

# Chemical shift of characteristic X-ray wavelength in silicon-containing ceramics due to neutron irradiation

Toyohiko Yano <sup>a,\*</sup>, Saisyun Yamazaki <sup>a</sup>, Hiroko Kawano <sup>b</sup>, Keiichi Katayama <sup>b</sup>

<sup>a</sup> *Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1, O-Okayama, Meguro-ku, Tokyo 152-8550, Japan*

<sup>b</sup> *Faculty of Engineering, Tokai University, Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan*

## Abstract

The characteristic wavelength of silicon in neutron-irradiated and non-irradiated ceramics was precisely measured to detect any change in materials induced by neutron irradiation. The wavelength of characteristic silicon K $\beta$  X-rays emitted from materials was measured by electron probe microanalysis, using a WDX-equipped scanning electron microscope. The crystal used to disperse silicon X-rays was PET (pentaerythritol). Specimens were non-irradiated metallic silicon, vitreous silica, quartz,  $\beta$ -silicon carbide and  $\beta$ -silicon nitride. Neutron-irradiated vitreous silica and quartz were also used. Measurements were conducted successively during while monitoring the temperature of PET. A chemical shift of peaks from that of metallic silicon was observed for unirradiated materials, for longer wavelength in case of  $\beta$ -silicon carbide,  $\beta$ -silicon nitride, quartz and vitreous silica in this order. The chemical shift of vitreous silica due to neutron irradiation was reduced but that of quartz increased to those of the unirradiated specimens.

© 2007 Elsevier B.V. All rights reserved.

## 1. Introduction

Several ceramic materials will be applied in fusion reactors as structural and functional components to sustain fusion plasma under the very severe environment such as intense radiation, high temperature and high heat load [1–4]. Properties of the ceramics will be influenced by irradiation with a high flux of fast neutrons, which produces crystalline defects and transmutation products. It is known that volume increase, reduction of thermal diffusivity, changes of mechanical properties, and degradation of electric properties are induced. Therefore,

evaluation of the defects induced in crystalline and amorphous materials is highly desirable for use with a variety of evaluation methods.

In the present study, a change in peak wavelength of characteristic X-rays emitted from materials was measured by electron probe microanalysis. Characteristic wavelengths of silicon in neutron-irradiated and non-irradiated ceramics were precisely measured to detect any change in materials induced by neutron irradiation. The merit of this method is its applicability for materials independent of crystallinity. Furthermore, this method is one of microanalyses so the chemical shift can be detected with high spatial resolution on the order of a micrometer. Wavelength of characteristic X-rays is influenced by atomic coordination for a specific ion/atom in materials (chemical shift). The chemical shift of

\* Corresponding author. Tel.: +81 3 5734 3380; fax: +81 3 3734 2959.

E-mail address: [tyano@nr.titech.ac.jp](mailto:tyano@nr.titech.ac.jp) (T. Yano).

characteristic X-rays of Si or Al in silicate minerals and several compounds was observed by White et al. [5,6], Day [7], Fukusihma et al. [8] and Okura et al. [9]. It was concluded that it was influenced by the valence number, coordination and/or electro-negativity of cations. Okura and Sudoh [10] and Leone [11] observed the chemical shift of Si-K $\alpha$  and Si-K $\beta$  in oxides and glasses and that of six-coordinated silicon showed a higher energy shift than four-coordinated silicon.

Although the chemical shift is a well-known and established phenomenon, it has not been applied to detect the neutron irradiation effects up to the present. Thus, the aim of the present study is to clarify the applicability of the chemical shift measurement for neutron-irradiated ceramics to detect any changes of atomic coordination. The obtained results were compared and discussed based on the volume change reported separately.

## 2. Experimental procedures

The wavelength of silicon K $\beta$  characteristic X-rays emitted from materials was measured by electron probe microanalysis using wavelength dispersive X-ray spectroscopy (WDX) (Oxford Instruments, Microspec WDX-450) in a scanning electron microscope (Hitachi, S-3500H). Accelerating voltage of incident electron beam was 30 kV and specimen current was 90–170  $\mu$ A. The crystal used to disperse silicon X-rays was PET (pentaerythritol,  $2d = 25.75$  Å). The scanning rate was 13.57 mÅ/min and the scanning range was 6.70–6.85 Å. Specimens used in this study were non-irradiated single crystal Si (metallic silicon), vitreous silica (SiO<sub>2</sub> glass), single crystal  $\alpha$ -quartz (SiO<sub>2</sub>),  $\beta$ -silicon carbide and  $\beta$ -silicon nitride. Neutron-irradiated specimens of the same vitreous silica and quartz were also observed. Measurement was conducted successively while monitoring the temperature of PET.

Neutron irradiation of quartz and vitreous silica was conducted in the Japan Materials Testing Reactor (JMTR) up to a fluence of  $6.9 \times 10^{23}$  n/m<sup>2</sup> at an irradiation temperature of 300 °C in a He filled capsule.

Obtained profiles were analyzed by standard method as follows. First, the profile was smoothed by the Savitzky–Golay method, and then second and third order differential curves were obtained to determine the number of peaks (maxima more than one tenth of the highest peak was identified as peaks). Each profile was fitted as a Gaussian

distribution. Then, the observed profile was convoluted to fit with several independent profiles using the Marquardt least-square method. The number of peaks, peak height, peak position, peak width were obtained.

## 3. Results and discussion

The observed Si-K $\beta$  profiles from metallic silicon, quartz, vitreous silica,  $\beta$ -silicon carbide and  $\beta$ -silicon nitride obtained at a PET crystal temperature of about 25 °C are compared in Fig. 1. All specimens were unirradiated. Intensities were normalized to obtain the same main peak intensity as each other. It is obvious that there is a large main peak at around 2.75–2.77 Å and small separate satellite peaks at 6.79–6.82 Å. Both peaks were shifted specimen to specimen. The degree of the shift was large in small and long wavelength peaks, which can be attributed to the Si-sK $\beta'$ . Shift of main large peaks, which can be attributed to Si-K $\beta$ , was relatively small.

An example of the profile analysis is shown in Fig. 2, which contains as-observed, deconvoluted and convoluted profiles of the Si-K $\beta$  spectrum observed for the neutron-irradiated quartz. The main Si-K $\beta$  spectra were deconvoluted into two or three peaks. The highest and sharpest peak was observed at  $\sim 6.75$  Å with medium and broad peak at  $\sim 6.77$  Å in metallic silicon and silicon carbide. The former could be attributed to Si-K $\beta$  and the latter to Si-K $\beta$ 1 in the case of metallic silicon. Almost the same highest peak at  $\sim 6.77$  Å was observed in both SiO<sub>2</sub> along with a small peak at 6.75 Å. The former peak can be attributed to Si-K $\beta$ 1 and the latter to Si-K $\beta$ . In the case of silicon nitride, these two peaks were mostly overlapped. Furthermore, in the case of quartz, vitreous silica and silicon nitride, a separate small peak was observed at  $\sim 6.82$ , 6.80 and 6.79 Å, respectively, which was attributed to Si-sK $\beta'$  [11], as shown in Fig. 1.

Fig. 3 indicates the change in the peak-wavelength of the Si-K $\beta$  main peaks from metallic silicon, unirradiated quartz and vitreous silica,  $\beta$ -SiC and  $\beta$ -Si<sub>3</sub>N<sub>4</sub> against the temperature of PET. The wavelength was influenced directly by the temperature of the dispersed crystal. In this study a PET crystal was used, thus the effect of crystal temperature was non-negligibly large for the measurement of a small chemical shift. Thus we obtained profiles serially while increasing the PET crystal temperature, which was monitored by Pt-resistance temper-

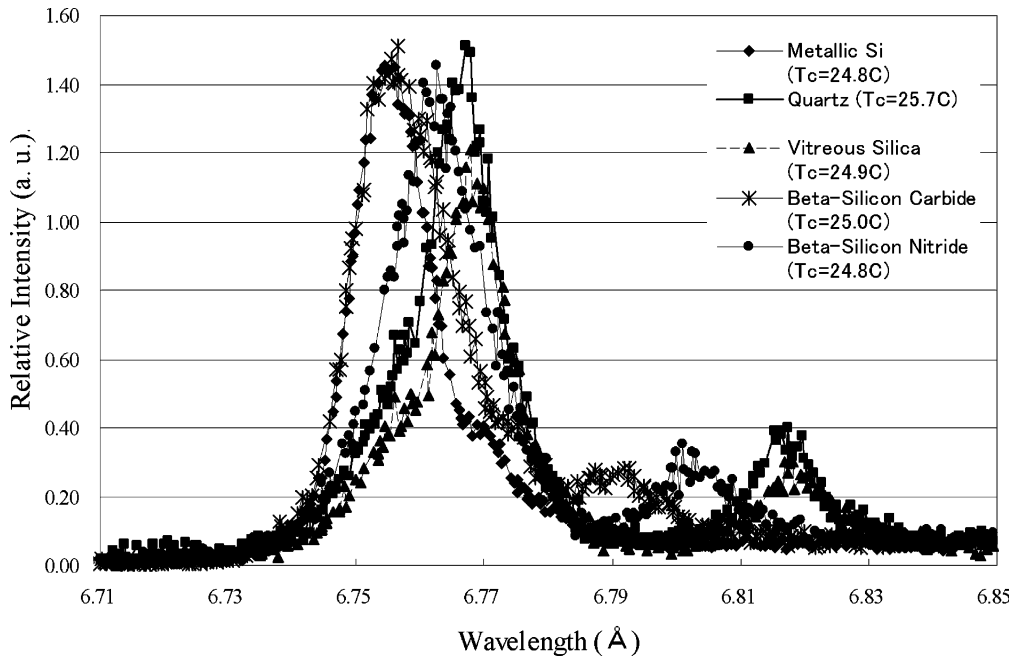


Fig. 1. Observed Si-K $\beta$  profiles from metallic silicon, quartz, vitreous silica,  $\beta$ -silicon carbide and  $\beta$ -silicon nitride at PET crystal temperature of  $\sim 25$  °C. All specimens were unirradiated.

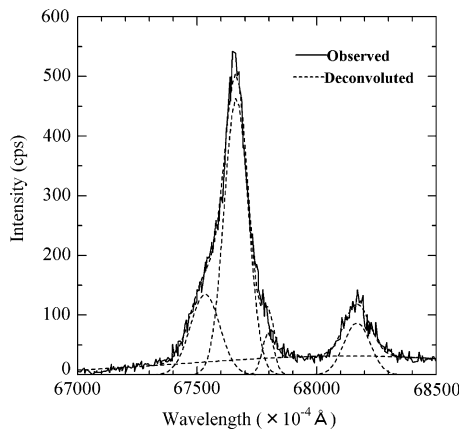


Fig. 2. An observed and deconvoluted profiles of Si-K $\beta$  spectrum observed for the neutron-irradiated quartz (temperature of crystal was 25.1 °C).

ature monitor. Then, each obtained profile was analysed the same way. As shown in Fig. 3, the fitted line showed mostly the same decreasing slope with increasing PET temperature. The slope agreed well with the expected value based on the thermal expansion coefficient of PET. Therefore, it was understood that the wavelength should be compared at the same PET temperature condition. From the

straight fitting lines shown in the figure, the peak wavelength of the main peak at a PET temperature of 25 °C was obtained.

Fig. 4 shows the chemical shift, which is the difference in peak wavelength from that of metallic silicon. The chemical shift of unirradiated specimens are increased in longer wavelength direction in the order of  $\beta$ -silicon carbide,  $\beta$ -silicon nitride, quartz and vitreous silica. The chemical shift was very small in  $\beta$ -silicon carbide, and large in crystalline and non-crystalline SiO<sub>2</sub>, and that of  $\beta$ -silicon nitride was intermediate. The trend and order of the chemical shift agreed well with the reported values [12]. Because the coordination of the Si polyhedron in all these compounds was a four-coordinated tetrahedron, the difference was explained by the difference in electro-negativity of these materials [12].

Fig. 5 shows the observed Si-K $\beta$  profiles of irradiated and non-irradiated quartz and vitreous silica at nearly 25 °C. Intensities were normalized to the same main peak intensity. A small peak shift was observed. As mentioned above, since the wavelength was influenced by the PET temperature, so that the same procedure as shown in Fig. 3 was applied to obtain the peak wavelength at a PET temperature of 25 °C, after the peak deconvolution. The obtained values are included in Fig. 4. The

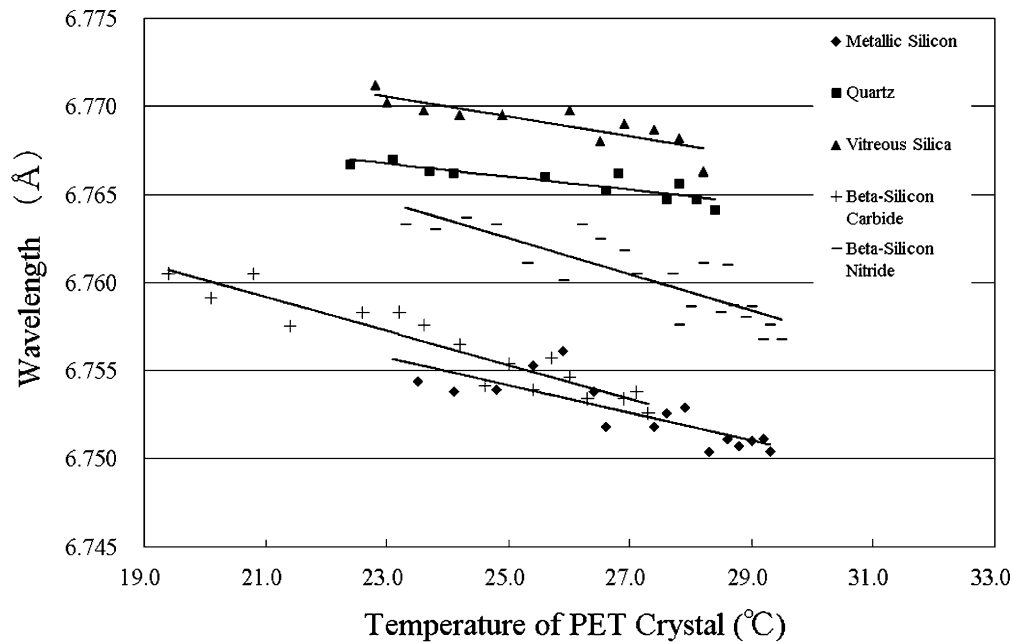


Fig. 3. Change in the peak-wavelength of the Si-K $\beta$  main peaks from metallic silicon, irradiated and unirradiated quartz and vitreous silica against the temperature of the PET crystal.

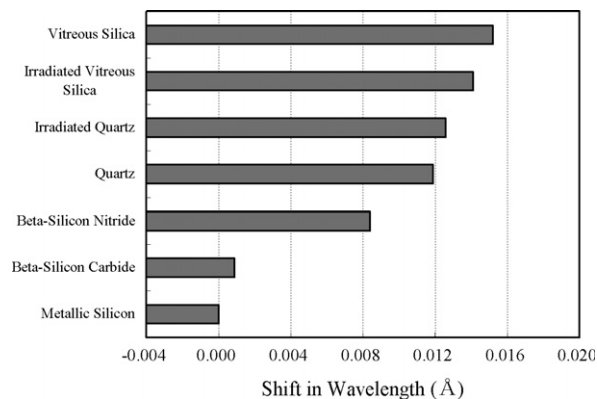


Fig. 4. Chemical shift of Si-K $\beta$  peaks of the specimens from that of metallic silicon at the PET temperature of 25 °C.

change in chemical shift due to the neutron irradiation was relatively small. The main peak of the irradiated quartz was shifted to a longer wavelength, while the main peak was shifted to a shorter wavelength in the case of vitreous silica. The satellite peaks shifted the same way as those of the main peaks. The width of the main peaks for unirradiated quartz and vitreous silica were 60 Å and 76 Å, respectively. After irradiation, the width of the main peaks for quartz and vitreous silica were 76 Å and 90 Å, respectively. Thus, the peak width was broadened by the neutron irradiation in both specimens.

In a separate report, it was observed that the vitreous silica shrunk  $\sim 2.2\%$  in volume and the quartz expanded  $\sim 1.3\%$  in volume after the same irradiation condition [13]. The original density of the vitreous silica was lower than that of quartz. Therefore, the density increased in vitreous silica but it decreased in quartz. It is known that both quartz and vitreous silica suffer large volume changes, contraction (maximum  $\sim 3\%$  increase in density) in the case of vitreous silica and swelling (maximum  $\sim 14\%$  decrease in density) in the case of quartz, and both saturated densities are the same  $\sim 2.26 \text{ g/cm}^3$  [14,15]. The change in density of the present specimens agreed well with these previous studies. The tendency of the peak shift observed by WDX in this study was consistent with the density change of the specimens, as shown in Fig. 6. Therefore, it was confirmed that the chemical shift of the characteristic X-ray wavelength can detect the effects of neutron irradiation of the materials. Basically the wavelength of the characteristic X-rays depends on the difference in energy levels between electron orbitals of the specific atom, in this case Si. The K $\beta$  wavelength corresponds to the transition from the M (3s and 3p) shell to the K(1s) shell. The change in chemical shift indicates that the electron orbital should be slightly modified by the neutron irradiation. The chemical shift in shorter wavelength

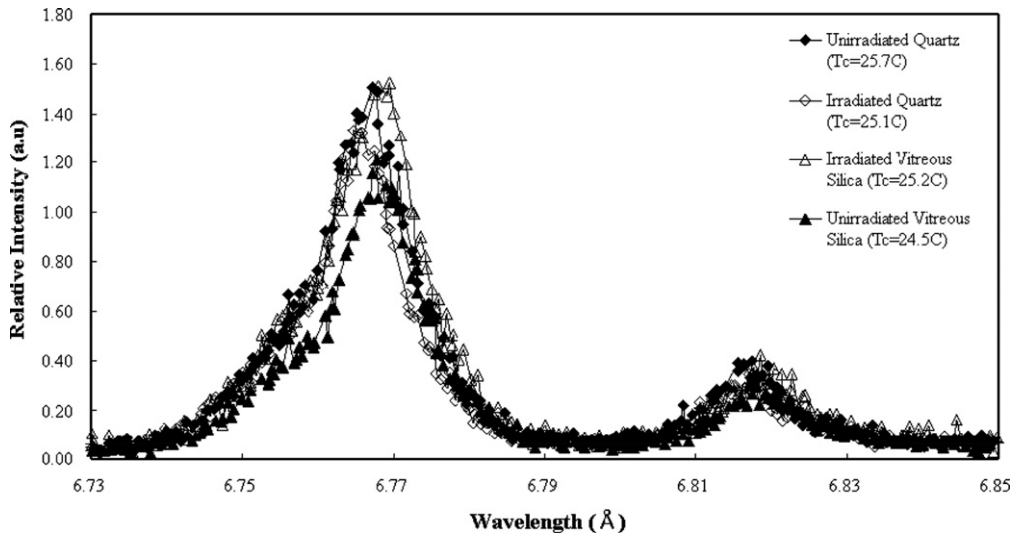


Fig. 5. Observed Si-K $\beta$  profiles for the irradiated and non-irradiated quartz and vitreous silica obtained at the PET crystal temperature of nearly 25 °C.

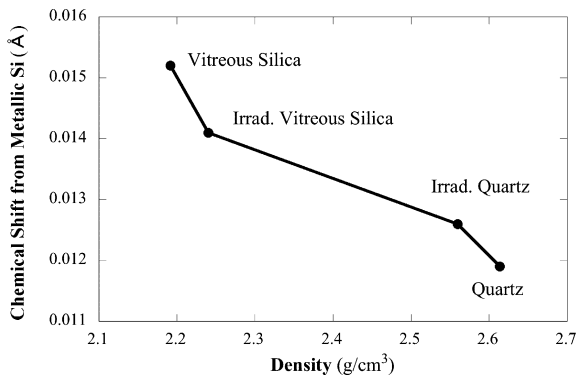


Fig. 6. Relation between the chemical shift of quartz, irradiated quartz, vitreous silica and irradiated vitreous silica at 25 °C and corresponding density.

direction in the case of vitreous silica indicates tighter tetrahedron formation, although the formation of a looser tetrahedron is indicated in the case of quartz. The increase in peak width in both cases suggests an increase in the variation of the coordination due to the irradiation, i.e., the change was non homogeneous.

In the present study, only the PET crystal could be used to detect wavelength shift of Si-K $\beta$  X-rays due to the limitation of crystals in the equipment. If more proper crystal will be applied to diffract characteristic X-rays, the temperature drift may be minimized, and then it enables us to detect the change in coordination of atoms in irradiated materials which show usually very slight property change

by the neutron irradiation. Further study should be necessary.

#### 4. Conclusions

It was confirmed that the chemical shift of the characteristic X-ray wavelength can be applied to observe neutron irradiation effects of materials. A chemical shift of the main K $\beta$  peaks from that of metallic silicon was observed for unirradiated materials, with increasing wavelength for  $\beta$ -silicon carbide,  $\beta$ -silicon nitride, quartz and vitreous silica in this order. The chemical shift of K $\beta$  wavelength from vitreous silica due to neutron irradiation was reduced but that of quartz increased compared to these of unirradiated specimens. The change corresponded with the change in density.

#### Acknowledgements

The work was partly supported by the Grant-in-Aids for Scientific Research from the JSPS, and partly by the JNC. Thanks are due to the staffs of the International Research Center for Nuclear Materials Research, Tohoku University for irradiation of the specimens.

#### References

- [1] F.W. Clinard Jr., E.H. Farnum, D.L. Griscom, R.F. Mattas, S.S. Medley, F.W. Wiffen, S.S. Wojtowics, K.M. Young, S.J. Jinkle, *J. Nucl. Mater.* 191–194 (1992) 1399.

- [2] F.W. Clinard Jr., W. Dienst, E.H. Farnum, *J. Nucl. Mater.* 212–215 (1994) 1075.
- [3] S. Yamamoto, T. Shikama, V. Belyakov, E. Farnum, E. Hodgson, T. Nishitani, D. Orlinski, S. Zinkle, S. Kasai, P. Stott, K. Young, V. Zaveriaev, A. Costley, L. deKock, C. Walker, G. Janeschitz, *J. Nucl. Mater.* 283–287 (2000) 60.
- [4] M. Decreton, T. Shikama, E. Hodgson, *J. Nucl. Mater.* 329–333 (2004) 125.
- [5] E.W. White, R. Roy, *Solid State Commun.* 2 (1964) 151.
- [6] E.W. White, H.A. Mackinstry, T.F. Bates, *Advances in X-Ray Analysis*, Vol. 2, Plenum, New York, 1960.
- [7] D.E. Day, *Nature* 200 (1963) 695.
- [8] Y.-Z. Bai, S. Fukushima, Y. Gohshi, *Yogyo-Kyokai-Shi* 92 (1984) 475.
- [9] T. Okura, H. Inoue, T. Kanazawa, *Spectrochim. Acta* 45B (1990) 711.
- [10] T. Okura, G. Sudoh, *J. Mater. Sci.* 30 (1995) 1033.
- [11] E.A. Leone, *Scann. Electron Micros.* 3 (1984) 1023.
- [12] S. Kawai, M. Motoyama, *Prog. X-ray Spectrosc.* 20 (1988) 103 (in Japanese).
- [13] T. Yano, K. Fukuda, M. Imai, H. Miyazaki, *J. Nucl. Mater.*, these Proceedings, doi:10.1016/j.jnucmat.2007.03.090.
- [14] W. Primak, L.H. Fuchs, P. Day, *J. Am. Ceram. Soc.* 38 (1955) 135.
- [15] E. Lell, N.J. Kreidl, J.R. Hensler, *Prog. Ceram. Sci.* 4 (1966) 1.