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A study on irradiation-induced structural change of lithium orthosilicate by infrared spectroscopy analysis with MNDO calculation

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Abstract

Properties of lithium orthosilicate, Li_4SiO_4, as a tritium breeding material will be substantially affected by structural change due to irradiation. An infrared absorption at 1040 cm^{-1} appeared in the FT-IR PAS spectra of Li_4SiO_4 irradiated with high energy oxygen ions. The semi-empirical molecular orbital method, MNDO, was applied to the interpretation of the changes of FT-IR PAS spectra of irradiated Li_4SiO_4. Vibrational frequencies and force constants have been calculated for the silicate clusters model: SiO_4 isolated tetrahedron, Si_2O_7 dimers, Si_2O_6 chain links, Si_2O_5 sheet units, and Si_2O_4 three-dimensional (3D) framework units. The calculations show that the Si–O–Si stretching vibrations are dependent on the degree of polymerization of the tetrahedron and connection of Li atoms. By comparing the FT-IR PAS spectra obtained experimentally in this study with the calculated spectra, the absorption at 1040 cm^{-1} due to the irradiation was assigned to the Si–O–Si stretching vibrations in the Si_2O_5 sheet and Si_2O_4 3D-framework structures. © 1997 Elsevier Science B.V.

1. Introduction

Inorganic compounds containing lithium are among the candidate of ceramic breeders for production of tritium in thermonuclear reactions, and the ceramic breeders are exposed to high energy neutrons and energetic particles from nuclear reactions in the fusion blanket environment. Such neutrons and particles cause radiation damage in the ceramic breeders. The radiation damage may lead to changes of various materials properties, i.e., physico-chemical properties, mechanical properties, transport behavior, etc.

Formation and properties of radiation-induced defects and radiolysis products in lithium silicates that are candidates of breeder materials have been investigated using various types of irradiation [1–3]. In-site luminescence measurements of lithium ortho- and metasilicates during proton irradiation suggested formation of peroxy species in the silicates due to the irradiation [1]. Electroparamagnetic resonance spectra of lithium silicates irradiated with ^{60}CO γ-ray were characterized by oxygen radicals of the O_2^- type formed in $2Li_2O \cdot SiO_2$ and $Li_2O \cdot SiO_2$ silicates [2].

The structure of lithium orthosilicate (Li_4SiO_4) has been studied in detail by X-ray diffraction, electron diffraction and infrared (IR) spectroscopy [4–6]. The structure is known to be sensitively detected by vibrational spectroscopy in the mid-infrared region. Vibrational spectroscopy is a powerful tool for the investigation of silicate chemistry. In particular, infrared photoacoustic spectroscopy (IR PAS) is suitable for nondestructive analysis of irradiated materials [7,8]; however, there are few IR spectroscopic studies on the structure of irradiated Li_4SiO_4. Our study on the radiation effect on the structure of Li_4SiO_4 using the IR PAS has been the only reported [7]. In our previous study, the new phases due to the irradiation in Li_4SiO_4 and $Li_{3.7}Al_{0.1}SiO_4$ appeared with increasing fluence. A structure of the new phases due to irradiation was not clarified.

Many experimental and theoretical studies on IR and Raman spectra for the silica and alkali silicate glasses have

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been performed by Lazarev [9] and McMillan [10]. It is well known that silica glass consists of a three-dimensional (3D) framework structure of SiO_4 tetrahedra, and that introduction of alkali oxides to silica glass breaks the Si–O–Si bridging bonds, creating non-bridging oxygens.

Changes of Raman and IR spectra of alkali silicate glass due to increase of alkali ions were interpreted by theoretical Raman and IR spectra calculated for some silicate anion model clusters by Furukawa et al. [11]. Their calculations are carried out with the stretching and bending force constants between the nearest neighbor atoms under some assumptions.

On the other hand, some quantum chemical calculations can be applied to the analysis of IR spectra. For the silicate anion model clusters, harmonic frequencies and force constants were calculated by ab initio molecular orbital methods using the STO-3G basis set at the Hartree-Fock self-consistent field (SCF) level by Murakami and Sakka [12]. Uchida and Shinmei applied the semi-empirical SCF-molecular orbital (MO) MNDO method to IR spectra of silicates [13]. The MNDO method was found to be useful for theoretical interpretation on the IR absorption spectrum of silica glass.

In this study, FT-IR PAS spectra of Li_4SiO_4 irradiated with high energy oxygen ions were measured. The semi-empirical SCF-MO MNDO calculation on various silicate clusters has been extensively performed to obtain a general interpretation of FT-IR PAS spectra of irradiated Li_4SiO_4.

2. Experimental

Li_4SiO_4 powder was synthesized by the reaction of the amorphous SiO_2 and LiOH precursor products in methanol [14]. Sintering was carried out at 1353 K for 5 h in the air after pressing the powder at a hydrostatic pressure of 160 MPa to make the pellets. Thin disks cut from the sintered pellets (8 to 9 mm in diameter, about 0.4 mm in thickness) were used for irradiation.

Ion irradiation was performed in an irradiation vacuum chamber attached to a tandem accelerator at the Japan Atomic Energy Research Institute (JAERI). The samples were irradiated to the ion fluence in the range 10^{18} to 10^{20} ions m^{-2} at the ambient temperature with 120 MeV oxygen ions, and were characterized by FT-IR PAS.

The FT-IR PAS spectra were measured using a combination of a Perkin–Elmer model 2000 FT-IR Spectrometer and a MTEC model 200 PAS Detector. All spectra were measured in the wave number region 1500 to 450 cm^{-1} at room temperature with an optical path difference (OPD) velocity of 0.05 cm s^{-1} and resolution of 8 cm^{-1}. The photoacoustic cell was purged with helium gas selected for optimal signal generation efficiency and a carbon film reference is used for the background spectra.

3. Clusters and computational procedure

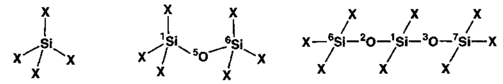
Irradiation effects on structure of alkali silicate glasses were examined by various surface analytical techniques such as secondary ion mass (SIMS), X-ray photoelectron (XPS) or Auger electron spectroscopies (AES) [15]. The structure of alkali-silicate glasses are significantly changed by irradiation. A dealkalization occurs by the irradiation and is accompanied by a structural rearrangement that results in the formation of new bridging oxygens.

Similarly the bridging oxygens will be expected to form in irradiated Li_4SiO_4. Thus we regard various silicate clusters with some bridging oxygens on the basis of the simplified silicate models [11]: SiO_4 isolated tetrahedra, Si_2O_7 dimers, Si_2O_6 chain links, Si_2O_5 sheet units and Si_2O_4 framework units. Such structures of the clusters are schematically presented in Fig. 1.

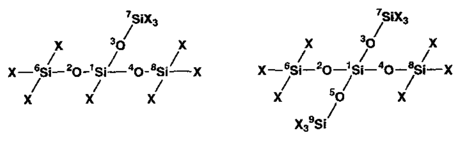
Three types of oxygen atoms exist in these clusters. The first type of oxygen atom is called bridging oxygen O(br) that means oxygens attached to two silicon atoms. The number of O(br) can vary between zero and four per tetrahedron containing one silicon atom. There are also the other types of oxygen atoms which are not attached to two silicon atoms; non-bridging oxygen (O(nbr)) such as oxygen atom of Si:–O^- linkages, oxygen bridging with Li atoms (i.e., Si–OLi).

The structure analyses of many silicate compounds including various types of lithium silicate have been experimentally performed [16–23]. The silicon atoms are attached to the oxygen atoms with covalent bonding. The distances Si–O are in the range 1.56 to 1.69 Å. The angle Si–O–Si in the range of 130 to 180°. The geometries of clusters used in this study were fully optimized with the experimental values selected as the parameters of initial geometries. Next vibrational analysis was performed.

The MNDO calculation was performed with the molecular orbital program package MOPAC93 on a Sun SPARC station 10 [24]. The vibrational frequencies of normal



(a) SiO_4 tetrahedra (b) Si_2O_7 dimer (c) Si_2O_6 chain



(d) Si_2O_5 sheet (e) Si_2O_4 3D-framework

Fig. 1. Silicate clusters used in the calculation of normal modes. X are terminating O^- or OLi.

modes, force constants and the relative intensity of absorption were derived from the second derivatives of the energy with respect to the geometry of the clusters and the value of the first derivative of the dipole moment for a normal mode, respectively [13,25]. The imaginary frequency did not appear in this calculation.

4. Results and discussion

4.1. Geometry

Equilibrium geometries were determined by a gradient optimization procedure using the Eigenvector Following routine [26]. As a whole, the geometries of the clusters optimized show a good agreement with the experimental values except for Si–O–Si and Si–O–Li bond angles. The Si–O–Si bond angles become about 180° for $Li_6Si_2O_7$ and $Si_2O_7^{6-}$. The Si–O–Li bond angles become 180° for Li_4SiO_4. However, the Si–O–Si average bond angle is experimentally estimated to 144° with a distribution of bond angles in the range 130 to 180°. Also, the experimental values of Si–O–Li bond angle are estimated in the 80 to 130° range. This discrepancy on the Si–O–Si bond angle has been discussed in detail with regard to MNDO and some ab initio methods [27]. It is mentioned that the Si–O–Si bond angle is flexible in the extreme and that the energy has a minimum value at 180°. And also, many compounds of alkali metals such as lithium are known as quasi-structureless moleculars [28]. However, IR spectra calculated by the MNDO method are useful for theoretical interpretation of experimental IR spectra of silicate compounds [13].

4.2. Vibrational analysis

The calculated IR spectra for the SiO_4^{4-}, $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$, $Si_4O_{13}^{10-}$ and $Si_5O_{16}^{12-}$ are shown in Fig. 2. These

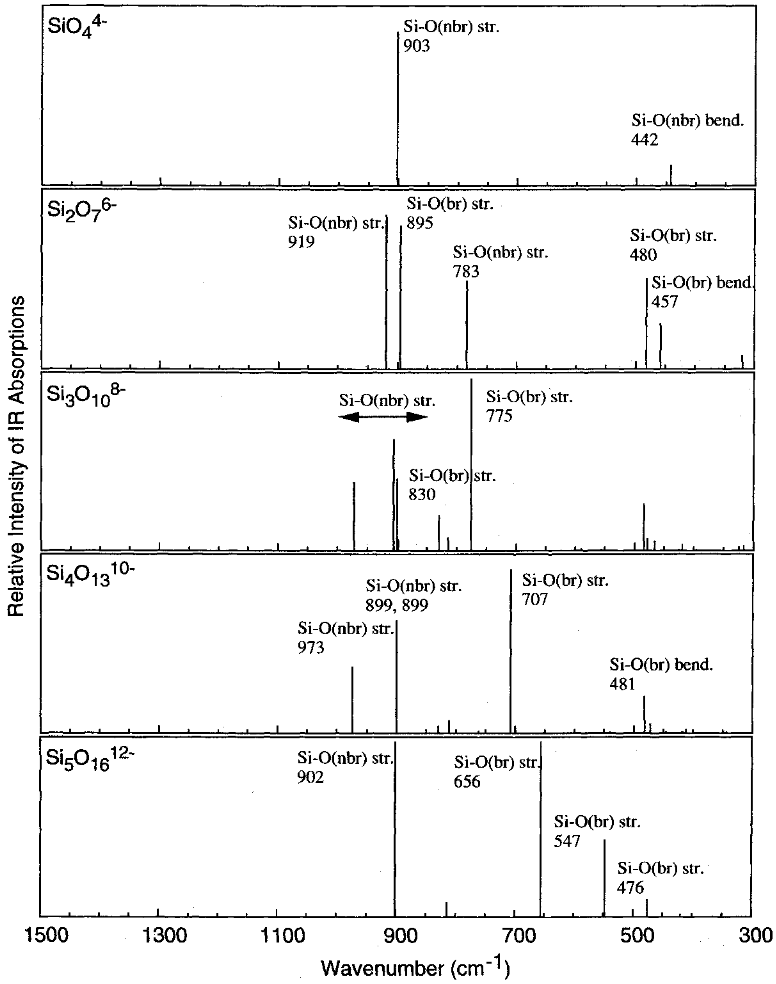


Fig. 2. Calculated IR absorption spectra for silicate anion clusters.

silicate anion clusters have two kinds of oxygen atoms, i.e., non-bridging oxygens O(nbr) and bridging oxygens O(br). The symmetries of structures of these optimized clusters are T_d, D_{3d}, C_{2v}, C_{3v}, T, respectively. The symmetries are lowered with the degree of polymerization.

In the theoretical IR spectra of SiO_4^{4-} cluster, the Si–O(nbr) bending vibration and stretching vibration are observed at 442 and 903 cm^{-1}, respectively. In the $Si_2O_7^{6-}$ clusters, the Si–O(br) stretching vibration due to the motion of bridging oxygen is observed at 895 cm^{-1}. The Si–O(nbr) stretching vibrations due to the non-bridging oxygens are observed at 783 and 919 cm^{-1}. The absorptions at 457 and 480 cm^{-1} are associated with the deformation vibration of the $Si_2O_7^{6-}$ unit.

With the progress of polymerization, the number of bridging oxygens increases. Two bridging oxygens exist in the $Si_3O_{10}^{8-}$ cluster. The $Si_4O_{13}^{10-}$ and $Si_5O_{16}^{12-}$ clusters have the three and four bridging oxygens, respectively. In the case of the $Si_5O_{16}^{12-}$ cluster with the four bridging oxygens, the SiO_4 unit of ^1Si is connected to the SiO_4 units of ^6Si, ^7Si, ^8Si and ^9Si through the bridging oxygens (Fig. 1e). The strong absorption at 902 cm^{-1} in the theoretical IR spectrum of the $Si_5O_{16}^{12-}$ cluster is due to the stretching vibration in the surrounding SiO_4 units. This vibration is associated with the motion between non-bridging oxygen and ^jSi atom ($j = 6, 7, 8, 9$). Thus, this absorption is not associated with the vibration of the SiO_4 unit of ^1Si whereas there are three absorptions associated with the vibration of the SiO_4 unit of ^1Si in the low wavenumber region. These absorptions at 476, 547 and 656 cm^{-1} are associated with the deformation vibration of the SiO_4 unit of ^1Si.

In the theoretical spectra of the $Si_3O_{10}^{8-}$ and $Si_4O_{13}^{10-}$ clusters, the Si–O(nbr) stretching vibrations are observed near 900 cm^{-1}. The Si–O–Si stretching vibrations are observed at 775 and 707 cm^{-1}, respectively.

The IR spectra calculated for the Li_4SiO_4, $Li_6Si_2O_7$, $Li_8Si_3O_{10}$, $Li_{10}Si_4O_{13}$, and $Li_{12}Si_5O_{16}$ clusters are shown

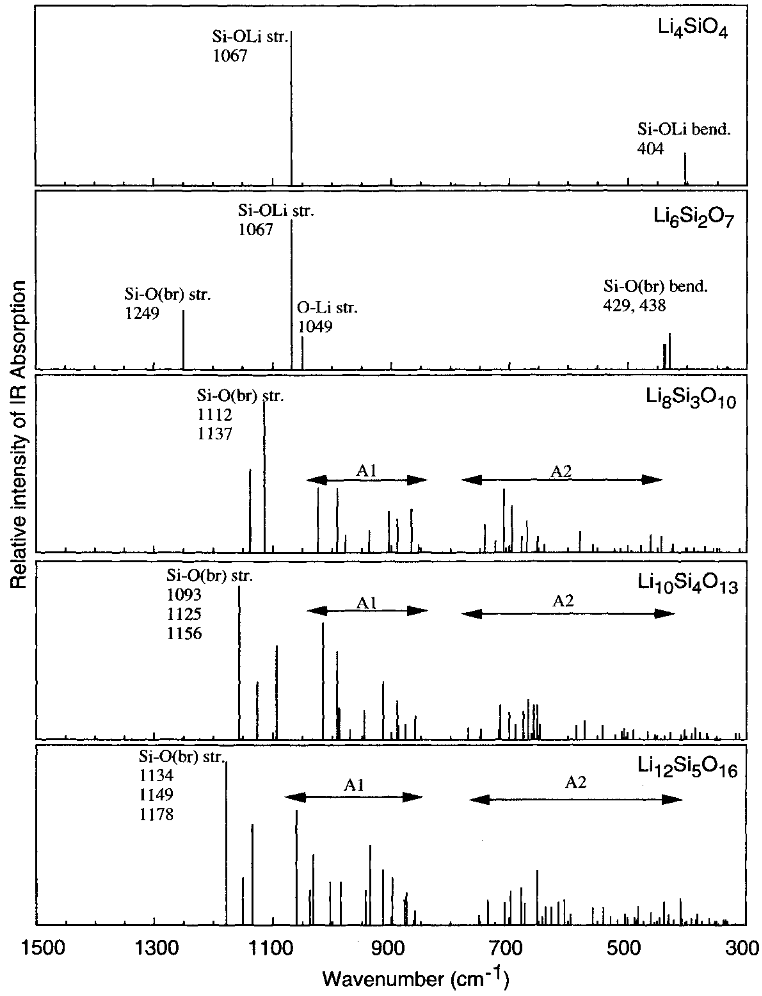


Fig. 3. Calculated IR absorption spectra for silicate clusters having OLi groups.

in Fig. 3. In the theoretical spectrum of Li_4SiO_4, the strong absorption at 1067 cm^{-1} is associated with the stretching vibration of the SiO_4 unit, while the weak absorption at 404 cm^{-1} is associated with the deformation vibration of the SiO_4 unit. The theoretical IR spectra for these silicate clusters having OLi groups also changes with polymerization. The changes are different from the theoretical IR spectrum for silicate anion clusters. In the theoretical IR spectra of the $Li_6Si_2O_7$ cluster with a bridging oxygen, strong absorption is observed at 1067 cm^{-1}. The absorption is associated with the Si–OLi stretching and Si–O stretching. The absorptions associated with the Si–O–Si stretching (1249 cm^{-1}) and Si–O–Si bending (429 and 438 cm^{-1}) are rather weak. In the theoretical IR spectra for the $Li_8Si_3O_{10}$, $Li_{10}Si_4O_{13}$ and $Li_{12}Si_5O_{16}$ clusters, strong absorptions associated with the Si–O–Si stretching vibrations are observed at 1200–1100 cm^{-1}. On the other hand, the A1 wavenumber region may be described as O–Si–O asymmetric vibration in the end SiO_4 units of each cluster, but these vibrations are strongly associated with the Si–OLi deformation motion. The deformation vibration of the end SiO_4 units are observed in the A2 wavenumber region. The absorptions in the A1 and A2 wavenumber regions are weaker than the ones associated with the Si–O–Si stretching vibration.

The vibration associated with the motion of bridging oxygens shifts to lower wavenumbers with increasing number of bridging oxygens in silicate anions. These vibrations are observed at 895, 775, 707 and 656 cm^{-1} for $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$, $Si_4O_{13}^{10-}$ and $Si_5O_{16}^{12-}$, respectively. In contrast with the calculations for silicate anion clusters, the vibration with the motion of bridging oxygens in silicate clusters having OLi groups shift to higher wavenumbers with increasing number of bridging oxygens, except $Li_6Si_2O_7$. These vibrations are observed at 1112, 1156, and 1178 cm^{-1} for, $Li_8Si_3O_{10}$, $Li_{10}Si_4O_{13}$ and $Li_{12}Si_5O_{16}$, respectively.

And also, the calculated IR spectra indicate that the force constants of vibration due to the bridging oxygens in silicate anion clusters become large by the connection of Li atoms to non-bridging oxygens. It is observed in this calculation that the Si–O(br) bond length decreases as the structure changes by the connection of Li atoms to the non-bridging oxygens. For the silicate clusters with 3D-framework structure, the Si–O(br) bond length in $Li_{12}Si_5O_{16}$ was estimated to be shorter than that of $Si_5O_{16}^{12-}$. The vibration due to the motion of bridging oxygens in $Li_{12}Si_5O_{16}$ was higher than that of $Si_5O_{16}^{12-}$. Thus, the increase of Si–O(br) bond strength is thought to be accounted for by the decrease of Si–O(br) bond length due to the connection of Li atoms to the non-bridging oxygens.

It has been reported that the Si–O stretching force constants of alkali silicate glasses which were evaluated experimentally by the normal coordinated treatments increased from 4.76 mdyn/Å (chain structure) to 5.94 mdyn/Å (3D-framework structure) with the decrease of alkali content [29]. And also, the Si–O bond length has been described to decrease from 1.66 to 1.61 Å with the decrease of alkali content. The decrease of alkali content causes the increase of bridging oxygen in alkali silicate glasses.

The changes of the Si–O bond length and Si–O stretching force constant also result from the connection of H atoms to the non-bridging oxygens of the SiO_4^{4-} cluster [12]. By the connection of H atoms, the Si–O bond length decreases from 1.80 to 1.66 Å. The Si–O stretching force constant increases by the connection of H atoms.

The relation between the Si–O(br) bond strength and the Si–O(br) bond length evaluated by the MNDO calculation in this study was consistent with the experimental and calculated results in other studies mentioned above.

4.3. FT-IR PAS spectra observed for oxygen-ion irradiated Li_4SiO_4

The crystal structure of Li_4SiO_4 is monoclinic with space group $P_{21/m}$ and contains isolated SiO_4-tetrahedra being connected by LiO_n-polyhedra ($n = 4, 5, 6$) [4,5]. The FT-IR PAS spectrum of Li_4SiO_4 before irradiation is shown in Fig. 4. In the range of wavenumber 1000–800 cm^{-1}, a group of some strong absorption is observed.

Many experimental and theoretical studies on the normal vibrational modes for some silicates report that the isolated SiO_4 structures (with symmetry T_d) have a strong absorption near 900 cm^{-1} [6,12,13,30–32]. The vibration due to the SiO_4 structure is a triply degenerate vibration and splits to three vibrations for Li_4SiO_4 structure having the lower space group. Lazarev et al. [6] showed that three absorptions near 900 cm^{-1} are due to the Si–O asymmet-

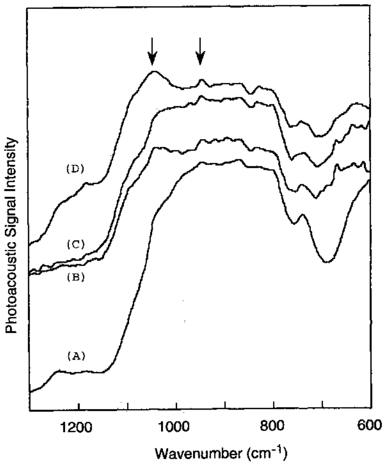


Fig. 4. Changes of FT-IR PAS spectra of Li_4SiO_4 irradiated to various fluences with 120 MeV ions (A) before irradiation, (B) 8.7×10^{18} ions m^{-2}, (C) 5.0×10^{19} ions m^{-2}, (D) 1.7×10^{20} ions m^{-2}.

ric stretching vibrations, and that an absorption near 800 cm^{-1} is due to the Si–O holosymmetric stretching vibration. In the FT-IR PAS spectra observed in this study, the absorptions due to the vibrations of SiO_4 tetrahedron are observed at 1000–800 cm^{-1}. The absorptions near 900 and 800 cm^{-1} are considered to be due to the Si–O asymmetric stretching vibrations and the Si–O holosymmetric stretching vibration, respectively. The absorption at 735 cm^{-1} is thought to be due to the CO_3^{2-} ion or to an admixture of Li_2SiO_3 [6].

The FT-IR PAS spectra of Li_4SiO_4 irradiated to the fluence of 8.7×10^{18}, 5.0×10^{19} and 1.7×10^{20} ions m^{-2} are also shown in Fig. 4. For Li_4SiO_4 irradiated to 8.7×10^{18} ions m^{-2}, many absorptions due to the irradiation appeared in the range 1100–800 cm^{-1} as shown in the spectra (B). The absorptions, especially the absorptions at 1042 and 950 cm^{-1} grew with fluence (see the spectra (C) and (D)). It is also recognized that the absorptions near 800 cm^{-1} are slightly grown with fluence. The absorption near 800 cm^{-1} seems to be formed with some small absorptions.

Theoretical line spectra of $Li_{10}Si_4O_{13}$ (sheet structure) and $Li_{12}Si_5O_{16}$ (3D-framework structure) are shown in Fig. 5 along with the experimental FT-IR PAS spectrum of Li_4SiO_4 irradiated to the fluence of 1.7×10^{20} ions m^{-2}. The absolute values of calculated frequencies have some systematic deviations from experimental ones. The systematic deviations can be reduced by using a simple correction function. The calculated frequencies (solid line) in Fig. 5 were corrected by using a scaling factor of 0.9 to account roughly for correlation effects and anharmonic correlations [33,34]. The strong absorptions at 1060(1178) and 1040(1156) cm^{-1}, which were calculated for $Li_{12}Si_5O_{16}$ and $Li_{10}Si_4O_{13}$ clusters, respectively, can be found in the experimental FT-IR PAS spectrum of irradiated Li_4SiO_4. The unscaled frequencies are shown in parentheses. The strong absorption near 1040 cm^{-1} can not be found in the theoretical IR spectra of another cluster. Thus, the prominent absorption which appeared near 1040 cm^{-1} with fluence is considered to be due to the Si–O–Si stretching vibration in the sheet and 3D-framework structures. And also, many weak absorptions appeared at 950–800 cm^{-1} corresponding to the absorptions observed in the A1 wavenumber region of IR spectra calculated for $Li_{12}Si_5O_{16}$ and $Li_{10}Si_4O_{13}$ clusters, which was shown in Fig. 3.

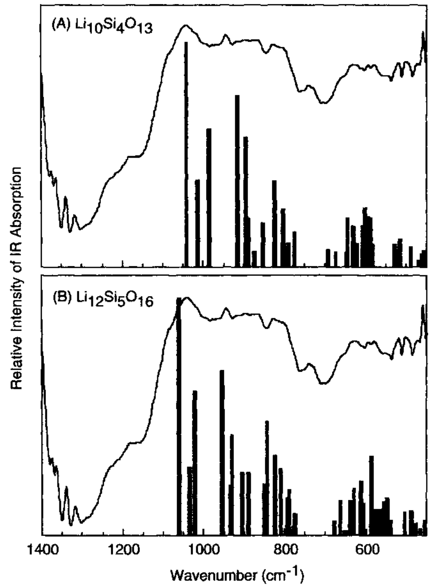


Fig. 5. Theoretical IR line spectra of (A) $Li_{10}Si_4O_{13}$, (B) $Li_{12}Si_5O_{16}$ together FT-IR PAS spectra obtained for Li_4SiO_4 irradiated to the fluences of 1.7×10^{20} ions m^{-2} with 120 MeV oxygen.

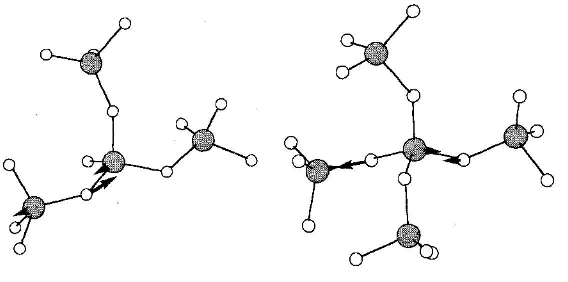

(a) 1040 cm^{-1} (b) 1060cm^{-1}

Fig. 6. Examples of vibrational modes due to motion of bridging oxygens in lithium silicate clusters with (a) sheet and (b) 3D-framework structures (terminating lithium atoms are not shown). Small open circles symbolize oxygen atoms, large circles symbolize silicon atoms.

Examples of the vibrational modes of the Si–O–Si stretching in the sheet and 3D-framework structures are shown in Fig. 6 using a computer program MOLCAT [35] to visualize results of vibrational analysis calculation. The vibration mode at 1040(1156) cm^{-1} can be assigned to the slightly deformed A_{2u} vibration of $Si_2O_7^{6-}$ with D_{3d} symmetry. The vibration mode at 1060(1178) cm^{-1} can be assigned to the slightly deformed F_2 vibration of the triply-degenerate Si–O asymmetric stretching vibration of SiO_4^{4-} with T_d symmetry. These vibration modes are governed by the vibration due to the basic structure units such as SiO_4^{4-} and $Si_2O_7^{6-}$, and are strongly associated with the motion of silicon atoms that binds to the oxygen atom of the SiO_4 unit.

A mechanism to account for the mobilization of the alkali ion under irradiation is proposed for the silicate glasses containing alkali ions such as Na^+, K^+ [36]. In this mechanism a positive hole as $\equiv SiO^0$ is created by the dealkalization due to ion irradiation. The alkali ion is considered to be no longer bonded to the non-bridging oxygen atom and to move into the glass. Electron irradiation of alkali silicate glasses is also known to result in the product of gaseous O_2. The $\equiv SiO^0$ groups recombine to form Si–O–Si bridges accompanied by the product of gaseous O_2 [37].

In high-energy ion irradiation, the energy of incident ions is dissipated by ionization and nuclear collision. During irradiation with high energy oxygen ions, the excitation of the atoms of Li_4SiO_4 structure and the creation of defects such as $\equiv SiO^0$ are caused by the dissipated energy. The $\equiv SiO^0$ created is considered to recombine to form the Si–O–Si bridges. This recombination will be assisted or enhanced by the excitation of electrons. Furthermore, the defect formation could occur due to the electron excitation. In such a case, the number of Si–O–Si bridges is larger than that expected only due to nuclear collision. However, such a possibility should be examined experimentally.

5. Conclusion

FT-IR PAS spectra of Li_4SiO_4 irradiated with high energy oxygen ions were measured. The semi-empirical SCF-MO MNDO calculation on various silicate clusters has been extensively performed to obtain a general interpretation of FT-IR PAS spectra of irradiated Li_4SiO_4.

The calculation of IR spectra for many silicate clusters shows that the shift of the Si–O–Si stretching vibration is accounted for by the degree of polymerization and the connection of Li atoms. The stretching vibrations in silicate anion clusters shift to a lower wavenumber with polymerization. In silicate clusters having OLi groups, the stretching vibration shifts to higher wavenumbers as the polymerization increases. By the connection of Li atoms to non-bridging oxygens in silicate anion clusters, the stretching vibrations shift to higher wavenumbers in the same structural unit.

The IR absorption near 1040 cm^{-1} observed for the irradiated Li_4SiO_4 which grew with the fluences was attributed to the changes of the SiO_4 structure due to the irradiation. By comparing the experimental FT-IR PAS spectra with the calculated spectra, the absorption is assigned to the Si–O–Si stretching vibration in the sheet and 3D-framework structures. Consequently, high energy oxygen ion irradiation is considered to lead to the formation of 3D-frameworks and sheet structures with bridging oxygens in Li_4SiO_4.

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