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Correlation between the Izumiyama porcelain ceramics and the red-overglaze enamels of the Kakiemon-style porcelains

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Abstract

The Kakiemon-style porcelains made from 17th century at Arita are famous Japanese porcelains, characterized mainly by their colored underglaze and overglaze and by their original design of coloring spatial patterns in the porcelain surface. Raw materials of the red-overglaze enamels have been investigated by means of X-ray diffraction and X-ray absorption spectra using synchrotron radiations. It is found that Izumiyama porcelain ceramics of yellow color can produce the Kakiemon red-overglaze enamels by thermal treatment and water-washing, where Izumiyama is a collecting place of the raw porcelain ceramic at Arita. The brightness of the red-overglaze enamels is related on the local structure around Fe ions and the electronic band states of Fe ions near a Fermi level in α-Fe_2O_3, in addition to the spatial density of the α-Fe_2O_3 fine particles. The structural and electronic properties are slightly affected by an electron-hybridization between Fe ions of α-Fe_2O_3 and oxygen ions of the (SiO_2–Al_2O_3) complexes in the red overglaze.

Keywords: Izumiyama porcelain ceramic; Koimari porcelain; Kakiemon-style porcelain; Red-overglaze

1. Introduction

Koimari porcelains had been produced at a special area localized at ‘‘Arita cho’’ in Kyushu Island, Japan from the beginning of 17th century. The Koimari porcelains are generally classified by four kinds of porcelain: Kokutani-style, Kinran-style, Kakiemon-style, and Nabeshima-style [1–8]. All of these porcelains were characterized by several elegant colors of red, yellow, green, violet, blue in the underglaze and overglaze, and own designs of spatial patterns on the porcelain surface. Thus, the Koimari porcelains were estimated to be very famous in high-level social classes and at museums sited in foreign countries, as Chinese porcelains. The basic body of the Koimari porcelains was of white color and was made of the Izumiyama ferromagnetic porcelain ceramics, called ‘‘Hakujikou’’, by thermal treatment at about 1000–1300 °C.

In Japan, it was considered that the red-overglaze enamels of old porcelains are mainly based on α-Fe_2O_3. Especially, at beginning of 18th, a lot of the red-overglaze enamels of α-Fe_2O_3, called by Fukiya-style Bengara, were produced by chemical treatment of $FeSO_4{\cdot}7H_2O$ to Fe_2O_3 by heating at about 650 °C in atmosphere [9–11]. After that, it was known that the Fukiya-style Bengara of α-Fe_2O_3 was also used on the Koimari porcelains [12]. However, the Koimari porcelains having the red-overglaze enamels were already made in 17th century. This suggests that there is another source of the Koimari-style red-overglaze enamels. If so, it is important to find it, in order to study historical developments of the porcelain

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techniques for the Koimari porcelains, especially Kakiemon-style. It is known that some of the Izumiyama porcelain ceramics are in white-yellow color, while the Hakujikou ceramics are in white color. It was reported that the white-yellow Izumiyama (WYI) porcelain ceramics include slightly FeS_2, and this is naturally transformed to $FeSO_4$ by oxidation in atmospheric air [13]. However, we deduced that WYI porcelain ceramics contributes to the red-overglaze enamels of the Koimari porcelains from the beginning of 17th century, being Izumiyama a small mountain area closed to the old porcelain factories at Arita.

Some researchers [1–5,14] reported a classification of body-style, color-design, firing techniques, and color appearance in the underglaze and overglaze for the Koimari porcelains, to study a historical and geometrical correlation of the traditional developments of porcelain techniques among the Koimari porcelains of Kokutani-style, Kinran-style, Kakiemon-style, and Nabeshima-style. As for material researches of the Koimari porcelains, the chemical compositions and the structural properties of the colored glaze enamels and the porcelain body have been studied by means of ordinary X-ray diffraction (XRD) and X-ray fluorescence analysis (XRF). However, it is not easy to estimate the color appearance of the glaze enamels at high-temperature region of about 1000–1300 °C, since the chemical reactions of the enamel compositions depend strongly on the thermal treatment of the glaze. Even at room temperature, the composition of the color-overglaze enamels in the fritted glaze or of the blue-underglaze enamels in the transplant glaze, called “Sometuke”, cannot be accurately estimated for the Koimari porcelain by using the XRD and XRF methods, because of X-ray absorption effects of the glaze materials.

More recently, Hidaka’s group [15–17] has studied the composition materials of the colored glazes in the transplant glaze of the Koimari porcelains made from 17th to 18th and modern Arita porcelains by using synchrotron radiation. They have studied the structures of the oxygen compounds including transitional metal ions in the Koimari and modern Arita porcelains by means of high-resolution X-ray diffraction (HXRD). They also measured the local structures around specific transition metal ions and the electronic band states near a Fermi level near X-ray absorption edges by means of X-ray absorption spectrum (XAS). In the present investigations, we study the structural and electronic properties of the Izumiyama porcelain ceramics of white color (Hakujikou) and white-yellow color, in order to find the origin of the red-overglaze enamels of the Koimari-style porcelains, especially Kakiemon-style one, in 17th century before the appearance of the Fukiya-style Bengara of α-Fe_2O_3, by HXRD and XAS using synchrotron radiation.

2. Experimental

In the present investigations, we used a block of the Izumiyama porcelain ceramics having a white color part (Hakujikou) and a white-yellow one (WYI in Plate 1). The specimen was collected at Izumiyama of Arita and its weight was about 55 g. It was considered that the WYI porcelain ceramics include FeS_2 and $FeSO_4$ naturally transformed from FeS_2 by oxidation in atmospheric air [13]. We got the red color porcelain ceramics by heating the white-yellow part above about 700 °C, as shown in Plate 1. We are interested in the color transition from yellow to red by thermal treatment. This suggests that $FeSO_4$ included in the WYI porcelain ceramics is chemically changed to α-Fe_2O_3, as occurred from Fukiya-style Bengara. In order to study the structural properties of the Izumiyama porcelain ceramics, we first carried out high resolution X-ray diffraction at room temperature, by using synchrotron radiations at the Pohang Light Source (2.5 GeV) of the Pohang Accelerator Laboratory (Korea). The incident X-ray beams had a wavelength of 1.5412 Å. The used specimens were a disc-like shape of 10 mm in diameter and 4 mm in thickness, prepared by pressing the fine powders obtained from the Izumiyama porcelain ceramics shown in Plate 1. In the present investigations, we called the red part, white-yellow one, and white one in the block of the porcelain ceramics by B1, B21, and B3, respectively. Thus, the X-ray powder diffraction patterns were obtained from a flat surface of the disc-like specimens at room temperature. The diffraction angles 2θ were in the region from 5.00 to 70.00°.

Plate 1. A porcelain block taken at Izumiyama of Arita, in Kyushu Island, Japan. The red part is heated at about 700 °C to the light yellowish one of the Izumiyama porcelain ceramics.

Before doing X-ray diffraction of the Izumiyama porcelain ceramics shown in Plate 1, we obtained powder diffraction patterns of the Fukiya-style Bengara, whose α-Fe_2O_3 have been used as the red-overglaze enamels for Japanese porcelain. Fig. 1(a) and (b) shows the diffraction patterns of the Fukiya-style Bengara and marketable pure α-Fe_2O_3. In Fig. 1(a), the reflections were indexed with the α-Fe_2O_3 type structure having a hexagonal symmetry of lattice parameters $a = 4.7780$ Å, $c = 12.504$ Å. Thus, it is confirmed that the brightness of the red color of the Fukiya-style Bengara is induced by a little additives of Al_2O_3 and SiO_2 to the pure α-Fe_2O_3, as reported [9,10].

However, the red-overglaze of the Koimari porcelains is slightly brighter than that of the Fukiya-style Bengara. We assume that the former red color results by a mechanism different from the later one. To confirm this assumption, we carried out measurements of X-ray diffraction patterns of the Koimari porcelains disc-like samples B1, B21, and B3. Fig. 2(a)–(c)

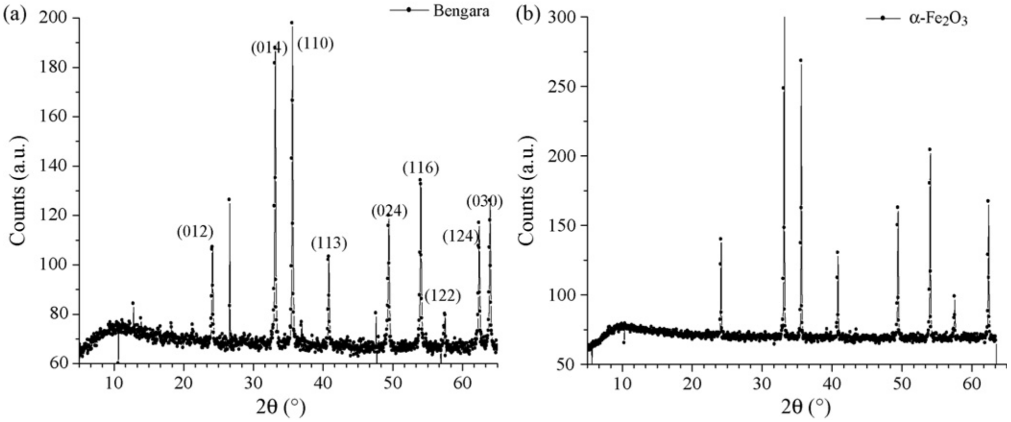

Fig. 1. X-ray diffraction patterns of the red-glaze materials: (a) Bengara and (b) marketable α-Fe_2O_3.

shows the powder diffraction patterns characterized by many reflections, in contrast to those in Fig. 1. The diffraction peaks having the large intensity result mainly from the reflections of the complexes of (SiO_2, Al_2O_3) systems and sulphurs in Fig. 2(a) and (b), where the sulphur reflections were indexed by a notation "S". The diffraction patterns in Fig. 2(c) showed the reflections of the (SiO_2, Al_2O_3) systems, but not those of the sulphur. Thus, it is deduced that the sulphur contributes partially to the appearance of the red color in B1. We also found that there is no reflection resulted from FeS_2, $FeSO_4$, and $FeSO_4\cdot 7H_2O$ in Fig. 2(a)–(c). This suggests that the Koimari red-overglaze enamel is arisen from different physical mechanism like those of the Fukiya-style Bengara [9–11]. However, we suspect that α-Fe_2O_3 should contribute to the appearance of the red color in the Koimari porcelains samples B1 and B21, but not B3. Thus, we re-checked whether the diffraction patterns in Fig. 2 include or not the reflections of α-Fe_2O_3. The results are shown in Fig. 3. We confirmed weak reflections belonging to the α-Fe_2O_3 type structure, denoted by small arrows. This means that the Izumiyama porcelain ceramics samples B1 and B21, even B3, include a little α-Fe_2O_3. Thus, we found that the red color in the overglaze results from the α-Fe_2O_3 fine particles, as in Bengara.

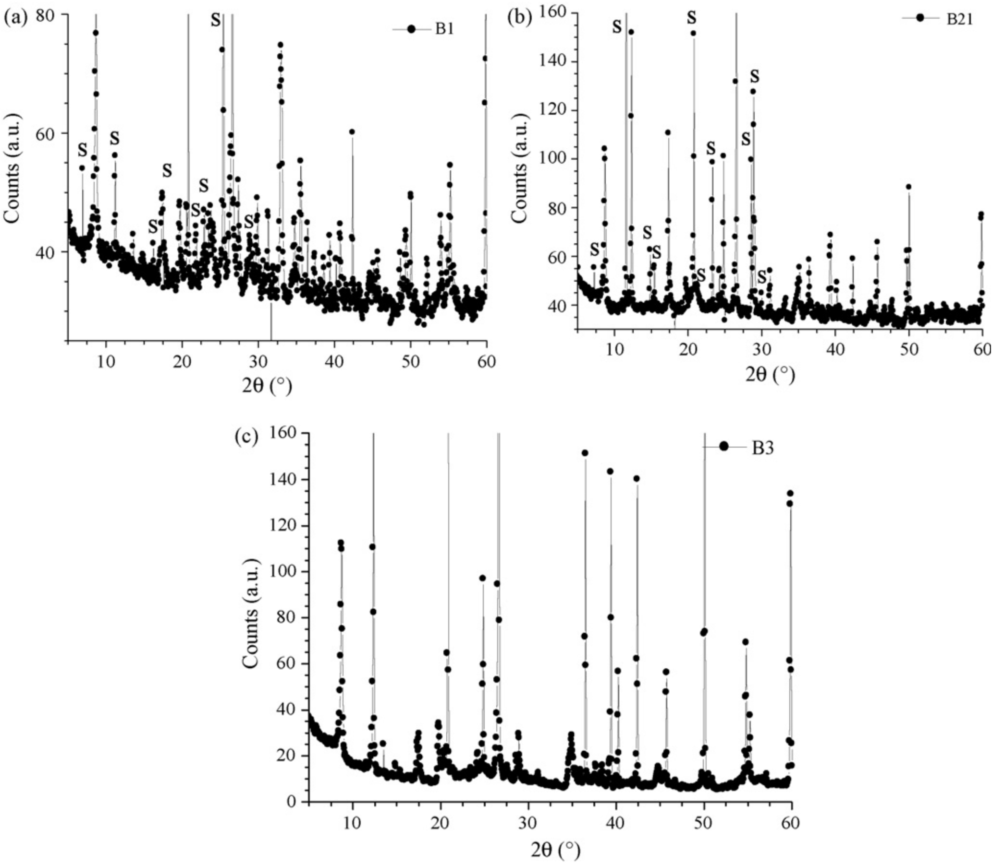

Fig. 2. X-ray diffraction patterns of the Izumiyama porcelains, B1, B21, and B3.

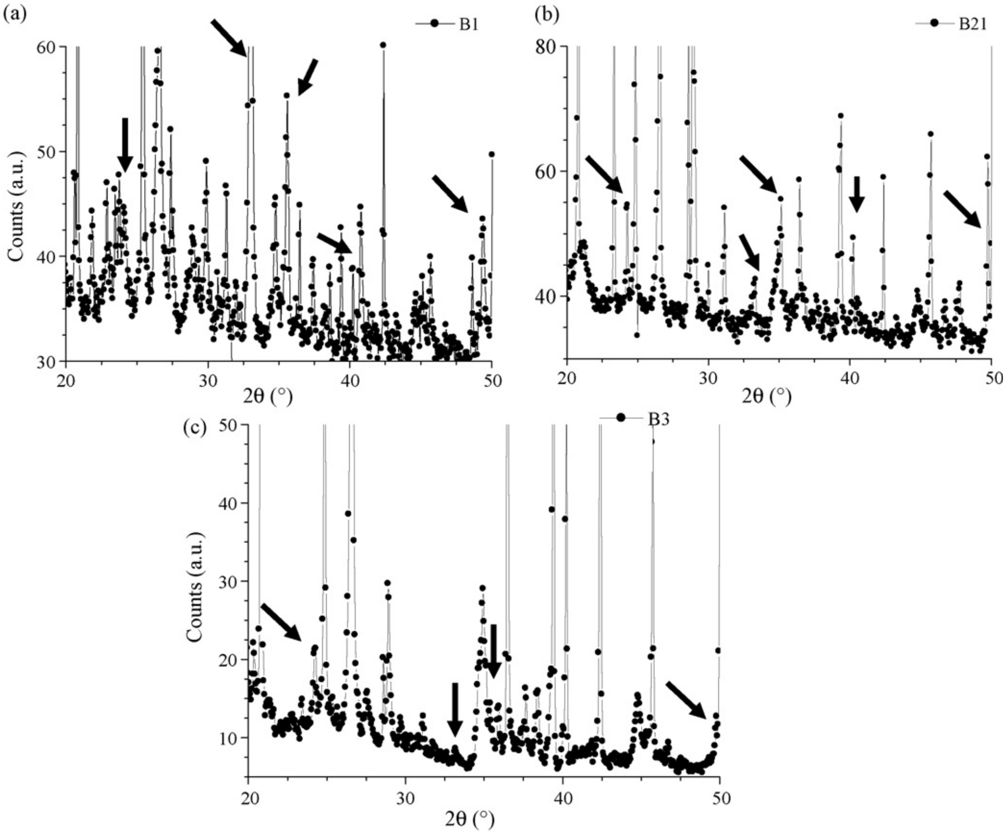

Fig. 3. X-ray diffraction patterns of the B1, B21, and B3 Izumiyama porcelains expanded to the ones in Fig. 2. The reflections of α-Fe_2O_3 are denoted by arrows.

In order to study the red-color transition from B21 to B1 by heating above about 650 °C, we determined temperature dependence of the diffraction patterns of the B21 sample by using a simple furnace, which was set on the 4-circle X-ray diffractometer. Fig. 4 shows the partial diffraction patterns continuously taken at 400, 500, and 550 °C. The notation "S" represents the reflections of the sulphur. Thus, the sulphur reflections disappear above 500 °C, not at about 650 °C, while the chemical reaction of $FeSO_4{\cdot}7H_2O$ to give Fe_2O_3 by heating above about 650 °C in atmosphere was reported for the Fukiya-style Bengara [9–11]. After testing at 550 °C, a lot of small sulphur crystals were observed inside the sample cell in the furnace at room temperature. We suspect that the disappearance of the sulphur reflections results from boiling at about 445 °C and, as cooling to room temperature, the sulphur gases re-crystallize. Thus, it is considered that the red-color transition from B21 to B1 by heating is partially induced by the nuclearization and growth of the clusters of α-Fe_2O_3 fine particles in the Izumiyama porcelain ceramics, since the sulphur particles are re-condensed as polycrystals at room temperature.

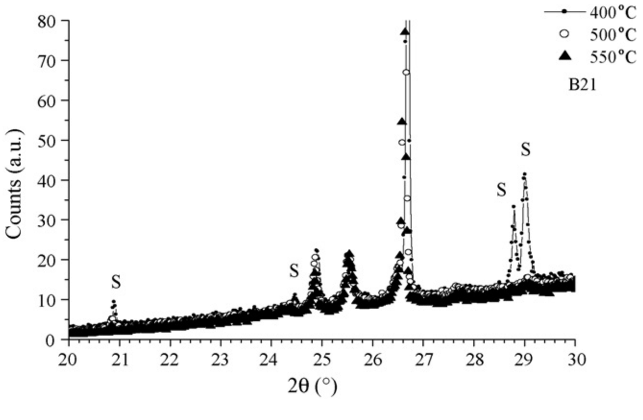

Fig. 4. Temperature dependence of the X-ray diffraction patterns of the B21 Izumiyama porcelain.

In order to study the compositions of the Izumiyama porcelain ceramics, we carried out X-ray fluorescence analysis (XRF) at room temperature of B1, B21, and B3. The results are listed in Table 1, where the sample "Rouha" will be described later. Since XRF gives information of only the component elements, we considered the chemical compounds listed in Table 1 as referring to the diffraction peaks induced by the reflections of (SiO_2, Al_2O_3) systems, α-Fe_2O_3, and sulphur S. Thus, the red-color of B1 depends on α-Fe_2O_3, CaO, and S having a largely weight content. However, the red-overglaze

Table 1
Chemical compositions in the Izumiyama porcelains of B1, B21, B3, and Rouha

wt%	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	S
B1	42	13	21	0.05	9.7	0.14	5.9	0.04	8
B21	45	14	22	0.05	6	0.06	6.3	0.05	7.1
B3	76	18	1	0.05	4.1	–	0.08	0.04	0.5
Rouha	48	11	14	0.04	5.5	0.09	14	0.04	7.3

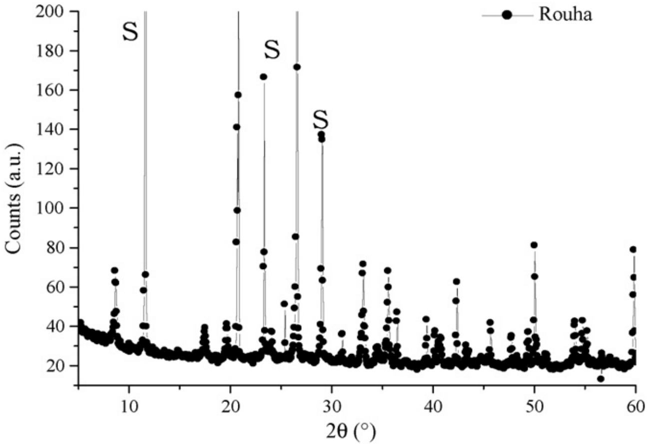

Fig. 5. X-ray diffraction pattern of Rouha, made by water-washing of the B1 Izumiyama porcelain.

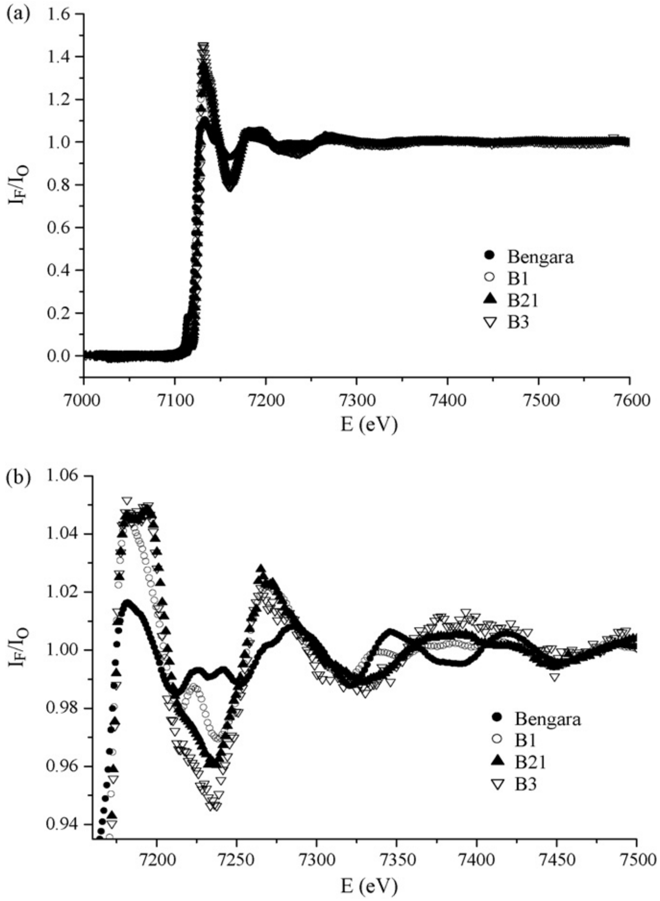

Fig. 6. X-ray absorption spectra of Bengara, B1, B21, and B3 at the Fe-K edge: (a) in the wide energy region of 7000–7600 eV and (b) in the EXAFS region of 7160–7500 eV.

enamels of the Kakiemon-style porcelain are brighter than those of B1 and the Fukiya-style Bengara. We prepared a new brighter material, called "Rouha", by water-washing the fine powders of the B1 porcelain ceramics in several hours. Rouha shows approximately a similar weight ratio of (SiO_2, Al_2O_3) to those of B1 and B21 in Table 1. Thus, we consider that the brightness is related mainly to the decrease of α-Fe_2O_3 and K_2O, and to the increase of CaO as for the relative concentrations. This suggests that a spatial distribution and clusters of α-Fe_2O_3 fine particles in the porcelain ceramics contribute to the brightness of the red-color. We obtained X-ray diffraction patterns of the pellet-like Rouha. The result is shown in Fig. 5, where the sulphur reflections were indexed by the notation "S". It is found that the number of reflections is correspondently reduced by the water-washing effect, when comparing the diffraction patterns of Rouha with those of B1 and B21 in Figs. 2 and 3. This means that there are enough spaces around α-Fe_2O_3 to make the crystallized cluster surrounded by CaO.

In general, the red-overglaze enamels are kept in a fritted glaze, which consists of the oxides in Table 1, with addition of PbO. Thus, we consider that, in the red-overglaze enamels of the porcelain, the fine particles of α-Fe_2O_3 are slightly affected by surrounding cations and anions. In order to study structural and electronic modulations of α-Fe_2O_3 in a microspace of the porcelain ceramics, we carried out measurements of X-ray absorption spectra (XAS) at the Fe–K edge for the disc-like specimens of B1, B21, B3, and Rouha. The XAS, including the X-ray absorption near edges structure (XANES) and the extended X-ray absorption fine structure (EXAFS), were measured near the Fe–K edge for the porcelain ceramics, by using synchrotron radiation at the Pohang Light Source (2.5 GeV). Double crystal monochromator of Si (1 1 1) gave an 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 disc-like specimens, while the X-ray fluorescence photons (I_F) emitted from the front flat-surface of the specimens were simultaneously detected with an X-ray fluorescence detector. The flat-surface of the discs was always set with 45.0° to the incident X-ray beam, of which the size was about 8 mm in horizontal and 1 mm in vertical on the specimen surface to the electron orbital of the accelerator. The K-edge of a free ion Fe is about 7111 eV, whose value depends slightly on the crystallographic structure of compounds including Fe ions. Fig. 6 clearly shows that B3 also includes α-Fe_2O_3, as those of B1, B21 and Bengara. The results consist with those of the X-ray diffraction patterns in Fig. 3. The EXAFS spectra in Fig. 5(b) suggests that there is a large difference of the local structure around Fe ions between Bengara and the Izumiyama porcelain ceramics. Furthermore, the local structures among B1, B21, and B3 are also slightly different each other. This means that the ionic coordinates of Fe ions in the α-Fe_2O_3 type structure are physically affected by the surrounding cations and anions of the (SiO_2, Al_2O_3) systems, the other oxides and sulphur in the porcelain ceramics, as in Table 1. Especially, the difference of the EXAFS spectra between B1 and B21 suggests that the thermal treatment of the Izumiyama porcelain ceramics (Plate 1) above about 445 °C gives the structural modulation localized around Fe ions. On the other hand, Fig. 7 shows the XAS near the Fe–K edge of B1 and Rouha. From the amplitude heights of the EXAFS spectra in Fig. 7(b), we suspect that the Rouha fine powders have a long-range order of the α-Fe_2O_3 type structure, in contrast to that of B1, though the local structure around Fe ions is slightly different between B1 and Rouha. This suggests that the water-

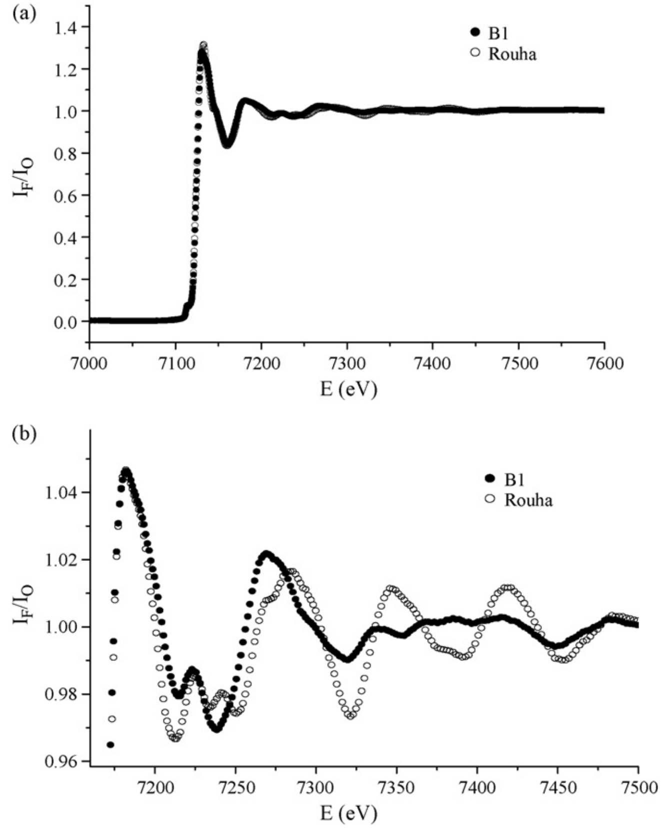

Fig. 7. X-ray absorption spectra around the Fe-K edge of B1 and Rouha: (a) in the wide energy region of 7000–7600 eV and (b) in the EXAFS region of 7160–7500 eV.

washing treatment induces more nuclearization of α-Fe_2O_3 clusters and growth of each cluster size in Rouha than in B1. Thus, it is considered that the brightness of the red-overglaze enamels in the Izumiyama porcelain ceramics also depends on the cluster size and its concentration of α-Fe_2O_3 in the microstructure of the specimens.

As described above, we found that the α-Fe_2O_3 type structure of the red-overglaze in the Izumiyama porcelain ceramics is slightly changed by the chemical composition of the overglaze and by the thermal treatment. In order to study quantitatively the deformation of the local structure around Fe ions, we carried out analyses of the EXAFS spectra of B1, B21, Rouha, and Bengara in Figs. 6 and 7, by using a Fourier transformation, after exchanging the energy of the incident X-ray photons with wavenumber $k\{ = 8\pi^2 m_e(E - E_o)/h^2\}$. Where E_o (about 7111 eV), m_e and h are a X-ray absorption threshold for Fe–K edge, an effective mass of electron, and Plank's constant, respectively. The results are shown in Fig. 8, where |F(R)| is a Fourier transformation spectrum and the abscissa is a radial distance (R(Å)) from a X-ray absorbing Fe ion to its surrounding cations and anions of the α-Fe_2O_3 type structure. We found that there is a slight difference of the local structure around Fe ions between the Izumiyama porcelain ceramics and Bengara. This means that the structural configuration of the α-Fe_2O_3 fine particles is different in both materials, as in Figs. 1 and 2. We also found that the local structures around Fe ions are slightly different among B1, B21, and Rouha. It is considered that the differences result from the weight-ratio of α-Fe_2O_3, K_2O, and CaO in each porcelain ceramics, as in Table 1. Thus, we deduced that the surrounding cations and anions around Fe ions slightly affect the α-Fe_2O_3 structure in the Izumiyama porcelain ceramics.

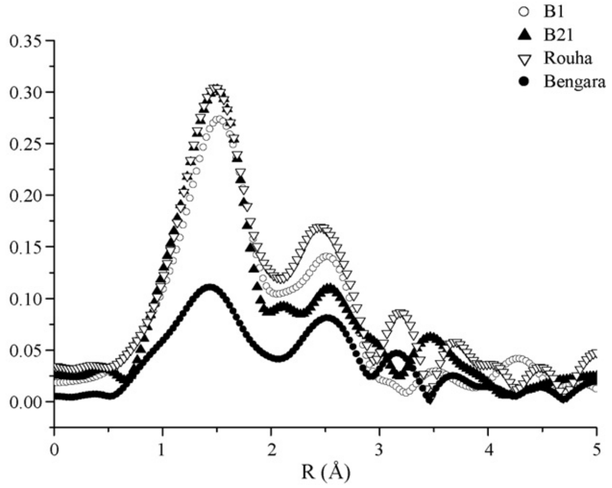

Fig. 8. Amplitudes |F(R)| taken from the Fourier transformation of the EXAFS spectra for Bengara and the Izumiyama porcelains of B1, B21, and Rouha.

In order to study the structural deformation of the α-Fe_2O_3 type quantitatively, we carried out refinements of the Fourier transformation spectrum |F(R)| taken from the oscillating EXAFS spectra, by using the *Artemis* and *Athena* software programs. It is well known that EXAFS spectrum results from a single scattering and multi-scattering paths by interference between a photoelectron wave emitted by an X-ray absorbing atom and a back scattered one induced by surrounding atoms. Therefore it is better to consider both scattering effects for the spectral analysis of the EXAFS data. However, we confirmed that the multi-scattering paths almost do not contribute to the interference in the α-Fe_2O_3 type structure. Thus, in the present investigations, we carried out refinements to the observed |F(R)| by considering only the single scattering paths. Fig. 9(a)–(c) shows the observed |F(R)| of the EXAFS spectra, denoted by solid circles, for B1, B21, and Rouha in Fig. 8, where solid lines show a theoretical |F(R)|. The refinement is satisfied by a good fitting between the observed and theoretical |F(R)|, except for the higher R-region. When doing the refinement, we always monitored a convergence factor RF; $\mathrm{RF} = \{\Sigma|k\chi_{\mathrm{obs}}(k) - k\chi_{\mathrm{cal}}(k)|^2\}/\Sigma|k\chi_{\mathrm{obs}}(k)|^2$, where the observed and theoretical EXAFS oscillating spectra at each wavenumber k are $\chi_{\mathrm{obs}}(k)$ with $\chi_{\mathrm{cal}}(k)$, respectively. The refinements were carried out for parameters of numbers (N_j) of ions sited on the shell having the same radial distance R_j, Debye-Waller factors (σ_j), characteristic temperature (ΘD_j), a passive electron reduction factor(S_o^2) Table 2 lists the refined main parameters. The final RF factors of Bengara, the marketable α-Fe_2O_3, B1, B21, B3 and Rouha were 0.020, 0.021, 0.035, 0.024, 0.011, and 0.015, respectively. The difference between the refined R_j and the radial distance R_{cal}, calculated for α-Fe_2O_3, results from a phase shift between the X-ray photoelectron wave emitted by the X-ray absorbing ions (Fe) and the back scattering one induced by the surrounding

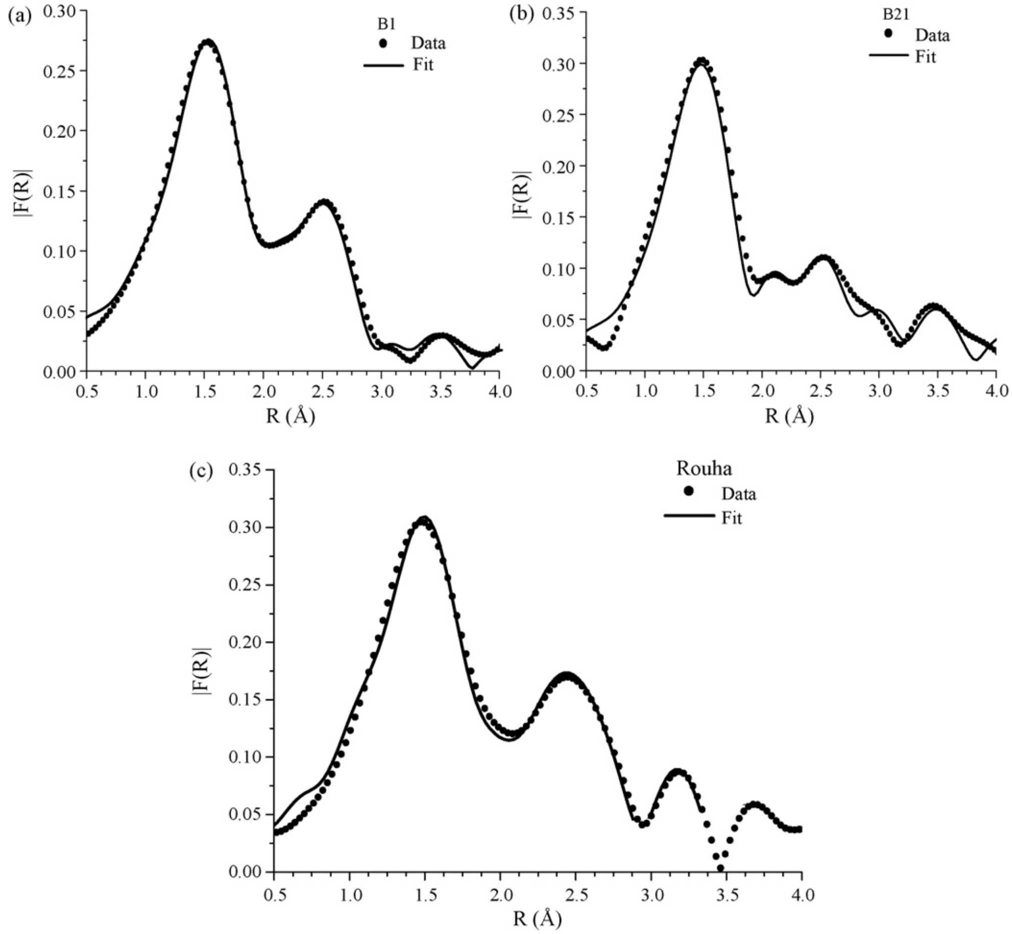

Fig. 9. Theoretical |F(R)| (solid line) of the EXAFS spectrum of the Fe ions in the α-Fe_2O_3 structure, taken by the least squares refinement to the observed |F(R)| (solid circles) for the Izumiyama porcelains of B1, B21, and Rouha in Fig. 8.

ions. From Table 2, we found that the α-Fe_2O_3 type structure of the Izumiyama porcelain ceramics has a slightly larger space than those of Bengara and the marketable α-Fe_2O_3. This suggests that the α-Fe_2O_3 type structure is deformed by the surrounding ions in the complexes of (SiO_2, Al_2O_3) systems, CaO, and sulphur.

Fig. 10(a) and (b) shows the XANES spectra near Fe–K edge. E_o is usually determined by differentiation of XANES curves and represented by a dotted line in Fig. 10(a). In Fig. 10(b), the abscissa of the spectra is the energy shift value from E_o ($\equiv 0$ eV). It is deduced that the Fermi level is close to E_o because α-Fe_2O_3 is insulated. Since the electronic transition between 1s and 4p bands of Fe ions is a dipole transition, the XANES peaks of P1 and P2 in the conduction band correspond to Fe-4pπ and 4pρ band of doublet, respectively. Thus, we considered that the empty electronic band states of Fe-4pπ (P1) and 4pρ (P2) are partially related to the bright difference of the red-overglaze between the Fukiya-style Bengara and the Izumiyama porcelain ceramics of B1, B21, and Rouha. On the other hand, the XANES spectra show two weak peaks of P3 and P4 in the pre-edge region of XAS. The P3 and P4 peaks of XANES appear at about −8.45 and −5.35 eV for B1 and Rouha, while these peaks at about

Table 2
Refined parameters R_j of the EXAFS spectra of the Fe ions in the α-Fe_2O_3 structure for the Bengara, the marketable α-Fe_2O_3, and the Izumiyama porcelain ceramics of B1, B21, and Rouha, as those in Fig. 8

	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
Bengara	1.95	2.08	2.87	2.95	3.35	3.37	3.58	3.68	3.79	3.96
α-Fe_2O_3	1.96	2.07	2.86	2.94	3.34	3.36	3.57	3.67	3.78	3.95
B1	1.97	2.10	2.89	2.98	3.38	3.40	3.61	3.72	3.82	4.00
B21	2.01	2.14	2.95	3.04	3.45	3.47	3.69	3.79	3.90	4.08
B3	1.99	2.12	2.92	3.01	3.41	3.43	3.65	3.75	3.86	4.04
Rouha	1.99	2.12	2.93	3.02	3.42	3.44	3.66	3.76	3.87	4.05

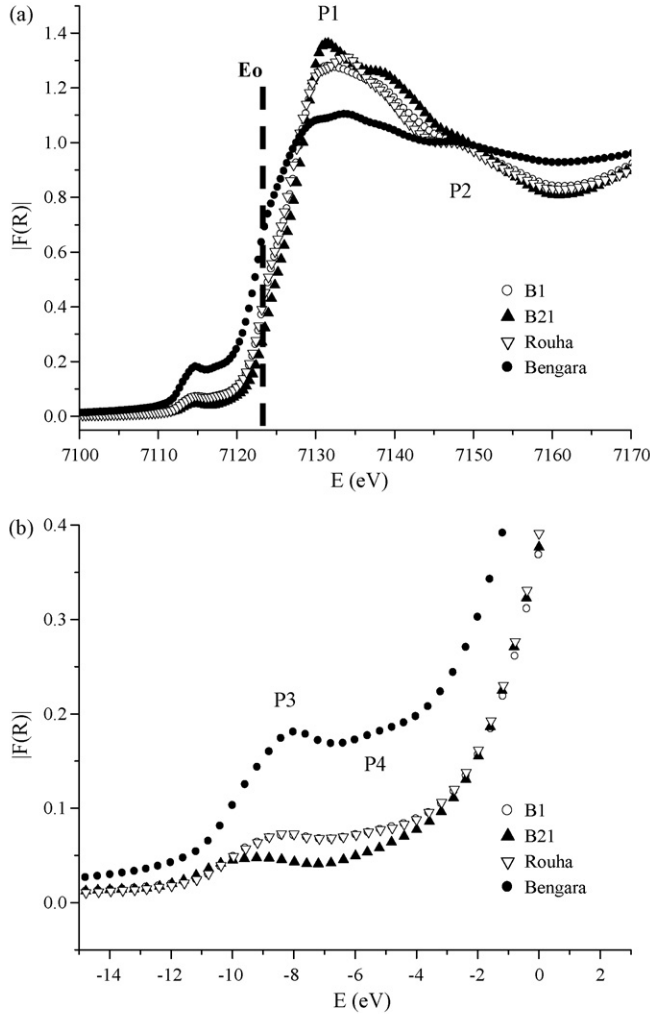

Fig. 10. XANES spectra around the Fe-K edge of B1, B21, Rouha, and Bengara.

−9.41 and −4.61 eV for B21 and at about −7.99 and −4.96 eV for Bengara. The pre-edge XANES peaks in the valence band are induced by the electronic transition between 1s and 3d bands of Fe ions. However, the 1s ($\ell = 0$) to 3d ($\ell = 2$) transition is not permitted by a forbidden condition $\Delta\ell = 1$ given from the quantum theory, where ℓ is a quantum number of electronic orbital. Thus, the pre-edge XANES peaks in Fig. 10(b) suggest that there are hybridized bands near the Fermi level in the α-Fe_2O_3 structure. The hybridization between Fe-3d orbitals of α-Fe_2O_3 and the outer orbitals of the surrounding ions, especially the anions of oxygen and sulphur ions, is induced by an electronic configuration interaction among the constituent compounds in the Izumiyama porcelain ceramics and Bengara. This means that the brightness of the red-overglaze enamels is affected by the ionic configuration of the surrounding ions to the α-Fe_2O_3 fine particles. Furthermore, it is interesting the consistency of the XANES spectra for B1 and Rouha, which were done by the high-temperature treatment above about 700 °C, though the EXAFS spectra and |F(R)| in Figs. 7–9 are slightly different between B1 and Rouha. This suggests for B1 and Rouha that the electronic band states are similar, while the local structure around Fe ions is deformed.

3. Discussion

In order to find the origin of the red-overglaze enamels of the Koimari porcelains, especially Kakiemon-style ones, in 17th century before the appearance of the Fukiya-style Bengara, characterized by α-Fe_2O_3, we studied the structural and electronic properties of the Izumiyama porcelain ceramics mainly by means of the high resolution X-ray diffraction (XRD) and the X-ray absorption spectra (XAS), using the synchrotron radiation. Although the Izumiyama porcelain ceramics include the α-Fe_2O_3 fine particles, the white-yellow one (B21), but not the white one (Hakujikou), showed the red color after thermal treatment above about 450 °C and its brightness was increased by the water-washing, as showed by Rouha. The Izumiyama porcelain ceramics are consisted mainly of the complexes of (SiO_2, Al_2O_3) systems, CaO, and sulphur. In the present investigations, we found that, by the thermal treatment and the water-washing, the surrounding ions of the compounds in the porcelain ceramics affect slightly the structural deformation of the α-Fe_2O_3 type structure and the electronic band states near the Fermi level in the conduction band and in the valence one of Fe ions in α-Fe_2O_3. The effects modify the brightness of the red color in Bengara and the Izumiyama porcelain ceramics of B1, B21, and Rouha. It is known that the red-overglaze enamels in the porcelain are stabilized only in the fritted glaze of (SiO_2, Al_2O_3) systems, and other oxides, in addition to PbO, at high temperature. Thus, it is expected that the surrounding ions around the α-Fe_2O_3 fine particles contribute the brightness of the red-color in the glaze.

In the present investigations, we suspect a possibility that the white-yellow porcelain ceramics (B21) is used as the red-overglaze enamels of the Koimari porcelains including the Kakiemon-style ones, which were made in 17th century. Recently, Hidaka's group [15–17] studied the red-overglazes for the Koimari porcelains. The results suggested that the Koimari porcelains show both types of the white-yellow Izumiyama porcelain ceramics and the Fukiya-style Bengara for the red-overglaze enamels with α-Fe_2O_3. This means that the raw α-Fe_2O_3 should be collected in the area closed to the old porcelain factories at Arita. It is known that the Izumiyama porcelain ceramics also produce celadon porcelains of green-color. The color appearance results from a chemical reduction from Fe_2O_3 to FeO in the transplant glaze at high temperature of 900–1200 °C. Thus, we consider that, in the 17th century, the potters used the Izumiyama white-yellow porcelain ceramics rich α-Fe_2O_3 for the Koimari porcelains.

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References

[1] H. Nishida, K. Ohashi, Old Imari Ware the SUN, Heibonsha, 1988 (Special issue 63).

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

[3] S. Yamashita, Ai-Kokutani and Ai-kakiemon, Soujusha Bijutushuppan, 1995.

[4] C. Shimizu, La Porcelaine Japonaise, Massin, 2002.

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

[6] The Kyushu Ceramic Museum, Nabeshima, Porcelain for the Shogunate, 2006.

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

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

[9] 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, in: Materials Research Society Symposium Proceedings, vol. 712, 2002, pp. 435–440.

[10] 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.

[11] P. Tae-Sung, S. Kobayashi, M. Koga, S. Kajkihara, T. Tsuru, A few trails of red pigment and Iroe or overglazed ensmel porcelain from Rouha of Arita Mt. Izumi for Early Kakiemon-style porclain, the Program of the Kakiemon-style Ceramic Art Research Center, Kyushu Sangyo University, 2006, ISSN 1880-3202.

[12] T. Nagatake, The Akae of Japan, Tozaigogasusha (1960).

[13] Saga Prefecturel Ceramics Research Laboratory, Reports of Materials Researches, 1969.

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

[15] M. Hidaka, K. Ohashi, R.P. Wijesundera, N.E.Sung, Red-underglaze enamels of Koimari Porclains, submitted for publication.

[16] M. Hidaka, K. Ohashi, R.P. Wijesundera, N.E. Sung, Red-overglaze enamels of Koimari Porclains, submitted for publication.

[17] M. Hidaka, K. Ohashi, S. Kajihara, R.P. Wijesundera, L.S.R. Kumara, J.Y. Choi, N.E. Sung, Red-overglaze enamels of HIZEN Porcelains, Ceram. Int. (2007), submitted for publication.