. These results illustrate that the improved Jonscher's model can well describe the relaxation process in the  $\text{Li}_5\text{La}_3\text{Bi}_2\text{O}_{12}$  compounds.

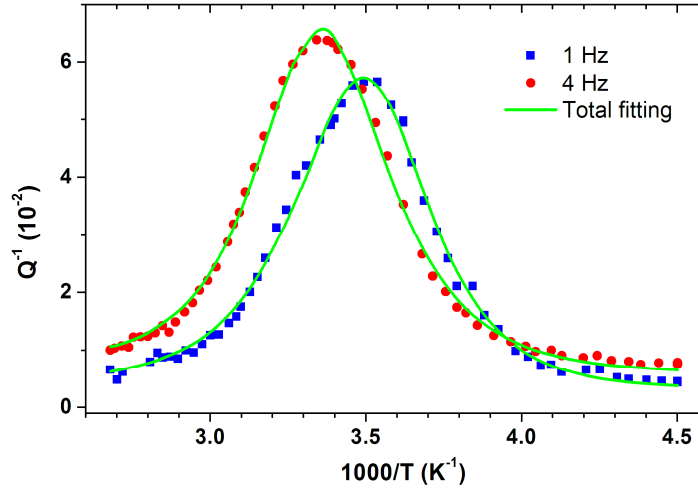


Fig. 4. The fitting results of experimental data at 1 and 4 Hz fitted by the improved Jonscher's model.

Table 1 Relaxation parameters of peaks in  $\text{Li}_5\text{La}_3\text{Bi}_2\text{O}_{12}$  compound deduced with different models

	Debye model	Coupling model		The improved Jonscher's model
		P <sub>1</sub> peak	P <sub>2</sub> peak	
E* [eV]	1.1	1.1	1.0	0.78
$\tau^*_0$ [s]	$2.4 \times 10^{-20}$	$5.8 \times 10^{-22}$	$1.8 \times 10^{-18}$	$3.3 \times 10^{-15}$
m, n, $\beta$	$\beta=2.8$	$\beta=0.52$	$\beta=0.52$	m=0.63; n=0.58
E [eV]	-	0.59	0.52	0.46
$\tau_0$ [s]	-	$2.4 \times 10^{-17}$	$1.3 \times 10^{-15}$	$3.6 \times 10^{-14}$

## Summary

In summary, a prominent and wide relaxation IF peak was observed in the garnet-like  $\text{Li}_5\text{La}_3\text{Bi}_2\text{O}_{12}$  electrolytes, which was associated with the short distance diffusion of lithium vacancies. The IF data were analyzed using the Debye model, the coupling model and the improved Jonscher's model, respectively. The high activation energy and small pre-exponential factor of the relaxation time obtained by fitting the data at different measurement frequency with Debye model indicate that the lithium vacancies do not relax independently and the mutual interaction among them exists. After comparing the fitting results with the coupling model and the improved Jonscher's model, both of which takes into consideration the mutual interaction of the relaxation species, it was concluded that the improved Jonscher's model is more suitable to describe the relaxation process in  $\text{Li}_5\text{La}_3\text{Bi}_2\text{O}_{12}$  based electrolytes. However, it is necessary to carry out more theoretical and experimental investigations to confirm the validation of the improved Jonscher's model and to clarify its physical basis in details.

## Acknowledgments

This work has been subsidized by the National Natural Science Foundation of China (grant nos. 50702061, 10874185, and 11075177) and the Anhui Provincial Natural Science Foundation (grant no. 090414181).

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## **Internal Friction and Mechanical Spectroscopy**

10.4028/www.scientific.net/SSP.184

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**Li<sub>5</sub>La<sub>3</sub>Bi<sub>2</sub>O<sub>12</sub>Lithium-Ion  
Conductor**

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