



Coloration Mechanism of Fe Ions in β -Quartz s.s. Glass-Ceramics with TiO_2 and ZrO_2 as Nucleation Agents

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Transparent β -quartz s.s. glass-ceramics in $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system have an undesirable brown color owing to Fe ions as a contaminant, whereas the mother glass normally has a clear appearance. Elucidation of the coloration mechanism during crystallization is important for industry to develop highly transparent materials. In this study, the mother glass contained SiO_2 , Al_2O_3 , and Li_2O as its principal constituents and TiO_2 and ZrO_2 as nucleation agents. The amount of contaminant Fe ions in the form of Fe_2O_3 was 0.03 wt%. It was confirmed that the coloration was appeared by the coexistence of Fe and Ti ions in the glass matrix based on the experimental results using Ti-containing and Ti-free glasses with a composition identical to that of the glass matrix. The coordination and oxidation state of the Fe ions were not changed by the coexistence of Ti ion according to the results of X-ray absorption near-edge structure measurement. The coloration is considered to be due to the formation of Fe–O–Ti by the concentration of Fe and Ti ions in the glass matrix phase during the crystallization process.

Keywords: $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass-ceramics, iron ion, coloration mechanism, glass matrix phase, coordination state, X-ray absorption near-edge structure

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INTRODUCTION

Although $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ low-expansion glass-ceramics having β -quartz s.s. or β -spodumene s.s. as main precipitated crystal were developed by Stookey more than 50 years ago, the research and development of the material is still active, particularly on their nucleation phenomena and improving their characteristics to apply them to various emerging applications (Bhattacharyya et al., 2010; Sakamoto and Yamamoto, 2010). The first developed $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass-ceramics contained 2–20 mass% TiO_2 as a nucleation agent, and their appearance was white and opaque. The ceramics were used for heat-resistant tableware (Stookey, 1960). The glass was crystallized homogeneously by heat treatment to induce the nucleation of Al_2TiO_5 as a precipitate (Doherty, 1967). Shortly after the work of Stookey, Tashiro and Wada (1963) found that ZrO_2 is an effective nucleation agent, and transparent β -quartz s.s. glass-ceramics in $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system can be easily obtained by the addition of ZrO_2 and TiO_2 (Petzoldt, 1963; Beall, 1967; Müller, 1972; Tashiro et al., 1976). By improving the transparency and other characteristics by optimization of the composition and the conditions of the heat treatment for crystallization through many basic studies on nucleation and crystal growth (Nakagawa, 1972; Riello and Hopfe, 2001; Dymshits, 2005), the application of the transparent glass-ceramics has become widespread, such as in electronic and optical devices, production equipment, and home and cooking appliances.

However, the transparent glass-ceramics have an undesirable brown color owing to Fe ions as a contaminant, whereas the mother glass normally has a clear appearance. This coloration, which occurs through the crystallization process, causes two problems for industry. One is that it prevents further expansion of the market for fire-rated windows due to the mismatch in appearance with normal bluish windows of soda lime silicate glass. The other is that it is difficult to avoid the use of toxic arsenic oxide and/or antimony oxide as a fining agent because the non-toxic alternative of tin oxide cannot be used on account of its enhancement of the coloration (Nakane and Kawamoto, 2015). It is therefore necessary to determine the coloration mechanism to develop environmentally friendly glass-ceramics with high transparency.

Many investigations have been conducted on Fe coloration in various glass systems from the viewpoints of changes in the valence and coordination number and the formation of clusters (Traverse et al., 1992; Ehrt et al., 2001; Schutz et al., 2004). It is well known that optical absorption spectra of Fe ions can be changed and shifted easily by adjusting the composition and melting conditions because the d-d transition in the outermost electron orbital is sensitive to the surrounding environment. This means that there are various possible explanations for the coloration mechanism. Furthermore, in the case of glass-ceramics, the effects of changes in the phase and composition in the microstructure upon crystallization should be considered to elucidate the coloration-appearance phenomena through the crystallization process. Although many previous works have provided various insights, it is difficult to directly specify the coloration mechanism in glass-ceramics from the literature.

The objective of the present investigation is to elucidate the mechanism of the strong brown coloration caused by Fe ions in transparent β -quartz *s.s.* glass-ceramics in $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. We determine the phase of the coloration and the key component responsible for the coloration. In addition, the relationship between the optical absorption and the valence and coordination state of Fe ions in the glass-ceramics is discussed on the basis of the results of Fe K-edge and Ti K-edge X-ray absorption near-edge structure (XANES) measurements and first-principles calculation.

EXPERIMENTAL

The specimens investigated in this study had a chemical composition (in mass percent) of 66SiO₂, 23Al₂O₃, 4Li₂O, 2TiO₂, 2ZrO₂, and small amounts of Na₂O, K₂O, MgO, BaO, and P₂O₅. Also, 0.03% of Fe₂O₃ was included as a contaminant. Mixture of raw materials was melted at 1,650°C for 20 h in air atmosphere, and then the melt were quenched with a metal roller. The obtained mother glass, which had a clear appearance, was crystallized in an electric furnace with a nucleation temperature of 780°C and a maximum temperature of 900°C. The heat-treatment times were 3 h at the nucleation stage and 1 h at the maximum temperature. After crystallization, the microstructure was observed using a scanning electron microscope to determine the crystallinity (SU8220, Hitachi). An X-ray diffractometer (RINT2000/PC, Rigaku) was used to analyze the crystalline phase. Optical

absorption was measured by a double-beam photospectrometer (UV-3100PC, Shimadzu). XANES measurement at the Fe K-edge (from 7,110 to 7,200 eV) and Ti K-edge (from 4,950 to 5,050 eV) was performed at beamline 24 of SPring8 in Hyogo Prefecture, Japan.

X-ray energy was monochromatized using a four-crystal of Si(111) and Si(400) in an anti-parallel setting (Galoisy et al., 2001).

RESULTS AND DISCUSSION

The broken line shown in **Figure 1** is the absorption spectrum for the sample after crystallization. A wide range of absorption from 2 to 3.5 eV, resulting in the brown color, and a strong peak at about 4 eV in the UV region were observed. According to the results of XRD, the sample mainly consisted of β -quartz *s.s.* (JCPDS 01-073-2336) and remained glass matrix phase. To specify which phase exhibits optical absorption, a glass with a composition identical to that of the glass matrix was prepared, and its optical absorption was measured. The glass matrix was assumed to have the following properties: the crystallinity was 75%, analyzed from the total area and the grain size of the precipitated crystal determined by SEM observation. The crystal composition was $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-6\text{SiO}_2$, estimated from the (406) peak position in the XRD pattern (Iwatsuki et al., 1974). The ratio of precipitated TiO₂ and ZrO₂ was 60%, quoted from the literature (Riello and Hopfe, 2001). All the Fe₂O₃ was assumed to remain in the glass phase. **Figure 1** shows the optical absorption spectrum of the glass with the matrix composition, which is almost identical to that of the glass-ceramics having a broad peak in the visible region and one sharp peak in the UV region, although there are slight differences in the peak position and shape, considered to be due to the deviation in the composition from the rough assumption. The absorption intensity in the visible region per Fe₂O₃ unit concentration was approximately 1.5 times larger than that of the glass-ceramics. This may indicate

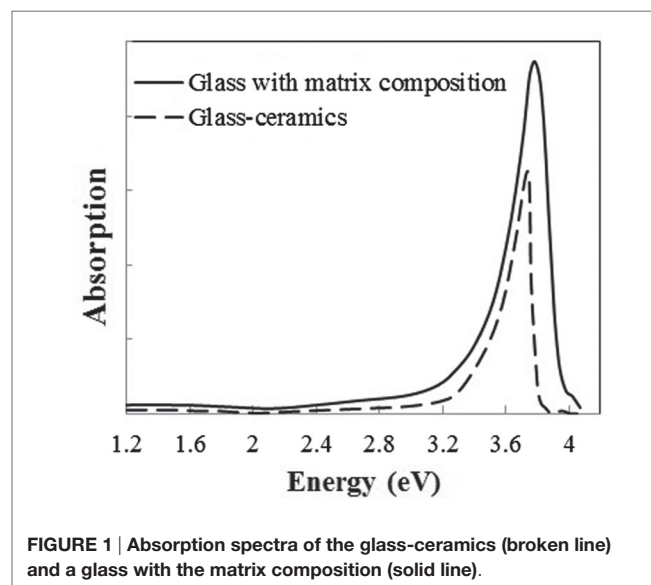


FIGURE 1 | Absorption spectra of the glass-ceramics (broken line) and a glass with the matrix composition (solid line).

that Fe content in the glass matrix phase was overestimated since some of the Fe ions precipitated to the crystal phase. However, no other absorption peak was observed in the spectrum of the glass-ceramics; therefore, it is concluded that most of the Fe ions remained in the glass matrix phase, resulting in the brown color of the glass-ceramics.

To determine which component in the glass matrix is responsible for the Fe ion coloration, the optical absorption spectra of various compositions, where the amount of only one component (Si, Al, Li, Ti, Zr, Na, K, or Ba) was changed from that in the above estimated matrix glass composition, were measured. Shown in **Figure 2** are the appearances of the Ti-containing and Ti-free glasses. In the case of the Ti-free glass, the coloration disappeared, while all the other glasses containing Ti had a brown color. **Figure 3** shows the optical absorption spectra of the Fe ions in the Ti-containing and Ti-free glasses, which were obtained by subtracting the Fe-free glass spectrum from the Fe-containing glass spectrum to eliminate the absorption from other components. The spectrum of the Ti-containing glass has a broad absorption

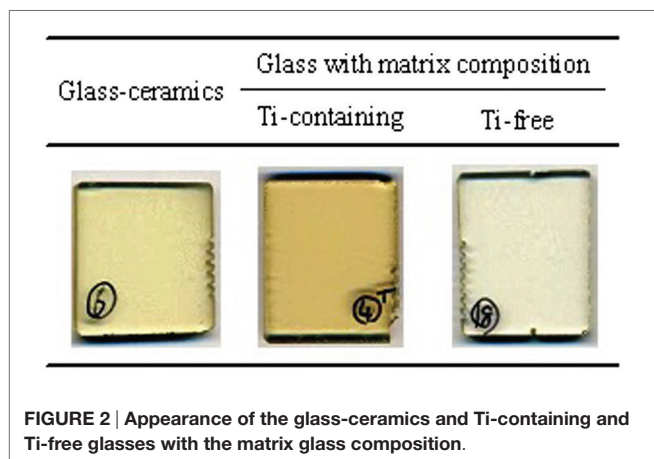


FIGURE 2 | Appearance of the glass-ceramics and Ti-containing and Ti-free glasses with the matrix glass composition.

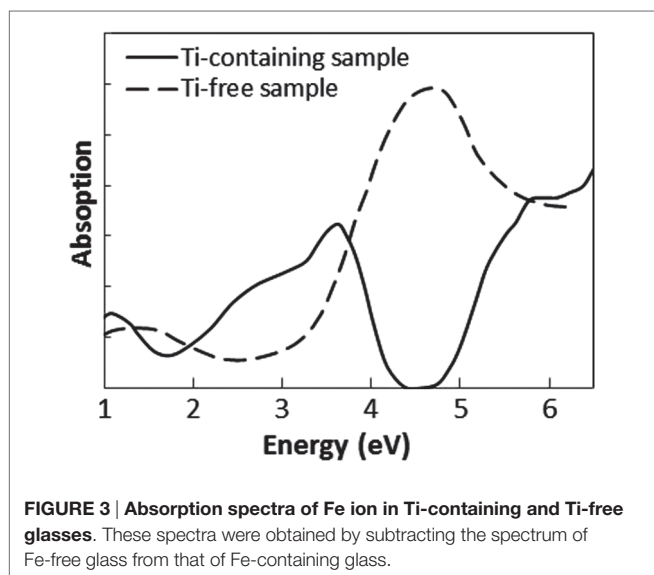


FIGURE 3 | Absorption spectra of Fe ion in Ti-containing and Ti-free glasses. These spectra were obtained by subtracting the spectrum of Fe-free glass from that of Fe-containing glass.

peak in the visible region from approximately 2 to 4 eV, whereas no peak in the visible region can be observed for the Ti-free glass. The amounts of Fe and Ti ions in the glass matrix were estimated to increase from 0.03 to 0.1% in the form of Fe_2O_3 and from 2 to 3% in the form of TiO_2 on the basis of the above. We speculate that the concentrations and the coexistence of Fe and Ti ions in the glass matrix phase may give the strong brown coloration in the glass-ceramics. Some previous works have mentioned a brown coloration due to the coexistence of Fe and Ti ions (Weyl, 1951). Weyl speculated that the coloration is caused by a change in the coordination number of Fe^{3+} from 6 to 4 due to the existence of Ti ions, but this was not sufficiently supported by experimental results. To determine the valence and coordination number in the Ti-containing and Ti-free glasses, XANES spectra at the Fe K-edge were measured. The other samples measured for reference were crystalline compounds of FeO and Fe_2O_3 . **Figure 4** shows the Fe-XANES spectra. The position of the XANES edge indicates the valence of the ions, in which the redox ratio is reflected in its position on the energy scale: 7,118 eV for Fe^{3+} in Fe_2O_3 and 7,114 eV for Fe^{2+} in FeO. The positions for both glasses were almost the same, 7,116 eV, which is almost halfway between those of the two minerals. The results clearly indicate that both Fe^{2+} and Fe^{3+} existed in the glasses, and that the ratio of the two ions did not change significantly with the existence or non-existence of Ti ions. **Figure 5** shows the pre-edge peak of Fe ions in the glasses around 7,110–7,120 eV. The pre-edge peak originated from a forbidden electron transition, which is partly allowed by making a hybrid orbital with p-electron, is affected by the coordination number. The pre-edge was extracted by fitting two Gaussian functions to the contribution of the main edge to the pre-edge feature. The peaks for both samples are made up of at least two peaks. Wilke et al. (2001) reported that four-coordinated Fe^{2+} and Fe^{3+} have two and one contributions, and six-coordinated Fe^{2+} and Fe^{3+} have two and three contributions, respectively. However, in this case, the coordination numbers of Fe^{2+} and Fe^{3+} in the samples could not be determined because of the insufficient S/N ratio to conduct peak separation owing to the small amount of Fe ions in the glass. Comparing the spectra of the two samples, no significant differences in the height and shape were detected.

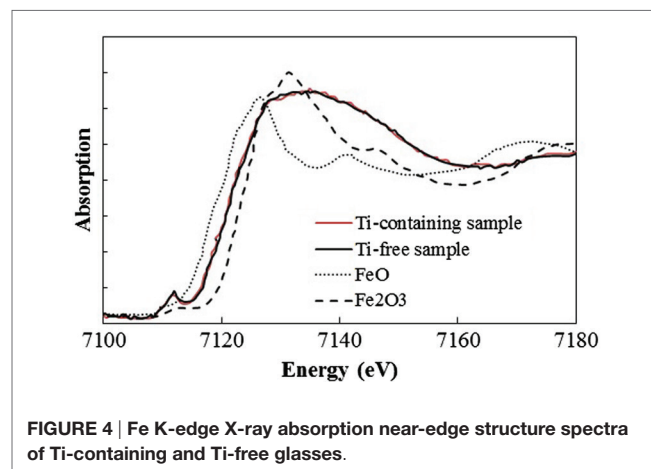


FIGURE 4 | Fe K-edge X-ray absorption near-edge structure spectra of Ti-containing and Ti-free glasses.

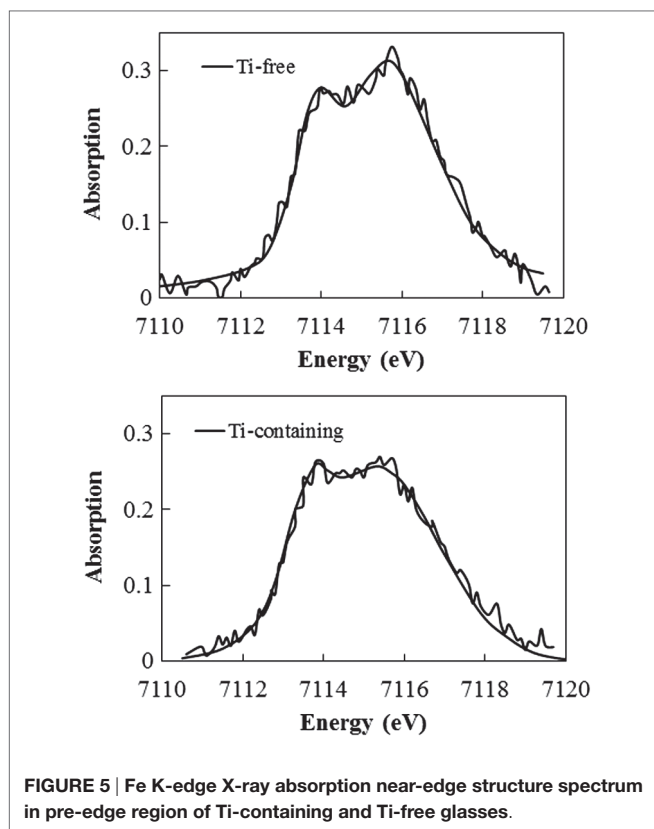


FIGURE 5 | Fe K-edge X-ray absorption near-edge structure spectrum in pre-edge region of Ti-containing and Ti-free glasses.

Wilke et al. (2005) suggested that the peak intensity significantly changes with the coordination number, with the peak intensity of a four-coordinated Fe ion being more than four times larger than that of a six-coordinated Fe ion. Their work indicates that the coordination number of the Fe ions in our samples is not changed by the coexistence of Ti ions. The peak position was shifted slightly to the lower-energy side by less than 0.3 eV with the coexistence of Ti ions. This shift may be a consequence of a very small decrease in the valence (Wilke et al., 2005).

In addition to the coloration from Fe ions, another past work showed that Ti^{3+} - Ti^{4+} mixed complexes cause a brown coloration (Bausa et al., 1991). To determine the valence of the Ti ions in our Ti-containing glass, the XANES spectra were measured at the Ti K-edge. The other samples measured for reference were crystalline Ti_2O_3 and TiO_2 . **Figure 6** shows the Ti-XANES spectra. The positions of the XANES edge indicating the valence are 4,972 eV for Ti^{3+} in Ti_2O_3 and 4,977 eV for Ti^{4+} in TiO_2 . The position in our glass is almost identical to that for Ti^{4+} in TiO_2 , where the existence of a certain amount of Ti^{3+} could not be confirmed. Similar results were reported for silicate glass systems prepared under normal melting conditions in a previous work (Schutz et al., 2004). In addition, we prepared Fe-free glass with the same composition to investigate the coloration by Ti ions, and it had a clear appearance without the strong brown coloration. These results indicate that Ti^{3+} - Ti^{4+} , which has an absorption band in the visible region, hardly exists in our glasses.

A first-principles calculation of the absorption of an Fe ion was conducted to clarify how Ti^{4+} ion affect the optical absorption of

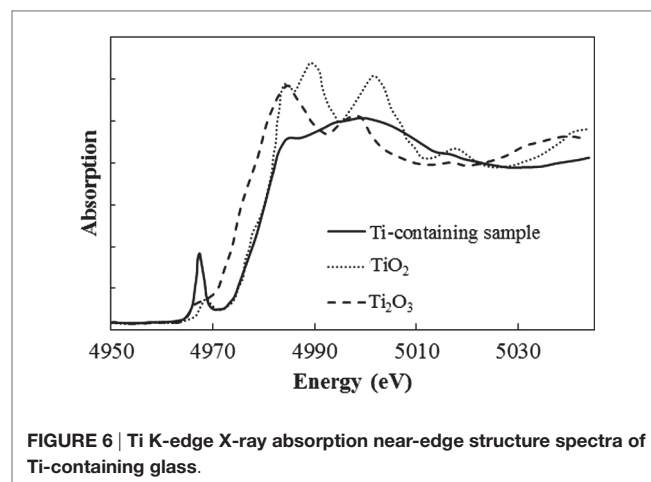


FIGURE 6 | Ti K-edge X-ray absorption near-edge structure spectra of Ti-containing glass.

Fe ions in the case of no changes in the valence and coordination conditions. The absorption spectra for Fe ions were obtained by the DV-ME method, which can be used to calculate absorption spectra while considering the d-d transition (Ogasawara et al., 1998). **Figure 7** shows the structure model used for the calculation, where a four-coordinated Fe^{3+} ion in the normal state in silicate glass (Schutz et al., 2004) is placed at the center of a SiO_4 tetrahedron, in which the bonding length of Si-O is 0.16 nm, obtained from CR912569 crystal code, and the Fe-O length is 0.18 nm from CR910311. To evaluate the effect of Ti, one Si^{4+} is substituted by Ti^{4+} at the second-nearest position from the Fe ion. **Figure 8** shows the calculated absorption spectra. Upon the substitution of the Ti ion, the absorption peak of the Fe ion from the d-d transition shifted to the lower-energy side that had qualitative agreement with the experimental results shown in **Figure 3**. This feature is caused by a change in the symmetry of the d-electron orbital in the Fe ion owing to the existence of a d-electron orbital in the Ti ion at the second-nearest position, even though the valence and coordination number are unchanged. Although this calculation does not have enough sufficient to give a definitive conclusion because of the oversimplified structure and components in the model, we tentatively conclude that the coloration is due to the formation of Fe-O-Ti in the glass matrix phase.

CONCLUSION

In this present work, the mechanism of the brown coloration of transparent β -quartz *s.s.* glass-ceramics in Li_2O - Al_2O_3 - SiO_2 system by Fe ions has been investigated. The preparation and evaluation of a glass with a composition identical to that of the glass matrix indicated that the concentration and coexistence of Fe and Ti ions in a glass matrix phase are the cause of the coloration. On the basis of this result, Nippon Electric Glass have developed and started to produce environmentally friendly glass-ceramics with high transparency (Nakane and Kawamoto, 2015). We hope that this finding will help understand the brown coloration in other glass-ceramics with TiO_2 in present applications including dental materials like lithium disilicate glass-ceramics where appearance is important. This study highlights the importance of the

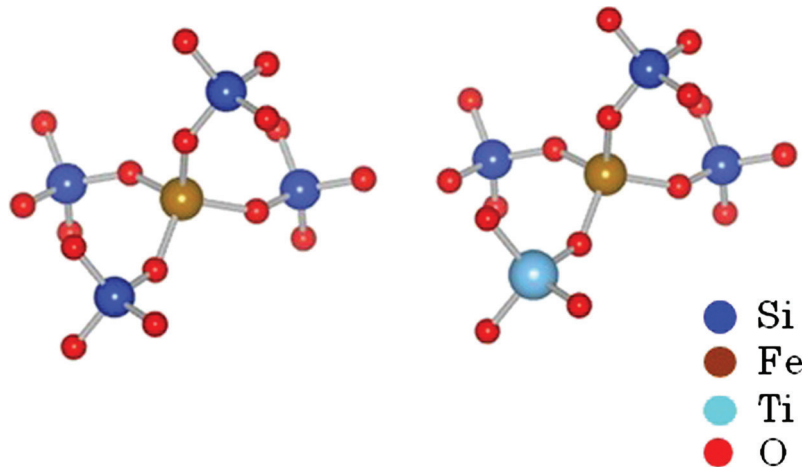


FIGURE 7 | Structure model for calculation of Fe ion absorption spectra.

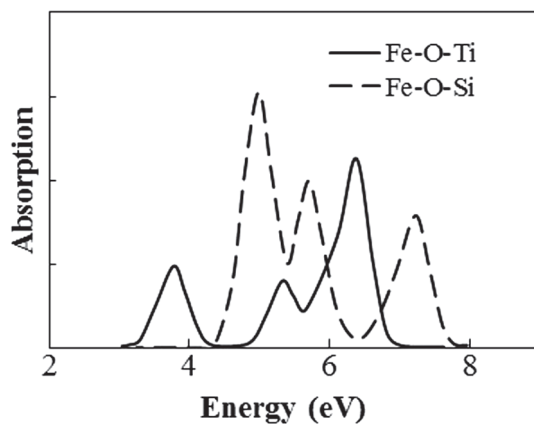


FIGURE 8 | Calculated absorption spectra of Fe ion with and without Ti at second-nearest ion position.

characteristics of the glass matrix phase in the development and improvement of various glass-ceramics for future applications.

AUTHOR CONTRIBUTIONS

SN: conception and design of the study, analysis and interpretation of data, collection and assembly of data, and drafting of the article. KK: conception and design of the study, analysis and interpretation of data, and collection and assembly of data.

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The reviewer CR and handling editor declared their shared affiliation, and the handling editor states that the process nevertheless met the standards of a fair and objective review.

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