

Vibrational Spectra and Energy Characteristics of the Superionics Li_4SiO_4 and Li_4GeO_4

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Infrared (IR) and Raman spectra of the superionic conductors Li_4SiO_4 and Li_4GeO_4 , including ^6Li -substituted compounds, have been studied. Results of the theoretical analysis of the spectra in conjunction with data on the electrostatic field calculations are presented. E_z and E_y components of the electrostatic field vector were found to be very small in the vicinity of the cation positions in the structures of Li_4SiO_4 and Li_4GeO_4 . Amplitudes of the lithium cation vibrations were calculated from the spectral data. Maximal amplitudes of vibrations were found in the [001] and [010] crystallographic directions for the Li_4SiO_4 and Li_4GeO_4 , respectively. The obtained results give information about mechanism of the lithium cations migration in the big group of superionic conductors. © 1997 Academic Press

INTRODUCTION

Lithium orthosilicate (Li_4SiO_4) and lithium orthogermanate (Li_4GeO_4) have low ionic conductivities at room temperature ($2.4 \times 10^{-10} \text{ Ohm}^{-1} \text{ cm}^{-1}$ (1) and $3.1 \times 10^{-12} \text{ Ohm}^{-1} \text{ cm}^{-1}$ (2) correspondingly). However, their solid solutions with lithium sulfate, lithium molybdate, and some other lithium salts show high cationic conductivity (2, 4–7). That is why the study of the vibrational spectra of the Li_4SiO_4 and Li_4GeO_4 can give information helpful for a better understanding of the mechanism of the cations transfer in the big group of cationic conductors.

Crystal structure of the Li_4GeO_4 (7) has a tetragonal symmetry, space group $Bmmb$ (D_{2h}^{17}) with two formula units in the unit cell. Discreet tetrahedra of the GeO_4 are located in the positions with C_{2v} symmetry. Lithium cations occupy the positions with C_2 and C_s point group symmetry and possess tetragonal oxygen coordination. Cationic transport in this compound is realized through the channels in the crystal structure.

Discreet tetrahedral groups (SiO_4) are also present in the crystal structure of the Li_4SiO_4 . In this structure, lithium cations have coordination numbers 4, 5, and 6, and their

positions are not fully occupied. The presence of the vacancies in the cationic sublattice is the reason for the conductivity in this compound. The crystal structure of Li_4SiO_4 was determined in the monoclinic space group $P2_1/c$ (C_{2h}^2) with two formula units in the unit cell (8). Superstructure with a seven times larger unit cell had been reported in an earlier investigation (9). However, in both cases, the crystal structure refinement had been carried out using the same space group, and geometrical parameters concerning the SiO_4 surroundings were found to be similar.

In the past, the vibrational spectra of silicates and germanates were the subject of several investigations (10–14). Vibrational spectra of the Li_4SiO_4 and Li_4GeO_4 were described earlier (15). However, only analysis of vibrations of the SiO_4 and GeO_4 groups was reported. Lack of experimental data from the ^6Li -substituted samples did not permit the authors to make complete band assignment, especially in the long wave length region.

Investigation of the lithium sublattice vibrations is mostly the focus of the present work. We have tried to combine spectroscopic results with the data obtained from the theoretical calculations of the electrostatic field in the crystal structure.

EXPERIMENTAL

Samples were obtained by the solid state reaction from the lithium carbonate (Li_2CO_3) and silicon or germanium oxides (SiO_2 , GeO_2). $^6\text{Li}_2\text{CO}_3$ which contained 95% of ^6Li served as a starting material in the synthesis of the isotope-substituted samples. Starting materials taken in the stoichiometric amounts were mixed in methanol in agate mortars till dryness. Obtained mixtures were kept in platinum crucibles for five hours at 750°C . In the next stage, Li_4SiO_4 was annealed at 1000°C for two hours, and then for two more hours at 1200°C (16). Lithium germanate was kept at 1150°C for four hours (17). Purity of the resulting samples was controlled by the X-ray powder diffraction method. Camera FR-552 with $\text{CuK}\alpha$ radiation was employed.

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Raman spectra from the polycrystalline samples were recorded using a multichannel spectrometer with triple monochromatization. The 5145-Å exciting line from the argon ILA-120M laser was used. Scattering spectra were measured using a slit width for the spectrometer of 100 μm . IR absorption spectra were measured on the Fourier spectrometer Bruker IFS-113v. Samples were prepared as pellets with KBr or as nujol mulls. The resulting spectra are presented in Figs. 1 and 2, while the wavenumbers of the bands of absorption are combined in the Tables 1 and 2. Calculations of wavenumbers of the normal vibrations were performed using a valence force field approximation. Final values of the force constants for which differences between calculated and experimental wavenumbers did not exceed 10 cm^{-1} are listed in the Table 3.

Calculations of the Madelung constants (related to the shortest Si–O and Ge–O distances), electrostatic potentials, and components of electrostatic field vector were done with a computer program based on Evald summation method (18,19). Formal ion charges were used. Components of electrostatic field vector were calculated with the 0.2-Å step in the planes parallel to the crystallographic (100), (010), and (100) and intersecting in the cation positions.

RESULTS AND DISCUSSION

Several factors have been taken into account during the analysis of the spectra of the Li_4SiO_4 and Li_4GeO_4 , and band assignment to the vibrations of certain sublattice. In our consideration we have based our calculations on the literature data, the shifts of the band positions in the spectra

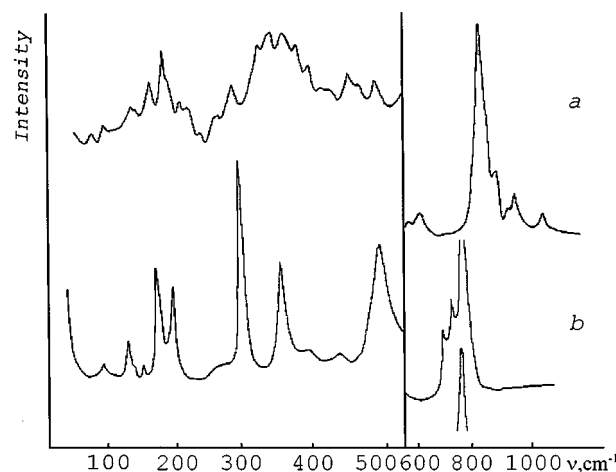


FIG. 2. Raman spectra of Li_4SiO_4 (a) and Li_4GeO_4 (b).

of ^6Li substituted samples, the group theory analysis, and the results of the calculations of the wavenumbers of the normal vibrations. Unfortunately, the absence of the single crystal data did not allow us to make full assignment of the vibrations with regard to their symmetry. Only types of vibrations were determined.

According to the results of the theoretical analysis, 27 modes are expected in Raman spectrum of the Li_4GeO_4 (at $k = 0$) and 20 in IR absorption spectrum:

$$\Gamma_{\text{vibr.}} = 8A_g(\text{R}) + 7B_{1g}(\text{R}) + 6B_{2g}(\text{R}) + 6B_{3g}(\text{R}) \\ + 4A_u(\text{inact.}) + 4B_{1u}(\text{IR}) + 8B_{2u}(\text{IR}) + 8B_{3u}(\text{IR}).$$

Modes of the lithium sublattice will be described by the following irreducible representation:

$$\Gamma_{\text{vibr. Li}} = 3A_g(\text{R}) + 3B_{1g}(\text{R}) + 3B_{2g}(\text{R}) + 3B_{3g}(\text{R}) \\ + 2A_u(\text{inact.}) + 2B_{1u}(\text{IR}) + 4B_{2u}(\text{IR}) + 4B_{3u}(\text{IR}).$$

Modes of the rotational vibrations of the GeO_4 tetrahedra will be given by the following irreducible representation:

$$\Gamma_{\text{rot.}} = B_{1g}(\text{R}) + B_{2g}(\text{R}) + B_{3g}(\text{R}) + A_u(\text{inact.}) \\ + B_{2u}(\text{IR}) + B_{3u}(\text{IR}).$$

Results of the factor group analysis of the internal vibrations of the GeO_4 groups are summarized in Table 4. According to the band assignment proposed earlier (11), three regions can be identified in the spectrum of the Li_4GeO_4 :

(1) Range from 850 to 650 cm^{-1} where bands corresponding to the valence vibrations of the GeO_4 tetrahedrons are located.

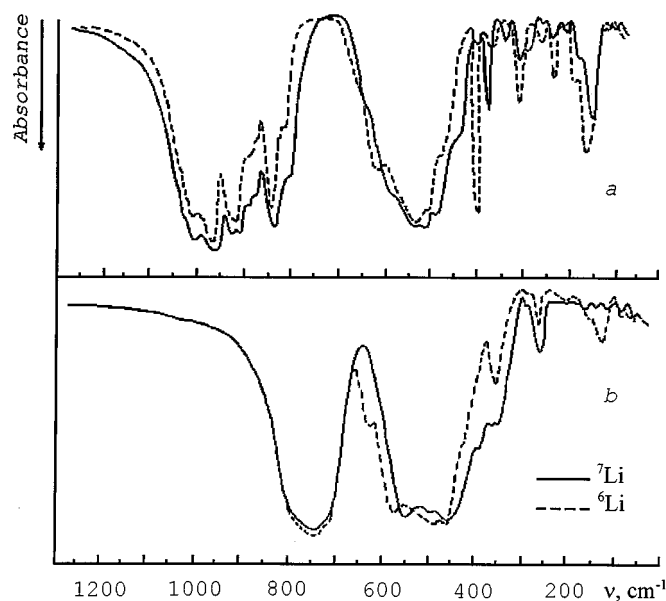


FIG. 1. IR absorption spectra of Li_4SiO_4 (a) and Li_4GeO_4 (b).

TABLE 1
Vibrational Wavenumbers of Li_4GeO_4 , $\nu \text{ cm}^{-1}$

Raman		IR		Assignment
^6Li 1	^7Li 2	^6Li 3	^7Li 4	
		790 sh	790 sh	$\nu_3 \text{ GeO}_4$
762	762			$\nu_1 \text{ GeO}_4$
		749	749	$\nu_3 \text{ GeO}_4$
725	725			$\nu_3 \text{ GeO}_4$
		715	715	$\nu_3 \text{ GeO}_4$
695	695			$\nu_3 \text{ GeO}_4$
		625	—	$T \text{ Li/Li}$
		571	543	$T \text{ Li/Li}$
		534	—	$\delta \text{ O-Ge-O}$
550 sh	550			$\delta \text{ O-Ge-O}$
517	491			$T \text{ Li/Li}$
		492	486	$T \text{ Li/Li}$
		459	459	$\delta \text{ O-Ge-O}$
451	438			$T \text{ Li/Li}$
		414	395	$T \text{ Li/Li}$
407	394			$T \text{ Li/Li}$
363	359			$R + T \text{ Li/Li}$
		—	359	$\delta \text{ O-Ge-O}$
		357	343	$T \text{ Li/Li}$
		331 sh	—	$\delta \text{ O-Ge-O}$
303	300			$R + T \text{ Li/Li}$
		277	277	R
275	265			$T \text{ Li/Li}$
		258	255	$R + T \text{ Li/Li}$
		207	—	$?$
201	198			$T \text{ Li/Li}$
187 sh	187 sh			$T \text{ Ge/Ge}$
174	174			$T \text{ Ge/Ge}$
160	155			$T \text{ Li/Li}$
		—	154	$T \text{ Ge/Ge}$
		149	131	$T \text{ Li/Li}$
133	133			$T \text{ Ge/Ge}$
		122	113	$T \text{ Li/Li}$
	117			$?$
111				$?$
		104	96	$T \text{ Li/Li}$
95	95			$T \text{ Ge/Ge}$
—	86			$?$
77	77			$T \text{ Ge/Ge}$
		76	—	$?$
60	—			$?$

(2) Range from 650 to 370 cm^{-1} where bands corresponding to the deformational vibrations of the GeO_4 groups are located.

(3) Range below 370 cm^{-1} where bands corresponding to the external modes are located.

IR spectra obtained in the course of our work were very similar to those reported earlier (15). We have observed 19 bands in each type of vibrational spectrum, IR absorption and Raman. It should be noted that several bands could be observed only in the spectrum of $^6\text{Li}_4\text{GeO}_4$, and they were

TABLE 2
Vibrational Wavenumbers of Li_4SiO_4 , $\nu \text{ cm}^{-1}$

Raman		IR		Assignment
^6Li 1	^7Li 2	^6Li 3	^7Li 4	
1040	1040			Components of $\nu_3 \text{ SiO}_4$
		1040	1040	
		1020	1020	
		1005	1005	
		985	985	
		956	956	
947	947			
929	929			
		920	920	
		908	908	
886	886			
		883	883	
		869	869	
		836	836	Components of $\nu_1 \text{ SiO}_4$
824	824			
		812	812	
		800	800	
		670	640	$T \text{ Li/Li}$
635	598			$T \text{ Li/Li}$
		610	585	$T \text{ Li/Li}$
598	554			$T \text{ Li/Li}$
		560 sh	560 sh	$\delta \text{ O-Si-O}$
		536	536	$\delta \text{ O-Si-O}$
		—	524	$T \text{ Li/Li}$
		518	498	$T \text{ Li/Li}$
486	486			$\delta \text{ O-Si-O}$
		468	445	$T \text{ Li/Li}$
468	468			$\delta \text{ O-Si-O}$
455	449			$T \text{ Li/Li}$
428	428			$\delta \text{ O-Si-O}$
		420	400	$T \text{ Li/Li}$
412	412			$\delta \text{ O-Si-O}$
		395	372	$T \text{ Li/Li}$
—	394			R
385	380			$T \text{ Li/Li}$
—	359			$T \text{ Li/Li}$
		365	353	$T \text{ Li/Li}$
353	340			$T \text{ Li/Li}$
348	323			$T \text{ Li/Li}$
		343	340	$T \text{ Li/Li}$
		307	302	$T \text{ Li/Li}$
296	286			$T \text{ Li/Li}$
		—	285	$T \text{ Li/Li}$
		266	262	$T \text{ Li/Li}$
266	261			$R + T \text{ Li/Li}$
237	237			R
		234	231	$R + T \text{ Li/Li}$
220	220			RSi
		216	210	$T \text{ Li/Li}$
207	207			$T \text{ Si/Si}$
192	192			$T \text{ Si/Si}$
		187 sh	—	$?$
181	181			$T \text{ Si/Si}$
		181	177	$T \text{ Li/Li}$
165	162			$T \text{ Li/Li}$
		156	152	$T \text{ Li/Li}$
135	135			$T \text{ Si/Si}$
96	96			$?$
75	75			$?$

TABLE 3
Force Constants (mdyn/Å)

Constant	Li_4SiO_4	Li_4GeO_4
$f_{\text{Si(Ge)-O}}$	5.6	3.9
	4.6	3.85
	4.5	
$f_{\text{Li-O}}$	0.48	0.85
	0.25	0.75
	0.22	0.65
	0.18	0.60
	0.10	
f_{OSiO}	1.10	0.80
	1.05	
$f_{\text{Si-O}}^{\text{Si-O}}$	0.35	0.10
$f_{\text{Li-O}}^{\text{Li-O}}$	0.05	0.04

masked by others in the spectrum of $^7\text{Li}_4\text{GeO}_4$ as a result of the isotope shift effect.

According to the results of the theoretical analysis (see Table 4), four absorption bands, corresponding to the valence vibrations of the GeO_4 group could be seen in each type of vibrational, Raman and IR spectrum. One component is observed corresponding to the symmetric vibration of the tetrahedral group $\nu_1(A_1)$, and three components are observed corresponding to the triply degenerate vibration $\nu_3(F_2)$. It is a well-known fact that in case of tetrahedral anions ratio of the frequencies, ν_1 and ν_3 depend on the mass of the central atom. In case of germanium, these frequencies are very close, and the positions of the bands (ν_1 and ν_3) depend on the splitting of the triply degenerate vibration into the components. Each of the observed spectra has three bands in this region in agreement with the previously reported data (15). The most intensive high wavenumber band at 762 cm^{-1} in Raman spectra is assigned to the symmetric valence vibration $\nu_1(A_1)$. It is possible that the weak shoulder at 790 cm^{-1} corresponds to this mode in the IR absorption spectrum. However, it is more probable and in accord with the results of our calculations of normal vibrations that

all three bands observed in the IR spectrum correspond to the $\nu_3(F_2)$ components. Perhaps the intensities of the missing bands are very weak and are completely masked in the spectrum.

Bands corresponding to the valence and deformational vibrations of the GeO_4 group show up in the regions expected (11), except the modes of the lithium sublattice which have higher wavenumbers.

According to the theoretical prediction, 10 bands in the IR absorption spectrum and 12 in the Raman can originate from the vibrations of the lithium sublattice. Experimentally, we found that 9 bands in IR and 8 in Raman are subject to the isotope shift. Relatively large isotope shifts were observed for these bands, up to 28 cm^{-1} for the high wavenumber band. Such a large isotope shift has never been observed in vibrational spectra of the ^6Li - ^7Li substituted compounds (20). This leads us to the conclusion that lithium vibrations are mostly localized on the cationic sublattice, and are very weakly mixed with vibrations of the GeO_4 tetrahedra. Results of our calculations of the wavenumbers of the normal vibrations also support this idea.

Observed high wavenumbers of the vibrations of lithium sublattice (up to 625 cm^{-1}) are in an agreement with the fact of tetrahedral coordination of the lithium cations.

It is more difficult to make an assignment of rotational vibrations of the GeO_4 groups. In case of the SiO_4 tetrahedra, corresponding bands are located in the range between 390 and 350 cm^{-1} and around 225 cm^{-1} (11, 21). Taking into account similarity of the SiO_4 and GeO_4 groups, we expect close values for their rotational wavenumbers. Generally speaking, these wavenumbers should not be affected by the isotope substitution in the cation sublattice, and their intensities should be higher in Raman spectrum than in IR absorption spectrum. Bands insensitive toward the ^6Li substitution were not observed in the specified region of the Raman spectrum of the Li_4GeO_4 . Obviously, rotational vibrations perturb movements of light lithium cations. However, it is possible to identify bands with relatively small isotope shifts. In Table 1, these vibrations are specified as the mixed $R + T$ Li/Li. Nevertheless,

TABLE 4
Results of the Group Theory Analysis of Internal Vibrations

Li_4GeO_4			Li_4SiO_4		
Point group T_d	Site group C_{2v}	Factor group D_{2h}	Point group T_d	Site group C_s	Factor group C_{2h}
A_1	A_1	$A_g(\text{R}) + B_{1u}(\text{IR})$	A_1	A'	$A_g(\text{R}) + B_u(\text{IR})$
E	$A_1 + A_2$	$A_g(\text{R}) + B_{1g}(\text{R}) + A_u(\text{IR}) + B_{1u}(\text{IR})$	E	$A' + A''$	$A_g(\text{R}) + B_g(\text{R}) + A_u(\text{IR}) + B_u(\text{IR})$
F_2	$A_1 + B_1 + B_2$	$A_g(\text{R}) + B_{2g}(\text{R}) + B_{3g}(\text{R})$ $+ B_{1u}(\text{IR}) + B_{2u}(\text{IR}) + B_{3u}(\text{IR})$	F_2	$2A' + A''$	$2A_g(\text{R}) + B_g(\text{R}) + A_u(\text{IR}) + 2B_u(\text{IR})$
F_2	$A_1 + B_1 + B_2$	$A_g(\text{R}) + B_{2g}(\text{R}) + B_{3g}(\text{R})$ $+ B_{1u}(\text{IR}) + B_{2u}(\text{IR}) + B_{3u}(\text{IR})$	F_2	$2A' + A''$	$2A_g(\text{R}) + B_g(\text{R}) + A_u(\text{IR}) + 2B_u(\text{IR})$

the number of identified bands (two in the Raman spectrum ($363\text{--}359\text{ cm}^{-1}$, $303\text{--}300\text{ cm}^{-1}$) and two in the IR absorption spectrum (277 cm^{-1} , $258\text{--}255\text{ cm}^{-1}$)) is less than the theoretically predicted number of rotational modes.

The spectra of Li_4SiO_4 are more complicated. Observed wavenumbers of the valence and deformational vibrations of the SiO_4 tetrahedra are in an agreement with the literature data for silicates (11). However, bands attributed as the valence vibrations have a complicated multiplet structure, and the number of observed bands is much larger than theoretically predicted for the two SiO_4 tetrahedra in the primitive cell. Nonequivalence of the SiO_4 groups can arise due to statistics in the distribution of lithium cations.

Theoretical analysis of the vibrations of the Li_4SiO_4 crystal has been done in the supposition that the cation sublattice is fully occupied. Presence of the statistically distributed vacancies in the lithium sublattice can result in a decrease of the intensities of the bands but should not change their total number. According to the following equation, 39 normal modes are expected in the IR absorption spectrum and 42 in the Raman spectrum of the Li_4SiO_4 :

$$\Gamma_{\text{vibr.}} = 24A_g(\text{R}) + 18B_g(\text{R}) + 17A_u(\text{IR}) + 22B_u(\text{IR}).$$

Irreducible representation for the modes of the lithium sublattice given as follows:

$$\Gamma_{\text{vibr.Li}} = 15A_g(\text{R}) + 12B_g(\text{R}) + 12A_u(\text{IR}) + 15B_u(\text{IR}).$$

Irreducible representation for the rotational modes of the SiO_4 groups given as:

$$\Gamma_{\text{rot.}} = A_g(\text{R}) + 2B_g(\text{R}) + 2A_u(\text{IR}) + B_u(\text{IR}).$$

The IR spectra of Li_4SiO_4 obtained in the course of our work were very similar to those reported before [15], although we observed a larger number of bands. Despite the fact that the total number of bands observed in IR and Raman spectra is less than theoretically predicted, it is clear that the presence of superstructure influences the spectra. For instance, in the region where bands corresponding to the valence vibrations of the SiO_4 groups are expected, we observed 5 bands in the Raman spectrum and 12 in the IR absorption spectrum instead of the 4 theoretically predicted in each spectrum. These bands can be divided into four groups: bands corresponding to the $\nu_1(A_1)$ modes of the tetrahedral anion at 824 cm^{-1} in the Raman spectrum and at $812, 810\text{ cm}^{-1}$ in the IR spectrum and $\nu_3(F_2)$ with the wavenumbers at $1040\text{--}869\text{ cm}^{-1}$. This assignment is in a good agreement with the calculated wavenumbers of the normal vibrations. Nevertheless, the number of bands observed in this region of the spectra is smaller than what is expected taking into account the superstructure. Probably it

is fair to say that the spectrum of Li_4SiO_4 can be satisfactorily described by the sublattice representation. The superstructure is responsible for the thin structure observed for certain bands.

At the same time the number of bands affected by the isotope shift, 16 in the Raman spectrum and 10 in the IR absorption spectrum, is less than that in the case of Li_4GeO_4 . The isotope shift is more pronounced in the spectrum of Li_4SiO_4 than in the spectrum of Li_4GeO_4 and can be as large as 41 cm^{-1} . Three regions with large isotope shift can be identified in the spectrum of Li_4SiO_4 . Bands in the region $670\text{--}550\text{ cm}^{-1}$ arise from the vibrations of tetrahedrally coordinated cations, in the range $520\text{--}370\text{ cm}^{-1}$ from penta coordinated cations, and below 360 cm^{-1} from the lithium cations with octahedral coordination.

Wavenumbers of the rotational vibrations of the SiO_4 groups turned out to be close to those reported for silicates (11, 21). Only one band of absorption in the corresponding region, at $234\text{--}231\text{ cm}^{-1}$, was the subject of the isotope shift. Three bands at $394, 237, \text{ and } 220\text{ cm}^{-1}$ in the Raman spectrum were insensitive toward the $^6\text{Li}\text{--}^7\text{Li}$ substitution.

Bands that are insensitive toward the $^6\text{Li}\text{--}^7\text{Li}$ substitution and are located below 210 cm^{-1} in the spectra of Li_4SiO_4 and Li_4GeO_4 we consider as the translational vibrations T Ge/Ge and T Si/Si.

According to the results of our calculations, the maximum amplitudes of the lithium cation vibrations (shift more than 0.2 \AA) are in the [001] crystallographic direction in the structure of Li_4GeO_4 . In the structure of Li_4SiO_4 , such preferential direction [010] with shifts up to 0.21 \AA was found only for the octahedrally coordinated cations. Amplitudes of the vibrations of the cations that are located in the other positions were found to be equal in all crystallographic directions.

These data strongly correlate with the results of our calculations of the electrostatic characteristics of the crystal lattices of Li_4SiO_4 and Li_4GeO_4 which are presented in the Table 5. Values of the electrostatic potential and electrostatic field in the vicinity of the lithium cations correlate with the migration ability of the cations. It is not enough to have low values of electrostatic potential in the vicinity of the cation position for them to be mobile. However, it is more important that this value does not change much within a certain distance. Change of the electrostatic potential within a certain distance is described by the electrostatic field which is a derivative of potential by distance. Low values of the electrostatic field in the vicinity of the cation positions mean that the cations can leave their sites easily. As a result of our calculations, we determined that the E_z component of the electrostatic field vector in the structure of Li_4GeO_4 and the E_y component for the octahedrally coordinated cations in the structure of Li_4SiO_4 are almost equal to zero. On the one hand, these directions coincide with directions of channels in the crystal structures, and on

TABLE 5
Electrostatic Characteristics

Characteristics	Li_4GeO_4			Li_4SiO_4		
Madelung constant	31.763			24.0–25.5		
Shortest distance Si(Ge)–O, (Å)	1.650			1.634		
Lithium coordination number	4	4	4	5	6	
Partial Madelung constants in the lithium positions	1.187	0.910		<0.8		
Potential in the lithium positions ($e/\text{\AA}$)	1.439	1.110		<1.0		
Components of the electrostatic field	E_x	10	$10\text{--}10^2$	10^5	10^2	10^2
in vicinities of lithium	E_y	10^6	10	10^2	10^2	0
positions, ($e/\text{\AA}^2$)	E_z	10	0	10^4	10^2	10

the other hand, they coincide with directions where the amplitudes of the lithium vibrations have maximum values. All of this implies that the cation transport realizes in the same directions. This is in agreement with the results of the previous study (9) based on the analysis of the crystal structure of Li_4SiO_4 .

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