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Structural properties of the red-color overglaze for the HIZEN porcelains produced in the early Edo period of Japan

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Abstract

HIZEN porcelains made in 1650s to 1750s (early Edo period) in Arita areas sited in south Japan (SAGA) are famous Japanese porcelains, which are characterized by elegant and bright colors in the overglaze and the underglaze. Red-overglazes and transparent glazes of the HIZEN porcelains have been investigated by means of X-ray diffraction (XRD) and X-ray absorption spectra (XAS) using synchrotron radiation. The results suggest that the red-color brightness of the Hizen porcelains is mainly induced by micro-structural correlation between α-Fe_2O_3 fine particles of red-color emission element and the oxide complexes of SiO_2–Al_2O_3–CaO–KNaO or SiO_2 in the fritted overglazes. The stability of the red-color overglaze on the porcelain body of white-color results from interfacial fusion between both glass-states in the fritted overglaze and the transparent glaze coating the porcelain body. The refined local structures around Fe ions of the α-Fe_2O_3 structure taken EXAFS spectra give the technical and historical relation among four kinds of the HIZEN porcelains for fritted materials of the overglazes and thermal treatment at high-temperature in the porcelain kilns.

Keywords: HIZEN porcelains; Red-overglaze enamels; Kokutani; Kakiemon; Nabeshima ware

1. Introduction

The HIZEN porcelains had been exported from the later 17th century and were estimated to be very famous for interior decorations and dinner-sets in Europe and America, as Chinese porcelains. The HIZEN porcelains are generally classified by four kinds of porcelains: Shoki-Iroe (Kokutani-style), Kakiemon-style, Kinran-style, and Nabeshima ware. Each porcelain shows elegant and bright color-patterns of the overglaze and the underglaze, which are spatially distributed over or under the transparent glaze coating the porcelain body. The Hizen porcelains are usually distinguished by its original color tone and its characteristic pattern-distribution drawn on the porcelain surface [1–16]. From the early 17th century, the HIZEN porcelains had been produced only at the Arita areas localized in SAGA prefecture (called ‘‘HIZEN-Han in the Edo period) of Kyushu island, Japan. The localization results from the Izumiyama ferromagnetic porcelain ceramics of white-color, called ‘‘Izumiyama Toseki’’, collected at Izumiyama of Arita as the basic body of the HIZEN porcelains. The Ceramics including α-Fe_2O_3 with several wt.% had been collected near Izumiyama and used to produce celadon porcelains, called SEIJI from the early 17th century, in which Korean potters discovered raw materials for the porcelain ceramics at Arita and found a possibility of the porcelain production. At the beginning, porcelains, called ‘‘Shoki-Imari’’, had been produced with a Korea porcelain technique. From 1640 to 1650s, the colored underglazes and overglazes were made by the porcelain technique due to Keitokuchin-kiln (China), while the celadon porcelains due to Ryusen-kiln (China).

It was considered that the red-color overglaze of old porcelains is usually based on α-Fe_2O_3 [17]. In the early 18th

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century, a lot of the red-color overglaze enamels of α-Fe_2O_3, called Fukiya-style Bengara, were produced at Fukiya in OKAYAMA prefecture of Honshu island, Japan mainly by heating treatment of $FeSO_4 \cdot 7H_2O$ to Fe_2O_3 at about 650 °C in atmosphere [18–21]. From the later18th century, it was deduced that the Fukiya-style Bengara of α-Fe_2O_3 was also used for the red-color overglaze enamels of the HIZEN porcelains [18,19]. However, the HIZEN porcelains having the red-color overglaze were already made in the early 17th century [22]. This means that there is another source of the HIZEN red-color overglaze enamels, which were imported from China or not. More recently, we found that the Izumiyama porcelain ceramics of white-yellow (WYI) show similar red-color brightness to those of KOIMARI porcelains (Kakiemon-style, Kinran-style, and Nabeshima ware) [23]. Thus, it is possible to consider that the KOIMARI red-color overglaze enamels consist of the WYI because these kilns were closed to Izumiyama porcelain field. It is also considered that the Fukiya-style Bengara was partially circulated at the Arita areas from early18th century.

Recently, we have studied the structural properties of the blue-color underglazes under the transparent glaze and the color overglaze on the transparent glaze of the Koimari porcelains made from the 17th to 18th century by means of high resolution X-ray diffraction (HXRD) and X-ray absorption spectrum (XAS), using synchrotron radiation. In the present investigations, we study the technical and historical correlations among the porcelain techniques for the red-color overglazes of the HIZEN porcelains by XRD and XAS using synchrotron radiation.

2. Experimental

In the present investigations, we used 11 broken pieces of the HIZEN porcelains produced mainly from the middle 17th to the early 18th century in the early Edo period. The specimens were the colored pieces of a small or large dish, cup, and a large bottle, as shown in Photo 1. The pieces were collected at the HIZEN kilns sited at Arita and its neighbor areas of Uresino, Imari (SAGA) and Hasami (NAGASAKI). The pieces in Photo 1a and b were made in 1640s and 1640–1650s and collected at Yamanbe kiln (Arita) and Mimata kiln (Hasami), respectively. The porcelains did not show any bright color and had a thicker

Photo 1. Broken pieces of the HIZEN porcelains taken at the local areas closed to Arita of Kyushu island in Japan; KOKUTANI-style [a, ARITA(1640s); b, HASAMI(1640–1650s); c, URESINO(1650s); d, URESINO(1650s)]; KAKIEMON-style [e, URESINO(early 18 century); f, KAKIEMON(1670–1680s)]; and NABESHIMA ware [g, (1670–1690s); h, (1680–1700s); i, (1690–1720s); j, (1690–1720s); k, (early 18 century)].

porcelain body, which was not made by the Izumiyama porcelain ceramics of white color (Izumiyama Toseki), often called ''Hakujikou''. The ones in Photo 1c and d were made in 1650s and collected at Yoshida kiln (Uresino) and the porcelain body was also not made by the Hakujikou. The HIZEN porcelains in Photo 1a–d are called ''Shoki-Iroe (Kokutani-style). Hasami is about 10 km away from Arita, while Uresino is about 10 km away from Hasami and about 20 km away from Arita. Thus, it is deduced that the colored underglaze and overglaze of the HIZEN porcelains were developed and produced in localized sites of the Arita area, after the Korean potters discovered raw materials of the Izumiyama porcelain ceramics at Arita and found a possibility of porcelain production in the early 17th century. The piece in Photo 1e was produced in the early18th century and collected at Sidanishi kiln (Uresino). It is confirmed that its body is thinner than those of the pieces in Photo 1c and d, and its color brightness is close to that of Kakiemon-style. This implies that the elegant and artistic color-technique of the underglaze and overglaze developed at Arita were distributed to its neighboring areas of Uresino, Hasami, and Okawauchi (Imari), where the later is about 10 km away from Arita.

It is considered that, after 1640–1650s, the development and improvement of the colored overglaze techniques and the production of the HIZEN porcelains were mainly carried out at the Kakiemon kiln and the Nabeshima-domain kiln (Odougu-yama). The piece in Photo 1f (Kakiemon ware) was made in 1670–1680s at the Kakiemon kiln, while the piece in Photo 1g (Early Nabeshima) was made in 1670–1690s at the Nabeshima Odougu-yama, sited at Ohkawauchi (Imari). Since the Nabeshima Odougu-yama was transferred from Nangawara (Arita) to Okawachi (Imari) in 1673–1681s, the piece in Photo 1g was made at Ohkawauchi Odougu-yama. This suggests that the color-techniques of the overglazes in Arita and Ohkawauchi areas were completed in 1670s. The pieces in Photo 1h–k were made at Okawauchi Odougu-yama to be the Nabeshima ware; h (1680–1700s), i (1690–1720s), j (1690–1720s), and k (the early 18 century). The Nabeshima wares as gifts only to the Tokugawa Shogun (Edo period) have different elegant characters compared to the Kakiemon-style porcelains. In the present investigations, we study the structural properties of the red-color emission enamels α-Fe_2O_3 in the fritted overglazes of the HIZEN porcelains (Kokutani-style, Kakiemon-style, and Nabeshima ware) by means of X-ray diffraction, using high bright X-ray of synchrotron radiation. For simplicity, we use following notations for the broken pieces of the HIZEN porcelains in Photo 1; a = KOKUTANI-A, b = KOKUTANI-B, c = KOKUTANI-C, d = KOKUTANI-D, e = URESHINO-E, f = KAKIEMON-F, g = NABESHIMA-G, h = NABESHIMA-H, i = NABESHIMA-I, j = NABESHIMA-J, and k = NABESHIMA-K.

All porcelain pieces in Photo 1 rented from the public museum are very important cultural assets in Japan. Thus, in the present investigations, we were strongly requested to use nondestructive methods for studying the structural and electronic properties of the present porcelains. This means that we cannot use an ordinary X-ray fluorescence analysis with X-ray beams of higher energy, because their X-ray photons slightly affect the chemical and structural properties of the present porcelains. We cannot also remove the partial overglaze on the porcelain surface to estimate the component materials of the porcelain glazes. However, the old documents for the ancient porcelain-techniques kept at the related kilns gave important information for the used raw materials. The results are listed in Table 1. The data were taken for the raw materials by the ordinary X-ray fluorescence spectroscopy. In Table 1, the Izumiyama Toseki had been used in the Kakiemon-style porcelains and the Nabeshima wares, as a porcelain body of white-color. Furthermore, at the early Edo period, the Sirakawa Yamatuti and/or the Taisyu Tyouseki had been used in the transparent glazes and the fritted colored overglazes, in addition to the Isubai (natural wood ash). More recently, Kajihara [24] succeeded the reproduction of the ancient transparent glaze in the early Kakiemon-style porcelains with components of 0.45KNaO, 0.53CaO, 0.02MgO, 0.56Al_2O_3, and 4.89SiO_2, in mol%, by using the raw materials in Table 1. It was also known that the ancient porcelains produced at the Arita areas have the following component region for the transparent glazes; 0.35–0.46KNaO, 0.52–0.65CaO, 0.02–0.04MgO, 0.56–0.99Al_2O_3, and 4.61–7.70SiO_2 in mol%. On the other hand, in wt%, it was known that the ideal fritted red-color overglaze of the ancient Arita porcelain consists approximately of 6.0K_2O, 0.34Na_2O, 0.04CaO, 0.04MgO, 3.2Al_2O_3, 70.0SiO_2 and 0.08Fe_2O_3, in addition to 20.5PbO[25]. The transparent glaze was heated at about 1300 °C, after coating the porcelain basic body. After that, the colored overglazes were painted on the glassy hard transparent glaze as characteristic patterns by hand and were heated in the temperature region of about 850–1000 °C, although the thermal treatment strongly depends on the porcelain technique developed by each kiln of the HIZEN porcelains. It is known that α-Fe_2O_3 of red-color emission materials are included by a few wt% in a fritted glaze, which consists mainly of lead oxide (PbO) and the other oxides of the SiO_2–Al_2O_3–CaO–KNaO complexes.

Table 1
Compositions of the raw materials used in the transparent glaze of the HIZEN porcelains

wt.%	SiO	Al_2O_3	K_2O	Na_2O	CaO	MgO	Fe_2O_3
Sirakawa Yamatuti	76.62	12.85	4.56	3.92	0.44	0.16	0.32
Taisyu Tyouseki	78.18	13.25	0.75	5.65	0.34	0.32	0.32
Izumiyama Toseki	79.08	14.00	2.76	0.42	0.12	0.06	0.56
Isubai	28.74	1.43	1.72	0.60	37.8	1.29	0.32

2.1. High-resolution X-ray diffraction

In order to study the structural properties of the HIZEN porcelains, we used a high-resolution 4-circle X-ray diffractometer at room temperature and the synchrotron radiation at the Pohang Light Source (2.5 GeV) of the Pohang Accelerator Laboratory (Korea). After setting the broken piece of the HIZEN porcelains in Photo 1 on the specimen stage of the 4-circle X-ray diffractometer, we accurately irradiated its red-color overglaze

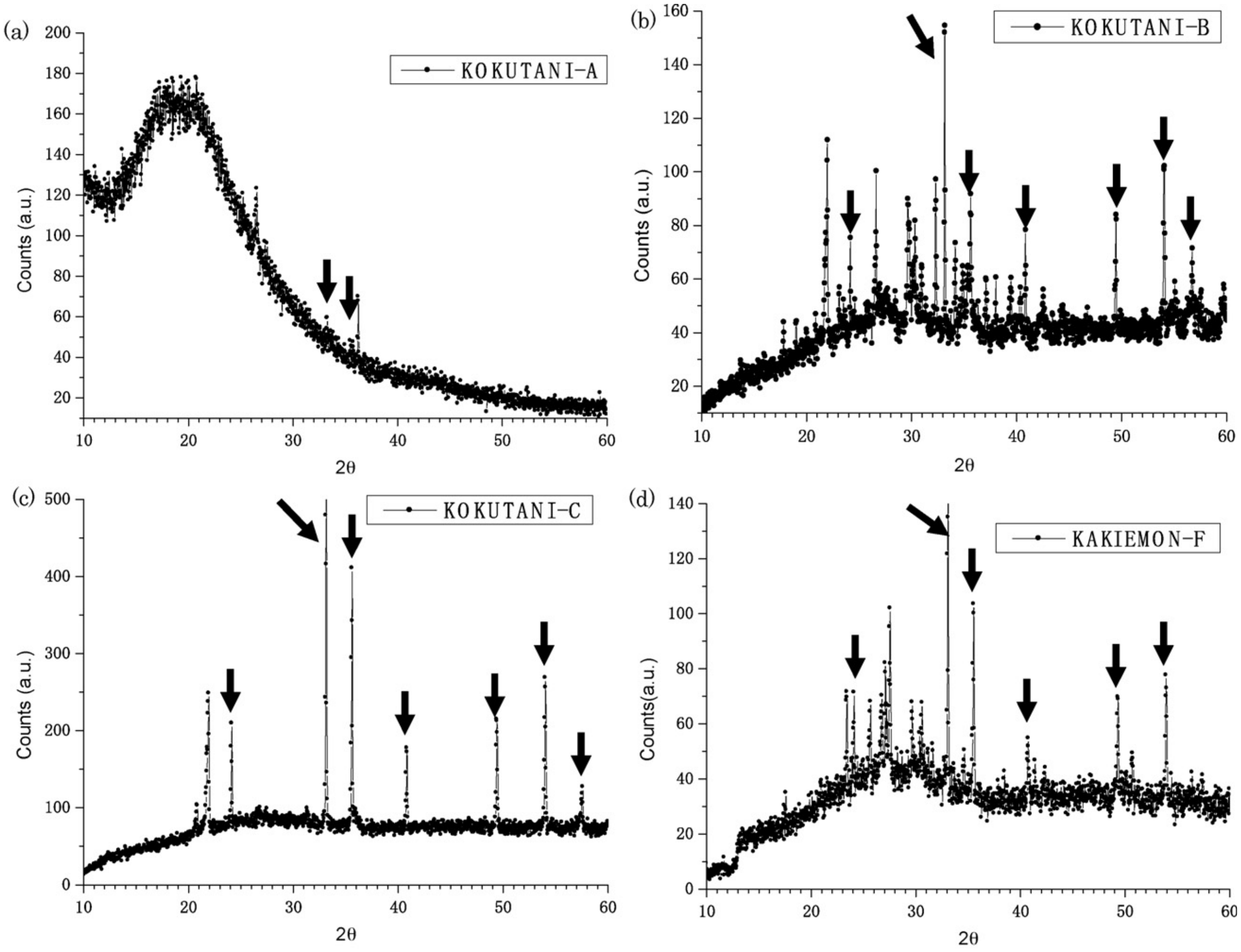

Fig. 1. X-ray diffraction patterns of the HIZEN porcelains: a, (KOKUTANI-A, 1640s); b, (KOKUTANI-B, 1640–1650s); c, (KOKUTANI-C, 1650s); and d, (KAKIEMON-F, 1670–1680s) in Photo 1a–c, and f, respectively. The arrows show the reflections of the α-Fe_2O_3 structure in the red-color overglazes.

with the incident X-ray beams having a size of about 1mm in diameter, and its monochromic X-ray photon energy was about 8.0457 keV (1.5412 Å). The diffraction method was a 2θ scan with each stepping angle of $\Delta 2\theta = 0.03^\circ$ in the region of $2\theta = 10.00$–70.00°, where the specimen was always fixed at an angle θ_s during measurements.

Fig. 1a–d show the X-ray diffraction patterns of the red-color overglazes of the HIZEN porcelains; a = KOKUTANI-A (1640s), b = KOKUTANI-B (1640–1650s), c = KOKUTANI-C (1650s), and d = KAKIEMON-F (1670–1680s) in Photo 1a–c, and f, respectively. In Fig. 1, the arrows represent the reflections of the α-Fe_2O_3 structure in the red-color overglaze. Although the lead oxides (PbO, melting about 880 °C) were usually included in the fritted red-color overglaze as a supporting material of the red-color emission, there is no reflection of PbO in Fig. 1. However, we confirmed Pb atoms in the red-color overglaze by means of the X-ray absorption spectrum, as described later. The X-ray diffraction patterns show extra peaks, but not the α-Fe_2O_3 reflections, and weak or strong halo-like scatterings. This suggests that the fritted overglazes in Photo 1a–c and f have different structural properties. The halo-like scattering means the structural short-range order mainly of other oxides (SiO_2, Al_2O_3, CaO, KNaO, MgO, PbO, etc.), but not α-Fe_2O_3, while the extra peaks result from the poly-crystals of the other oxides and/or the SiO_2–Al_2O_3–CaO–KNaO complexes. It is considered from Fig. 1a and c that, at Arita and Uresino in 1640–1650s, the reduced brightness of the KOKUTANI-style porcelains (Photo 1a and c) is related to the undeveloped fritted components in the red-color overglaze. However, Fig. 1b suggests that the fritted red-color overglaze of KOKUTANI−B had been considerably improved, though the Izumiyama Toseki of white-color in Table 1 were not yet used as a porcelain body ceramics. Thus, it is deduced that, in 1650s, the porcelain porters working at Hasami own jointly the porcelain techniques for the overglazes with ones at Arita because Hasami and Uresino are about 10 and 20 km away from Arita in the mountain area, respectively.

In 1650s, the KOKUTANI-style porcelains (Photo 1b–d) had the α-Fe_2O_3 fine particles in the reduced red-color overglazes, which were sufficiently heated up at high-temperature because of weak hallo-like scatterings. However, the colored overglazes were not well fixed on the surface of the porcelain body. The easily coming off of the overglazes was cleared later by improving the transparent glaze coating the porcelain body in the Arita area. It was known that, at that time, the colored overglazes drawn on the porcelain by hand were heated up at about 700–800 °C, after the porcelain body coated with the transparent glazes were preliminarily heated up at about 1300 °C. The porcelain body was made of the Izumiyama Toseki of white-color. In Photo 1f, the Kakiemon-style porcelain (KAKIEMON-F) in 1670–1680s shows the elegant brightness of the colored overglazes, and the colored overglazes were well fixed on the transparent glaze. Its thin porcelain body ceramics was the Izumiyama Toseki. Fig. 1d shows the extra peaks and the halo-like scatterings, in addition to the reflections of the α-Fe_2O_3 structure. We also found that the transparent glaze closed to the floral patterns of the red-color overglazes is in glass-state because of the halo-like diffraction pattern as like that in Fig. 1a [26,27]. Thus, it is considered that the stability of the colored overglazes on the transparent glaze coating the porcelain body results from interfacial fusion of both glasses in the fritted red-overglaze and the transparent glaze, as an adhesive ceramic.

We are also interested in the origin of many weak and strong extra peaks in Fig. 1b and d. Fig 2a and b show the expanded diffraction patterns of the KOKUTANI-B and KAKIEMON-F porcelains in Fig. 1b and d, respectively. All peaks cannot be indexed by each component structure of SiO_2, Al_2O_3, CaO, KNaO, MgO, PbO included in the fritted red-color overglaze, except the α-Fe_2O_3 peaks denoted by arrows. Although it was not easy to correctly index the extra peaks, we deduced that some extra peaks result from the poly-crystals of the SiO_2–Al_2O_3–CaO–KNaO complexes because EXAFS spectra of Pb in the red-color overglazes suggested that the local structure around Pb ions is in glass-state. If so, the complexes give information for the thermal treatment to the fritted overglazes, as like a ceramic thermometer of Hecht, Cramer, and Seger used in the kiln, where the ceramic thermometer is usually made of SiO_2, Al_2O_3, CaO, K_2O, Na_2O, MgO, B_2O_3, and its melting temperature depends on the composition-ratio of the components. At a moment, some peaks are approximately related to (K, Na)$AlSi_3O_8$ and $CaAl_2Si_2O_8$ structures as regarding the intensity ratio. However, we need to quantitatively study the origin of the extra peaks. Thus, we are now in progress to re-measure the X-ray diffraction patterns of KOKUTANI-B and KAKIEMON porcelains. At a moment, we assumed that the elegant brightness of the red-color overglazes in the HIZEN porcelains after 1670s (Photo 1e and f) is induced partially by the structural correlation between the α-Fe_2O_3 fine particles and the other complex oxides in the fritted red-color overglazes.

In 1660–1670s, the early Kakiemon families completed the porcelain techniques for the colored overglaze and the transparent glaze of the Kakiemon wares, and deeply contributed to establish the big production of the Kakiemon-style porcelains in the areas. It is considered that, officially and

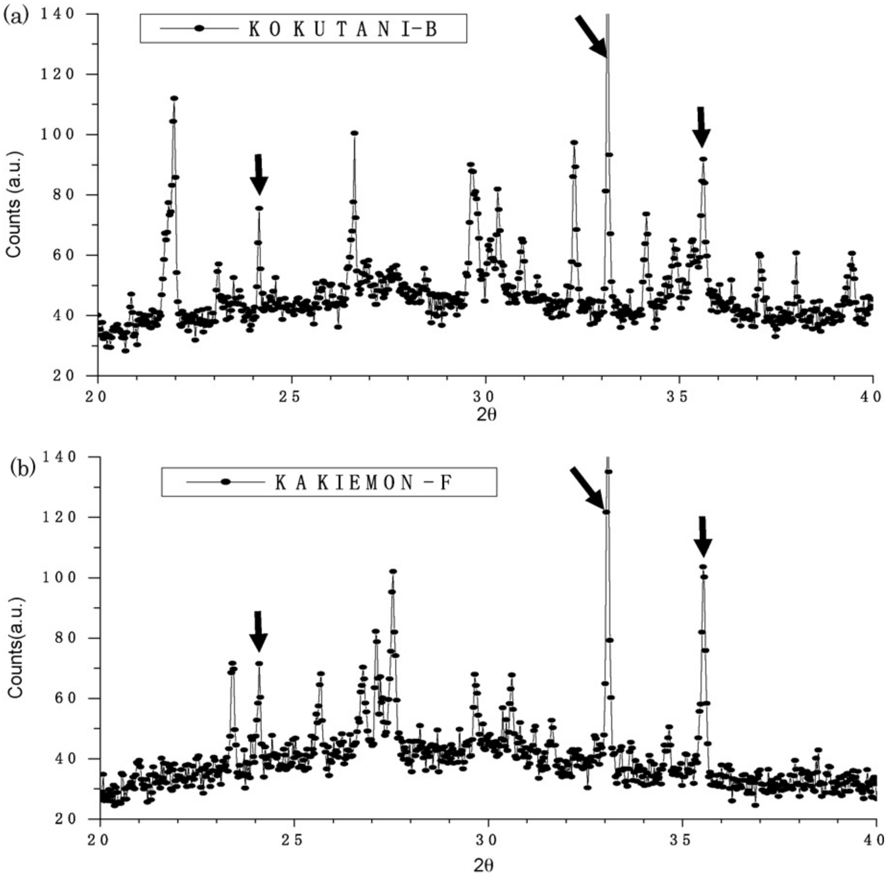

Fig. 2. X-ray diffraction patterns of the KOKUTANI-B and KAKIEMON-F porcelains in Fig. 1b and d, respectively. The arrows show the reflections of the α-Fe_2O_3 structure in the red-color overglazes.

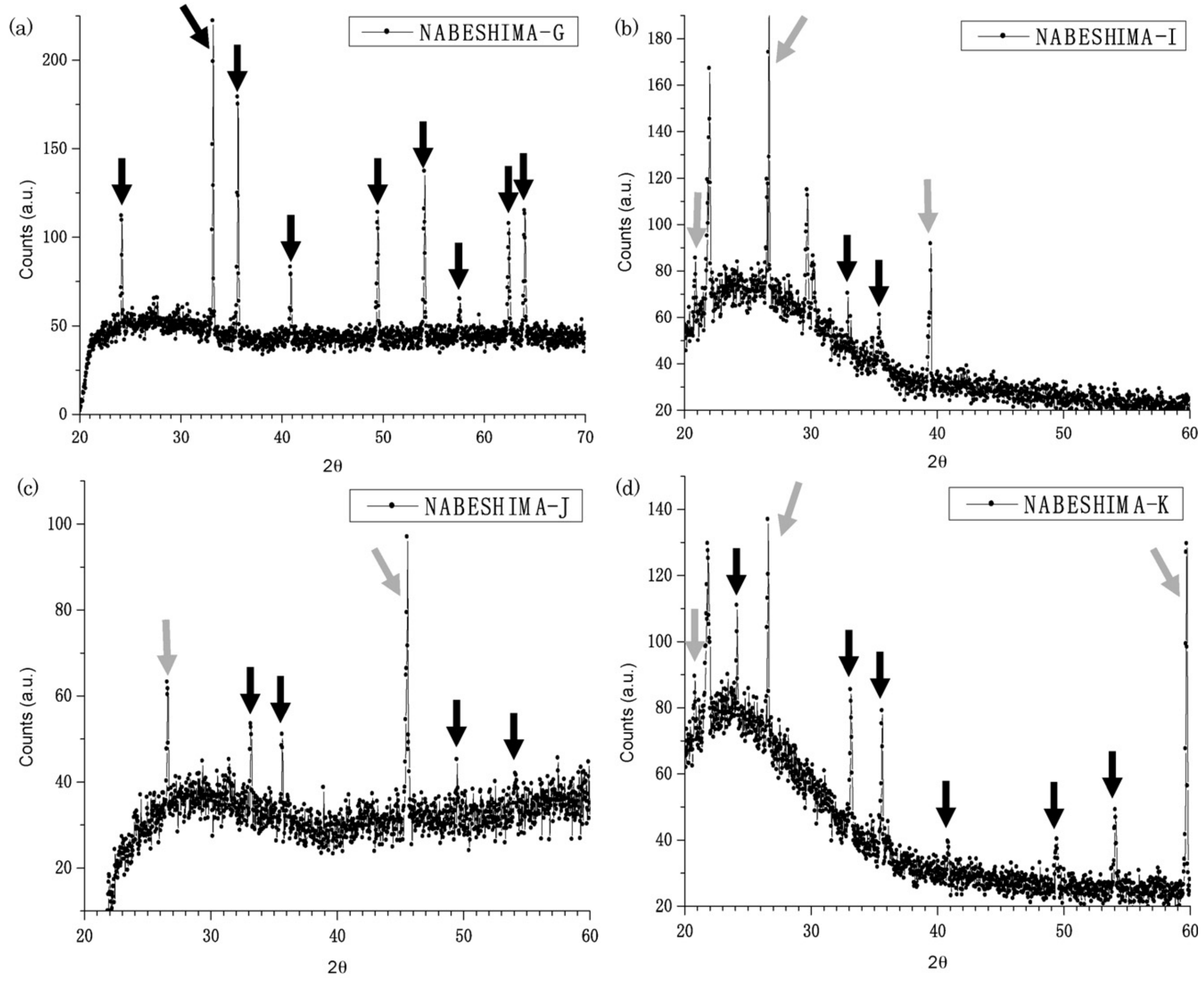

Fig. 3. X-ray diffraction patterns of the HIZEN porcelains: a, (NABESHIA-G, 1670–1690s); b, (NABESHIA-I, 1690–1720s); c, ((NABESHIA-J, 1690–1720s); and d, (NABESHIA-K, early 18th century) in Photo 1g and i–k, respectively. The dark- and gray-arrows show the reflections of the α-Fe_2O_3 structure and the SiO_2 one, respectively, in the red-color overglazes.

privately, the porcelain potters own jointly the porcelain techniques to shortly produce a lot of export HIZEN porcelains in the early Edo period. However, at the period, the Nabeshima wares were developed with slightly different porcelain techniques to that of the Kakiemon-style porcelains, after the Odougu-yama of the Nabishima-domain kiln was transferred from Nangawara (Arita) to Ohkawauchi (Imari) in 1673–1681s. Kakiemon kiln was sited at Nangawara. Thus, we are also interested in the structural difference between the Nabeshima wares and the Kakiemon-style porcelains. Fig. 3a–d shows the X-ray diffraction patterns of the red-color overglazes for the Nabeshima wares in Photo 1g and i–k, respectively, where NABESHIMA-G, I, J, K were made in 1670–1690s (the Early Nabeshima,), 1690–1720s (the Prime Nabeshima), 1690–1720s (the Prime Nabeshima,), and early 18th century (the Middle Nabeshima). In Fig. 3, the dark- and gray-arrows represent the reflections of the α-Fe_2O_3 structure and the SiO_2 one, respectively. It is found that Fig. 3a shows only the α-Fe_2O_3 reflections of strong intensity, as that in Fig. 1c. Thus, we consider that, in the Early Nabeshima (about 1670–1690s), the α-Fe_2O_3 particles were as a red-color emission element and the red-color overglaze technique was very similar of Kokutani-style, just when the Odougu-yama was transferred to Ohkawauchi (Imari) in 1673–1681s. However, the Odogu-yama already used the porcelain body ceramics of white-color, that is Izumiyama toseki, in Photo 1g. Comparison of the diffraction patterns in Figs. 1d and 3b–d, suggests that the Nabeshima wares were certainly produced by the different porcelain techniques to the Kakiemon-style porcelain. Especially, the Nabeshima wares in the Prime, Middle Nabeshima show the strong peaks of SiO_2 structure, denoted by the gray arrows in Fig. 3, in the fritted red-color overglaze. This suggests that the crystallization of SiO_2 particles give information of the thermal treatment at higher-temperature in the Odougu-yama kiln. On the other hand, the Kakiemon-style porcelains show the crystallization of the complexes of SiO_2–Al_2O_3–CaO–KNaO in the fritted red-color overglazes as the extra peaks in Figs. 1 and 2 [26,27]. It is known that the Nabeshima wares used the similar fritted materials in Table 1 to those of the Kakiemon-style porcelains. Thus, we suspect that the thermal treatment in the Nabeshima kilns induces a mixed phase of the crystalline SiO_2 and the glass-like Al_2O_3–CaO–KNaO–PbO complex because of the halo-like scatterings in Fig. 3b–d. Thus, the thermal treatment is probably related to the difference of the elegant and bright red-color emission between the Nabeshima wares and the Kakiemon-style porcelains. As described before, it is also considered that the stability of the colored overglazes results from interfacial fusion of both glasses in the fritted red-color overglaze and the transparent glaze.

2.2. High-resolution X-ray absorption spectrum

The X-ray diffraction patterns in Figs. 1–3 suggests that there is probably a high structural correlation between the red-color emission particles of α-Fe_2O_3 and their surrounding oxide particles of SiO_2, Al_2O_3, CaO, K_2O, Na_2O, MgO, PbO, etc. Thus, we carried out the study of the local structure around Fe ions. Such physical information can get by analyzing the X-ray absorption spectrum (XAS) measuring near an X-ray absorption edge of Fe–K. Generally, the XAS consists of XANES spectrum in the region of about −100 to +150 eV and EXAFS one in the region of about 50–700 eV around its X-ray absorption thresholds (E_o). In the present investigations, the XAS were measured near the Fe–K edge for the HIZEN porcelains, by using synchrotron radiation at the Pohang Light Source (2.5 GeV). A double crystal monochromator of Si (1 1 1) gave a relative energy resolution ΔE to be less than about 0.2 eV in the respective measurements for the XAS near the Fe–K edge. The incident X-ray photons (I_o) were detected with an ionic chamber set before the specimens of the broken pieces in Photo 1, while the X–ray fluorescence photons (I_F) emitted from the front surface of the specimens were simultaneously detected with an X-ray fluorescence detector. The surface was always set with about 45.0° to the incident X-ray beam, of which the size was about 1–3 mm in horizontal and 1 mm in vertical on the specimen surface to the electron orbital of the accelerator. The E_o of the α-Fe_2O_3 structure slightly sifts from 7111 eV (a free Fe ion) to about 7114 eV, since E_o depends on the crystallographic structure. The ratio (I_F/I_o) gives the XAS near the Fe–K edge.

Fig. 4 shows the XAS of the HIZEN porcelains in Photo 1a–c and f, which are KOKUTANI-A, B, C and KAKIEMON-F, respectively. All of the spectra result from Fe ions in the red-color overglaze enamels α-Fe_2O_3. Fig. 5 shows the EXAFS spectra partially expanded in Fig. 4. Thus, the results suggest that the local structures around Fe ions are slightly deformed in the fritted overglazes. As described in Fig. 1, the X-ray diffraction patterns suggest that the used fritted overglazes have

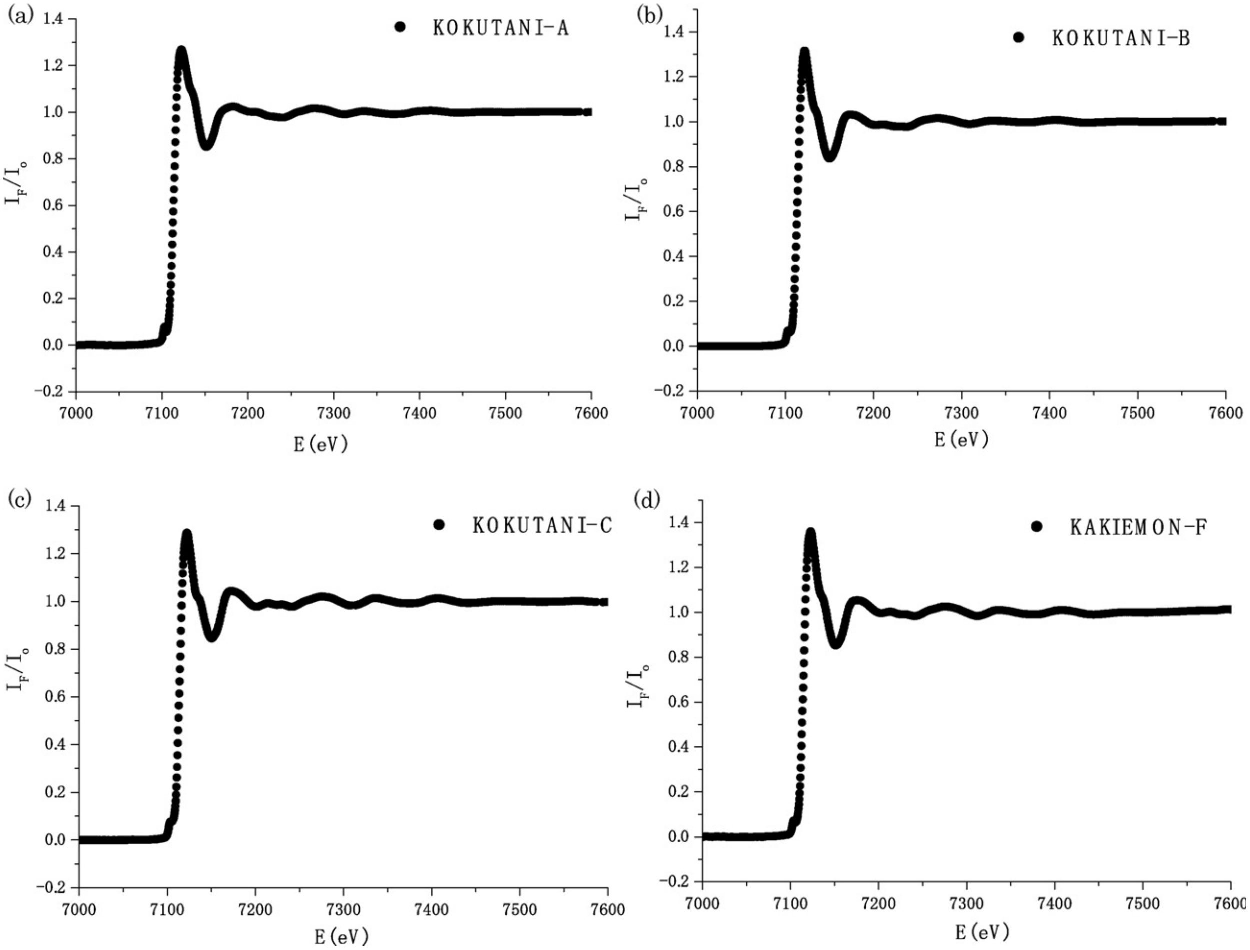

Fig. 4. X-ray absorption spectra around Fe–K edges of α-Fe_2O_3 in the HIZEN porcelains of KOKUTANI-A(ARITA, 1640s), B(HASAMI, 1640–1650s),C(URESINO, 1650s), and KAKIEMON-F(1670–1680s) in Photo 1a–c, and f, respectively.

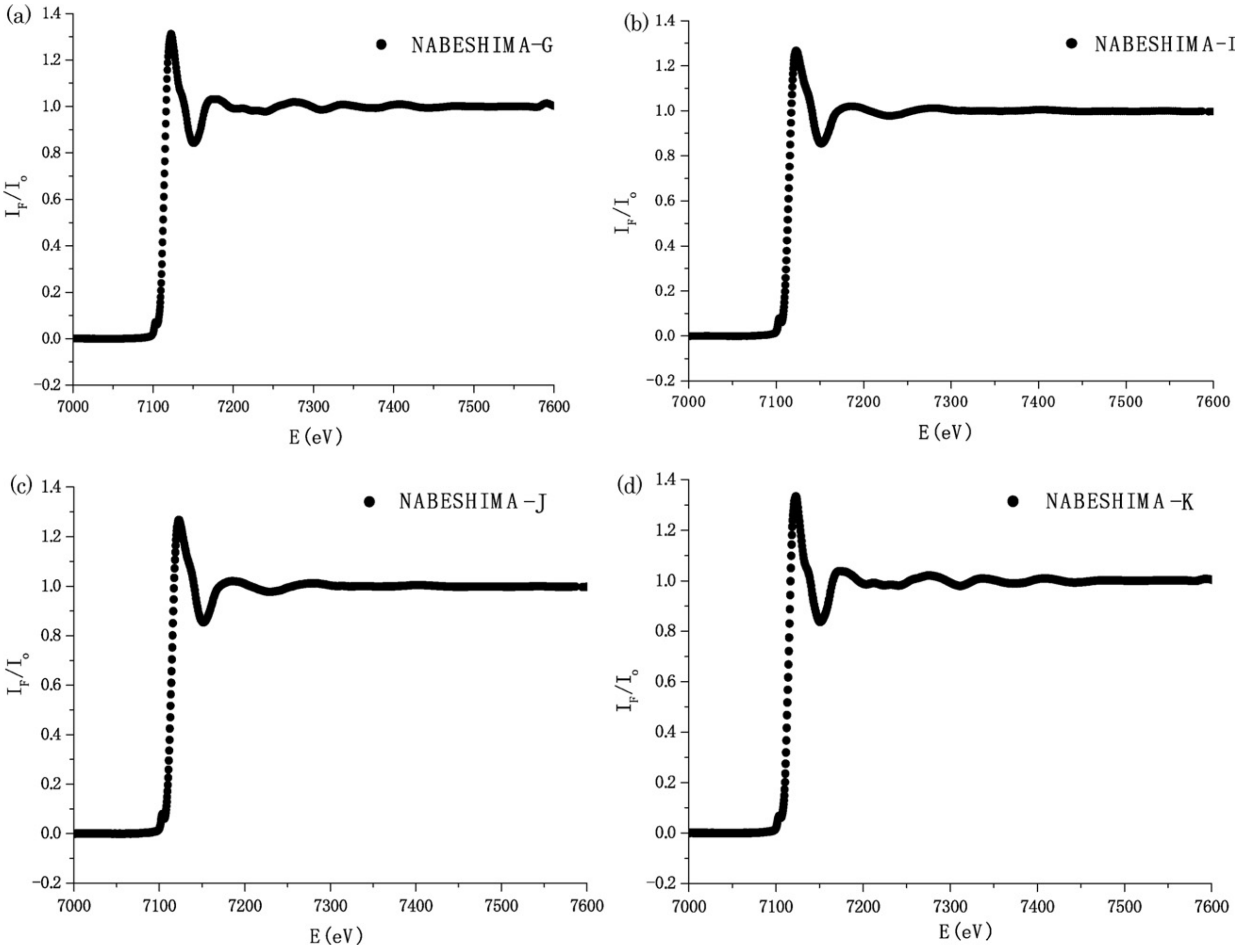

Fig. 5. Partial EXAFS spectra around Fe–K edges of α-Fe_2O_3 in HIZEN of KOKUTANI-A, B, C and KAKIEMON-F, expanded in Fig. 4.

different structural properties in the present porcelains, though the red-color emission enamels were the α-Fe_2O_3 particles. Thus, we consider that the α-Fe_2O_3 fine structure depends slightly on the material components of the overglaze and the thermal treatment at about 800–1000 °C in the porcelain kiln.

Fig. 6 shows the XAS around Fe–K edge in α-Fe_2O_3 for the Nabeshima wares in Photo 1g and i–k, which are NABESHIMA-G, I, J, and K, respectively. All of the wares were made at the Nabeshima Odougu-yama. Fig. 7 shows the EXAFS spectra partially expanded in Fig. 6. The results suggest that the

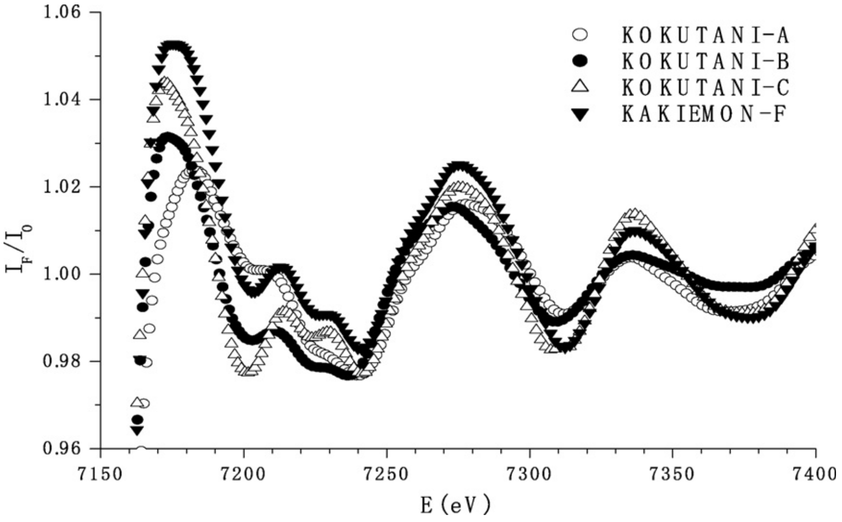

Fig. 6. X-ray absorption spectra around Fe–K edges of α-Fe_2O_3 in HIZEN of NABESHIMA-G(1670–1690), I(1690–1720), J(1690–1720), K(front-half of 18th century) in Photo 1g, i–k, respectively.

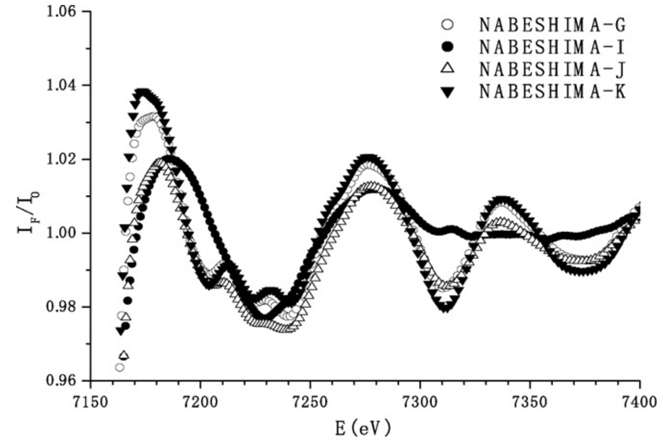

Fig. 7. X-ray absorption spectra of partial EXAFS around Fe–K edges of α-Fe_2O_3 in NABESHIMA-G and I–K, expanded in Fig. 6.

local structures around Fe ions are slightly deformed in the fritted overglazes, and that the porcelain technique for the fritted red-color overglaze of the Nabeshima wares was historically modified, as shown in the X-ray diffraction patterns (Fig. 3). It is known that the Nabeshima wares are classified approximately by the Early Nabeshima (1670–1680s), the Prime Nabeshima (1680–1720s), the Middle Nabeshima (1720–1770s), and the Latter Nabeshima (after 1770s). Thus, we are interested in a correlation between the red-color overglaze enamels and the producing periods of the Nabeshima wares. From comparison of the EXAFS spectra in Figs. 5 and 7, it is found that the Nabeshima wares (G and K) were made by the similar porcelain technique for the fritted red-color overglaze to that of KAKIEMON-F. Although NABESHIMA-G was produced in 1670–1690s, the Odougu-yama of the Nabishima-domain kilns were transferred from Nangawara (Arita) to Ohkawauchi (Imari) in 1673–1681s. In 1660–1670s, the early Kakiemon families completed the porcelain techniques, called ‘‘Kakiemon-style’’, producing the elegant and bright colored overglazes and the transparent glazes at Nangawara. Thus, it is deduced that, for the red-color overglaze, the Early Nabeshima wares were still affected by the Kakiemon-style porcelain technique, even after the Nabishima-domain kilns were sited at Ohkawauchi. On the other hand, NABESHIMA-K made in the front-half of 18th century also

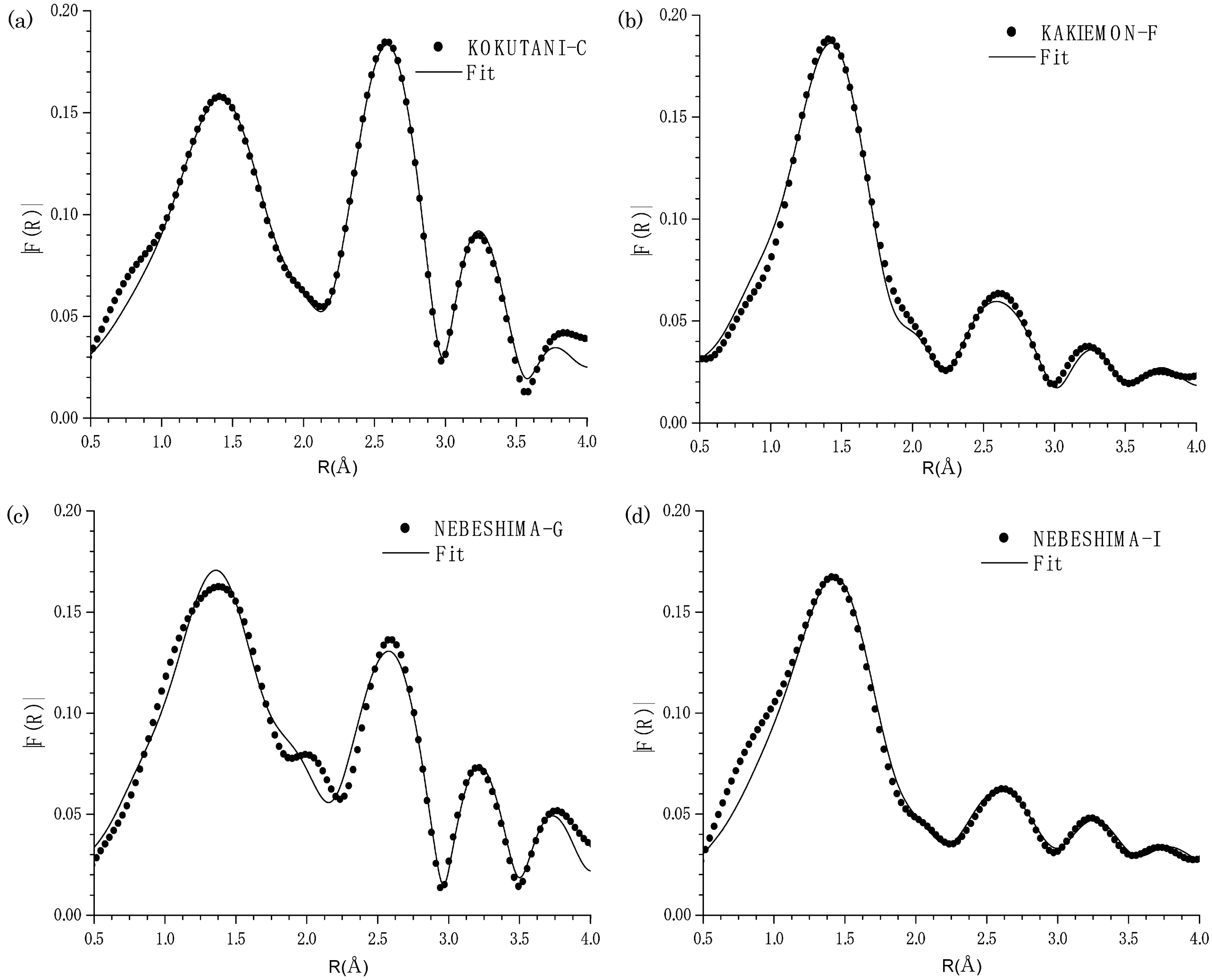

Fig. 8. Theoretical |F(R)|(solid line-fit) of the EXAFS spectrum, taken by the least squares refinement to the observed |F(R)| (solid circles) for the Fe ions in the α-Fe_2O_3 structure: a, (KOKUTANI-C); b, (KAKIEMON-F); c, (NABESHIMA-G); and d, (NABESHIMA-I).

Table 2
Refined parameters R_j(Å) of the surrounding ions (oxygen O_j and Fe ions Fe_j) around the X-ray absorber Fe ion to the ideal radial distance R_{calj}(Å) in the α-Fe_2O_3 structure for HIZEN porcelains of KOKUTANI-style (A–D), KAKIEMON–style (E and F), and NABESHIMA (G–K) in Photo 1

	RF	O1	O2	Fe1	Fe2	Fe3	O3	O4	Fe4	O5	Fe5
R_{cal}		1.96	2.09	2.88	2.97	3.36	3.38	3.60	3.70	3.81	3.98
N		3	3	1	3	3	3	3	6	3	1
A	0.003	1.875	2.080	2.871	2.957	3.352	3.372	3.585	3.686	3.795	3.965
B	0.005	1.967	2.095	2.892	2.978	3.376	3.396	3.610	3.712	3.822	3.993
C	0.004	1.910	2.082	2.873	2.959	3.354	3.374	3.587	3.688	3.797	3.968
D	0.004	1.880	2.082	2.874	2.960	3.355	3.375	3.589	3.690	3.798	3.969
E	0.006	1.910	2.092	2.888	2.974	3.371	3.391	3.605	3.707	3.816	3.988
F	0.005	1.880	2.090	2.885	2.971	3.368	3.388	3.602	3.703	3.813	3.984
G	0.011	1.880	2.089	2.883	2.969	3.366	3.386	3.600	3.701	3.811	3.982
H	0.010	1.910	2.110	2.913	2.999	3.401	3.421	3.637	3.739	3.850	4.023
I	0.003	1.910	2.109	2.912	2.998	3.399	3.419	3.635	3.738	3.848	4.021
J	0.007	1.900	2.098	2.896	2.982	3.381	3.401	3.616	3.717	3.827	3.999
K	0.015	1.910	2.093	2.889	2.975	3.373	3.392	3.607	3.708	3.818	3.989

shows the similar EXAFS spectrum to that of KAKIEMON-F. This suggests that the Middle Nabeshima wares were also affected by the Kakiemon-style porcelain technique. As described above, the HIZEN porcelains used the α-Fe_2O_3 particles as the red-color emission enamel. However, the X-ray diffraction patterns of the Nabeshima wares (G and K) in Fig. 3a–d are largely different to that of Kakiemon wares (F) in Fig. 1d, in contrast to the partial EXAFS spectra in Figs. 5 and 7. It is known that the Nabeshima wares and the Kakiemon-style porcelains used the similar raw materials and their component-ratio of the fritted overglazes at the Arita and Imari areas in the early Edo period. Thus, this evidence results mainly from the different thermal treatment between both porcelains. It is considered that the characteristic high-temperature environment in the porcelain kilns affects slightly the fine structure of the red-color emission element α-Fe_2O_3.

In order to study quantitatively the local structures around Fe ions of α-Fe_2O_3 in the red-color overglaze, we analyzed more accurately the EXAFS spectra of the HIZEN porcelains in Figs. 4 and 6. An observed Fourier transformation spectrum $|F_{obs}(R)|$was obtained from $X_{obs}(K)$, where the $X_{obs}(K)$ is an observed oscillating EXAFS spectrum $X_{obs}(K)$ with a wavenumber k-unit from the XAS spectrum. The details of its analysis were already reported in our paper [23]. The representative results are shown in Fig. 8. The $|F_{obs}(R)|$are denoted by solid circles for KOKUTANI-C, KAKIEMON-F, NABESHIMA-G, and NABESHIMA-I in Fig. 8a–d, respectively. The abscissa is a radial distance (R(Å)) from a X-ray absorbing Fe ion to its surrounding shells including the cations or anions of the α-Fe_2O_3 structure. The peak profiles of the $|F_{obs}(R)|$ suggest that there is an intrinsic difference of the local structure around Fe ions for the HIZEN porcelains of Kokutani-style, Kakiemon-style, and Nabeshima ware.

In the present investigations, we used software programs of *Artemis* and *Athena* to analysis the XAS data and refine the $X_{obs}(K)$ with a theoretical $X_{cal}(K)$ [28]. We carried out a curve fitting between the $X_{obs}(K)$ and the $X_{cal}(K)$ by mean of a least squares method for several refined parameters, which consist of numbers (N_j) of ions sited on the shell having the same radial distance R_j, Debye–Waller factors (σ_j), characteristic temperature (Θ_Dj), a passive electron reduction factor (S_o^2). The refinements were monitored by a convergence factor RF; $RF = \{\Sigma|SX_{obs}(K) - SX_{cal}(K)|^2\}/\Sigma|SX_{obs}(K)|^2$, where S is a scale factor. The details were also reported in our paper [23]. In Fig. 8, the solid lines represent the theoretical Fourier transformation spectrum $|F_{cal}(R)|$ for each porcelains, when getting at the best refinements. The RF-values were about 0.004, 0.005, 0.011 and 0.003 in Fig. 8a–d, respectively. We confirmed that the present spectral analyses were successfully done in Fig. 8.

We carried out refinements of the EXAFS data taken for the HIZEN porcelains in Photo 1. The results are shown in Table 2, where the alphabet notations of A–K mean those of the HIZEN porcelains in Photo 1. The O_j and Fe_j (j = integer) represent the surrounding oxygen and Fe ion in the shell sited at the radial distance R_j away from the origin of the X-ray absorbing Fe ion, respectively. When refining the local structures based on the EXAFS spectra, it is important to obtain a phase between the photoelectron waves emitted from the X-ray absorbing Fe ions and the backscattering waves produced by the surrounding shells. Thus, we also refined the phase parameter. In the present refinements, the calculated radial distances R_{calj} are due to the ideal α-Fe_2O_3 structure of hexagonal symmetry to be $a = 5.035$ and $c = 13.72$ Å. Thus, a slight difference between R_j and R_{calj} results from the effect of the phase parameters. We found from Table 2 that the radial distances R_j are characterized by Kokutani-style (Shoki-Iroe), Kakiemon-style, and Nabeshima ware. The R_j difference of the HIZEN porcelains suggests that the α-Fe_2O_3 structure is slightly deformed in the fritted red-overglaze by the surrounding cations (Si, Al, Pb, Ca, etc.) and/or the anions (oxygen), although the characteristic porcelain techniques were developed and improved by each porcelain kiln producing the HIZEN porcelains.

Fig. 9 shows the historical dependence of the R_j of the surrounding Fe ion (Fe5), R(Fe5), in Table 2, where the alphabet notations of A–K are corresponded to a–k in Photo 1 of the HIZEN porcelains. The results suggest that the α-Fe_2O_3 structures in the red-color overglaze were slightly deformed chronologically from Kokutani-style (KOKUTANI-A,B,C,D), Kakiemon (KAKIEMON-F), Nabeshima wares (NABESHIMA-G, H, I, J) to Kakiemon-style ware (URESHINO-E) and

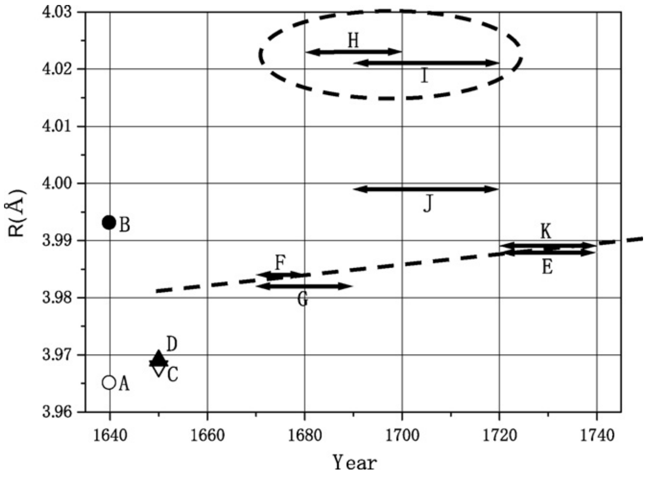

Fig. 9. Historical dependence of the R_j (Å) for the surrounding Fe ion (Fe5), R(Fe5), listed in Table 1. The symbol A–K are defined for the HIZEN porcelains, where the KOKUTANI-style (A–D), KAKIEMON-style (E), KAKIEMON (F), NABESHIMA-style (G–K) in Table 2.

NABESHIMA ware (NABESHIMA-K). It is considered that the heating expands the crystallographic lattice constants of the porcelain oxides or complexes, and that the interfacial fusion between both glass-states in the fritted overglaze and the transparent glaze induced at high temperature slightly keeps the thermal expansion of the lattice constants even at room temperature, after the porcelain is gradually cooled from high-temperature (about 800–1000 °C) in the porcelain kiln. Thus, the R_j of the α-Fe_2O_3 structure gives information for the thermal treatment of the porcelains at high-temperature. We consider in Fig. 9 that the HIZEN porcelains were produced by the different heating techniques for Kokutani-style (before 1650s), Kakiemon-style (1670–1740s), and Nabeshima wares (1680–1720s). The extrapolated dotted line in Fig. 9 indicates a historical succession between the Kakiemon ware (F) and the Kakiemon-style (E). More recently, we have been studying the local structure around Fe ions in the red-color overglazes of several Kakiemon-style porcelains produced in 1670–1730s, and the results showed that the R(Fe5) of the Kakiemon-style porcelains are in the region of about 3.988–3.992 Å [26,27]. The early Kakiemon families completed the porcelain techniques of the Kakiemon-style porcelains having the elegant and bright colored overglazes in 1660–1670s and considerably contributed the mass production of the Kakiemon-style porcelains in the Arita areas in the Edo period. This is consistent with the distribution of the R(Fe5) in Fig. 9. Recently, we also confirmed the unstable R_j-value of the Kokutani-style ones produced before 1650s, as like those in Fig. 9. On the other hand, the Nabeshima wares (H–J) produced in the Prime Nabeshima period (1680–1720s) show a large shift value of the R(Fe5) to those of the Kakiemon-style porcelains (E and F). Thus, we suspect that the noblest elegance and brightness of the colored porcelain pattern in the Prime Nabeshima wares strongly depend on the characteristic thermal treatment at higher temperature than that of the Kakiemon-style porcelains. However, the elegant and bright patterns of the colored overglazes of the Nabeshima wares were gradually reduced in the Middle Nabeshima period (1720–1770s). Fig. 9 also indicates the reducing process of the Middle Nabeshima wares by the consistency of the R(Fe5) between the Kakiemon-style porcelain (E) and NABESHIMA ware (K). This means that the red-color overglazed porcelain technique of the Middle Nabeshima wares were combined with that of the Kakiemon-style porcelain in 1720–1740s.

3. Discussion

In order to study the historical and geometrical correlation of the red-color overglaze techniques among the Kokutani-style porcelains, Kakiemon ware, Kakiemon-style porcelains, and the Nabeshima wares of the HIZEN porcelains, we carried out the X-ray diffractions (XRD) and the measurements of the X-ray absorption spectra (XAS) near the Fe–K edge, by using the synchrotron radiation. The results suggest for the HIZEN porcelains that the red-color emission material is certainly the α-Fe_2O_3 fine particles of a few wt.% in the fritted red-color overglaze, and that the elegance and brightness of red-color depend on the fritted materials in the overglazes and the thermal treatment of the porcelain kilns at high-temperature. It is found from XRD that the fritted red-color overglazes show the largely structural difference among four kinds of the HIZEN porcelains. Especially, in the red-color overglazes, the Kakiemon-style porcelains indicate the crystallization of the fritted components SiO_2–Al_2O_3–CaO–KNaO complexes, while the Nabeshima wares indicate the crystallization of SiO_2. This suggests that the thermal treatment of the porcelain kiln is slightly different between the Kakiemon-style porcelains and the Nabeshima wares, since the raw materials of the fritted overglazes are almost similar for both porcelains at the Arita (Kakiemon) and Imari (Nabeshima) areas in the early Edo period. The EXAFS analyses in Fig. 9 indicate that the Prime Nabeshima wares (1680–1720s) were produced at higher-temperature than that of the Kakiemon-style porcelains, and that the Middle Nabeshima wares (1720–1770s) and the Latter Nabeshima wares (after 1770s) were produced by the same porcelain technique for the red-color overglaze with that of the Kakiemon-style porcelains. It is also found that, for the Kakiemon-style porcelains and the Nabeshima wares, the structural stability of the red-color overglaze on the porcelain body of white-color results from interfacial fusion between both glass-states in the fritted overglaze and the transparent glaze coating the porcelain body, as an adhesive ceramic.

References

[1] H. Imaizumi, Iro-Nabeshima and Matsugadani, Yuzankaku-Shupan, 1969

[2] H. Nishida, A pageant of Japan Ceramics—Imari Ware, Nippon Toji Zenshu 23, Choukouronsha, 1976.

[3] H. Nishida, A pageant of Japan Ceramics–Kakiemon Ware, Nippon Toji Zenshu 24, Choukouronsha, 1977.

[4] Y. Yabe, A pageant of Japan Ceramics–Nabeshima Ware, Nippon Toji Zenshu 25, Choukouronsha, 1976.

[5] I. Ogi, From Early Imari to Kokutani-style, Soujusha Bijutushuppan, 1990

[6] The Kyushu Ceramic Museum, Polychrome Porcelain in Hizen—Its Early Type and Change of Style, 1991.

[7] H. Nishi, Y. Ohashi, Old Imari ware, The Sun special issue 63, Autum'88, Heibonsha, 1994.

[8] H. Kurita, Collection of Imari and Nabeshima, Kurita Meseum, 1997.

[9] I. Ogi, Imari, Ribun Shuppan, 2000.

[10] Y. Yabe, Imari ware, Kadogawa-Shoten, 2000.

[11] C. Shimizu, LA PORCELAINE JAPONAISE, Massin, 2002.

[12] The Society of Kyshu Early Modern Ceramic Studies, Hizen Porcelains in Japan, 2002.

[13] Idemitu Musuem of Arts, Ko-kutani, 2004.

[14] K. Ohashi, M. Arakawa, Early Imari, the origins of Underglaze Cobalt-blue and Overglaze Polychrome Enamels, Japan Broadcasting Corporation (NHK), 2004.

[15] Y. Imura, *Kakiemon*, Rokusho 5, Maria Shobou, 2005.

[16] The Kyushu Ceramic Museum, *NABESHIMA*, *Porcelain for the Shogunate*, 2006.

[17] M. Ohnishi, Porcelain Glaze, Rikogakusha, 2006.

[18] Y. Kondo, A. Yoshida, *History of Okayama Prefecture*, History of Japan 33, Kawade Shobo Shinsha, 1990.

[19] H. Yamasaki, K. Takahara, Fukiya, Sanyo-Sinbun, 2006.

[20] H. Asaoka, M. Nakanishi, T. Fujii, J. Takada, Y. Kusano, R. Murakami, Reproduction of Japanese traditional pigment based on iron oxide powders with yellowish red color, Mater. Res. Soc. Symp. Proc. 712 (2002) 435–440.

[21] H. Asaoka, Y. Kusano, M. Nakanishi, T. Fujii, J. Takada, Characterization and Reproduction of "Fukiya Bangara", Noble Red Color Pigment, by Fe_2O_3–Al_2O_3 System, Jpn. Soc. Powder Metall. 50 (2003) 1062–1067.

[22] T. Nagatake, The Akae of Japan, Tozai gogasusha, 1960.

[23] S. Kajihara, M. Hidaka, R.P. Wijesundera, L.S.R. Kumara, M. Koga, S. Kobayashi, T. Tsuru, K. Koga, K. Shimomura, Jae-Young Choi, Nark Eon Sung, Young Jun Park, *Correlation between the Izumiyama porcelain ceramics and the red-overglaze enamels of the Kakiemon-style porcelains*. Ceram. Int. 34 (2008) 1681–1689.

[24] S. Kajihara, The comparative study of glaze and porcelain body in the early Kakiemon-style porcelain, J. Kakiemon-style Ceram. Art Res. Center, ISSN 180-3202, (2006) 227–234.

[25] P.K. Soung, S. Kobayashi, M. Koga, S. Kajihara, T. Tsuru, A few trials of red pigment and Iroe or overglazed enamel porcelain from a Rouha of Arita Mt.Izumi for Early Kakiemon-style porcelain, Jounal of the Kakiemon-style Ceramics Art Reserach Center, ISSN 180-3202 (2006) 235–242.

[26] M.Hidaka, H.Horiuchi, K.Ohashi, R.P.Wijesundera, L.S.R.Kumara, Jae-Young Choi, Yong Jun Park, *Structural properties of the red-color overglazes on the Kakiemon-style porcelains produced in the later 17th century by means of X-ray diffraction*, Ceramica, submitted for publication (2008).

[27] M.Hidaka, H.Horiuchi, K.Ohashi, R.P.Wijesundera, L.S.R.Kumara, Nark Eon Sung, *Local structures and electronic band states of α?Fe2O3 polycrystalline particles included in the red-color overglazes and the transparent glazes of the Kakiemon-style porcelains by means of X-ray absorption spectra*, Ceramica, submitted for publication (2008).

[28] C.H. Booth, F. Bridges, Phys. Scr. T115 (2005) 202.