Local structures and electronic band states of α-Fe_2O_3 polycrystalline particles included in the red-color overglazes and the transparent glazes of the Kakiemon-style porcelains by means of X-ray absorption spectra (Π)

(Estruturas locais e estados de banda eletrônica de partículas policristalinas de α-Fe_2O_3 inclusas em esmaltes vermelhos e transparentes de porcelanas do estilo Kakiemon por meio de espectros de absorção de raios X (II))

M. Hidaka[1], H. Horiuchi[2], K. Ohashi[3], R. P. Wijesundera[1,5], L. S. R. Kumara[1], Nark Eon Sung[4]
[1]Department of Physics, Graduate School of Science, Kyushu University, 33, Fukuoka 812-8581, Japan
[2]Archaeological Research Unit, The University of Tokyo, Tokyo, Japan
[3]The Kyushu Ceramic Museum, Arita, Saga, 844-8585, Japan
[4]Beamline Department, Pohang Accelerator Laboratory, Pohang University of Science and Technology, San31, Hyoja-doing, Pohang, 790-784, Korea
[5]Department of Physics, University of Kelaniya, Kelaniya, Sri Lanka
hidaka@phys.kyushu-u.ac.jp

Abstract

Kakiemon-style porcelain is mainly characterized by the porcelain body of white color or milky-white color and the elegant and bright patterns of the colored overglazes on its white body. The porcelains were first developed and completed by Kakiemon-kiln family in 1650-80's. The red-color overglazes and the transparent glazes of the present porcelain pieces, which were produced in the early 17th century to the middle 18th century, have been investigated by means of X-ray absorption spectrum using synchrotron radiation. The structure of α-Fe_2O_3 as red-color emission element is slightly deformed in the red-color overglazes by the other surrounding oxides (SiO_2, Al_2O_3, K_2O, Na_2O, MgO, PbO), and/or the new complexes of (SiO_2-Al_2O_3,) systems constructed by the raw materials. The Fe ions in the transparent glazes are in the glass-state with the other oxides. However, the electronic valence, Fe^{3+}, of Fe ions is the same with that of the α-Fe_2O_3 in the red-color overglazes. The lead oxides (PbO, Pb_3O_4) used in the Edo period to increase the brightness in the fritted red-color overglazes were perfectly decomposed, and Pb ions were in the glass-state of the porcelains.
Keywords: Kakiemon-style porcelains, red-overglaze, transparent glaze

Resumo

A porcelana do estilo Kakiemon e caracterizada principalmente pelo corpo de porcelana de cor branca ou branco-leitosa e os motivos elegantes e brilhantes dos esmaltes coloridos no seu corpo branco. As porcelanos foram primeiramente desenvolvidas e completadas em forno pela família Kakiemon em 1650-1680. Os esmaltes vermelhos e transparentes das peças de porcelana que foram produzidas no começo do século XVII até o meio do século XVIII foram analisadas em espectros de absorção de raios X com radiação síncrotron. A estrutura do α-Fe_2O_3 como elemento emissor de cor vermelha é levemente deformada nos esmaltes vermelhos por outros óxidos presentes (SiO_2, Al_2O_3, K_2O, Na_2O, MgO, PbO), e/ou novos sistemas complexos de (SiO_2-Al_2O_3,) que fazem parte da matéria-prima. Os íons Fe nos esmaltes transparentes pertencem ao estado vítreo nos outros óxidos. Entretanto, a valência eletrônica, Fe^{3+}, dos íons Fe é a mesma que a do α-Fe_2O_3 nos esmaltes vemelhos. Os óxidos de chumbo (PbO, Pb_3O_4) usados no período Edo para aumentar o brilho e a resistência dos esmaltes vermelhos estavam completamente decompostas, e os íons Pb estavam no estado vítreo das porcelanas.
***Palavras-chave**: porcelanas do estilo Kakiemon, esmaltes vermelhos, esmaltes transparentes.*

INTRODUCTION

Hizen porcelains produced in the early Edo period of Japan are classified mainly by 4 kinds of porcelain-styles; Shoki-Iroe (Kokutani-style), Kakiemon-style, Kinran-style, and Nabeshima ware. A lot of the Kakiemon-style 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. In the Edo period, the white porcelain body of the Hizen porcelains was made of the Izumiyama ferromagnetic porcelain ceramics of white color, Hakujikou, which Korean-potters discovered at Izumiyama just near Arita in the early 17th century as a raw porcelain material of the porcelains.

Thus, the Kakiemon-style 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 Izumiyama porcelain ceramics were grouped by content of α-Fe_2O_3 as a raw material; about 0.6wt% for Kakiemon-style porcelain and Nabeshima ware, and several wt% for celadons, called SEIJI, which were made in the Arita areas from the early 17th century. The Kakiemon-style porcelains had the elegant and bright patterns of the colored overglazes painted on the porcelain body of white color or milky-white color. The Kakiemon-style porcelain-techniques creating its elegance and brightness were developed in 1650's (Edo period) first by Kakiemon-kiln family, and quickly distributed in the localized areas around Arita [1-17].

In the middle 18th century, a large quantity of α-Fe_2O_3 fine powders, called Fukiya-style Bengara, were produced at Fukiya village in Okayama prefecture of Honshu island, Japan, by chemical treatment from $FeSO_4 \cdot 7H_2O$ to Fe_2O_3 at about 650 °C in atmosphere [18-21]. It was considered that, from 1760's, the Fukiya-style Bengara was used as the red-color emission enamels of the Hizen porcelains [18, 19]. However, in the Arita area, the red-color overglazes had been used for the Hizen porcelains even in the early 17th century [22]. It is known that, in 1661 to 73's, Akae Machi was located at Arita to quickly produce a lot of the export Kakiemon-style porcelains of high quality. At Akae Machi, there were about 11 to 16 Akae Ya, which were porcelain traders having a special kiln and were called "Kin gama", permitted by Nabeshima domain. This means that there was another source of the Hizen red-overglaze enamels, which were imported from China or not. More recently, we found that the Izumiyama porcelain ceramics of white-yellow, called Izumiyama Rouha, show similar red-color brightness to those of the Hizen porcelains [23]. Since the Izumiyama sites at the center of Arita area and near the Akae Machi, we deduced that some porcelain kilns already used the Izumiyama Rouha as the red-overglaze enamel in the early 17th century to the early 18th century.

In order to know a mechanism of the elegance and brightness of the colored overglazes on the Kakiemon-style porcelains and to find applications of its porcelain-techniques to modern ceramic sciences, we carried out investigations of the local structures around Fe ion and the electronic band states near a Fermi level of the red-color overglazes and the transparent glazes on the Kakiemon-style porcelains by means of X-ray absorption spectra using synchrotron radiation.

MATERIALS

It is known that the patterns as flowers, leaves, climbers are spatially distributed in asymmetry on the surface of the Kakiemon-style porcelains, and the white-color porcelain body increases the elegant brightness of the colored overglazes. As already described above, in the Edo period, the white porcelain body of the Kakiemon-style porcelains was made of the Izumiyama porcelain ceramics of white color. In the present investigations, we used 5 broken pieces of Kakiemon-style and one of Arita, collected at a Hongou campus of the University of Tokyo at Tokyo in Japan. All of the porcelains were produced at the Arita region in the end 17th century to the early 18th one. The photographs are already shown in our other paper [24]. At a moment, we called the porcelains by following notations in the present paper; A(bowl, Kakiemon-style, 1670-90's), B(bowl, Kakiemon-style, 1670-90's), C(bowl, Kakiemon-style, 1670-90's), D(bowl, Arita, 1690-1730's), E(dish, Kakiemon-style, 1670-90's), and F(rice-bowl, Kakiemon-style, 1670-90's). The samples were the broken porcelain pieces of a bowl, a dish, and a rice-bowl having colored overglazes and the blue-color underglazes.

The Hongou campus sites at Edo-premises of Kaga domain in the Edo period. A lot of Kakiemon-style porcelains were bought by the premise owners. However, the premises were suffered four times from big fires occurred in 1650, 1682, 1703 and 1730 years. Many porcelains of high quality lined under the ground have been excavated at the campus. The four fires strongly contribute to establish the produced date of the lined porcelains. Thus, it could be more exactly estimated that the present broken porcelains were produced mainly from the end 17th to the early 18th century. The porcelain bodies of A, B, and D are clearly white-color, while those of C, E, and F are white-color slightly including light-blue. This suggests that the body ceramics of C, D, and F have a slightly larger content of α-Fe_2O_3 than those of A, B, and D as a raw material. However, the red-color overglazes of the porcelain piece F show dark-brown color, but not red-color brightness. This means that the red-color overglazes

Table I - Composition of the raw materials used in the transparent glaze of the Kakiemon-style and Arita porcelains [17, 25].
[Tabela I - Composição das matérias-primas usadas no esmalte transparente das porcelanas de estilo Kakiemon e Arita [17, 25].]

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
Izumiyama rouha	48.0	11.0	5.5	0.09	14.0	0.04	14.0

were chemically changed by the big fires occurred in 1703. The blue-color of the underglaze did not show any chemical reaction induced by the fires and has the similar brightness to the other porcelain pieces of A to E.

The different thermal effect between the overglaze and underglaze results from the difference of the producing procedure of the porcelain. It is known that the porcelain body painted with the blue-color underglaze is first coated with the transparent glaze, and secondly heated at higher temperature of about 1300 ºC with the porcelain body. After that, the color-overglaze is heated at about 900 to 1000 ºC, but to about 1200 ºC for some porcelain kilns. Thus, the blue-color underglaze is shield by the coated transparent glaze to the fire oxidation in air, while the red-color overglazes is affected by the fire oxidation. As described latter, the fire oxidation of the porcelain piece F gives important structural information for the overglaze materials of the Kakiemon-style and Arita porcelains produced in the early Edo period from the end 17th to the early 18th century.

The present porcelain pieces are very important cultural assets in Japan. Thus, we needed to study the structural and electronic properties of the present porcelains by means of nondestructive methods. Thus, we cannot remove the partial overglaze on the porcelain surface to estimate the component materials of the porcelain glazes. Since ancient porcelain-techniques of the kiln were very strictly initiated a next successor, it is not easy to correctly investigate the techniques. However, some old documents gave important information for the used raw materials of the Kakiemon-style and Arita porcelains. In Table I, the Izumiyama Toseki collected at the Arita area had been used as a porcelain body of white-color from the early 17th century at the Arita areas. At the Edo periods, the Sirakawa Yamatuti and/or the Taisyu Tyouseki had been used in the transparent glazes and the fritted color-overglazes, in addition to the Isubai (natural wood ash). More recently, Kajihara [25] succeeded the reproduction of the ancient transparent glaze in the early Kakiemon-style porcelains with components of 0.45 KNaO, 0.53 CaO, 0.02 MgO, 0.56 Al_2O_3, and 4.89 SiO_2 in mol%, by using the raw materials in Table I. It is known that the ancient porcelains produced at the Arita areas have the following component region for the transparent glazes; 0.35-0.46 KNaO, 0.52-0.65 CaO, 0.02-0.04 MgO, 0.56-0.99 Al_2O_3, and 4.61-7.70 SiO_2 in mol%. On the other hand, in wt%, the fritted red-color overglaze of the ancient Arita porcelain consists approximately of 6.0 K_2O, 0.34 Na_2O, 0.04 CaO, 0.04 MgO, 3.2 Al_2O_3, 70.0 SiO_2 and 0.08 Fe_2O_3, in addition to 20.5 PbO [25].

EXPERIMENTAL

The X-ray diffraction patterns of the Kakiemon-style porcelains produced in the later 17th century suggested that there is the intrinsic structural correlation between the red-color emission particles of α-Fe_2O_3 and the raw porcelain materials of SiO_2, Al_2O_3, K_2O, Na_2O, MgO, and PbO in the fritted red-color overglazes [24]. Some Kakiemon-style porcelains indicated that the new oxygen complexes were grown in the red-color overglazes by the fritted raw porcelain materials at high-temperature treatment. Thus, we carried out the study of the local structure around Fe ions and the electronic band states of Fe ions near the Fermi level (E_F), especially 3d bands at the top region of the valence band in the α-Fe_2O_3 structure.

It is known that X-ray absorption spectrum (XAS) gives the local structural and the electronic information of the X-ray absorbing ions, Fe ions, in the present investigations. Generally, the XAS consists of XANES spectrum in the region of about -100 to +50 eV and EXAFS one in the region of about 50 to 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 porcelains, by synchrotron radiation at the Pohang Light Source (2.5 GeV). A double crystal monochromator of Si (111) gave a relative energy resolution $\Delta E/E$ 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 porcelain broken pieces, while the X-ray fluorescence photons (I_F) emitted from the porcelain surface were simultaneously detected with an X-ray fluorescence detector. The incident X-ray beam was always set with about 45.0° to the irradiated part of the porcelain surface, of which the size was about 2 mm in horizontal and 1 mm in vertical. Thus, the beam size of the incident X-ray beams was about 3 mm on the sample surface in horizontal. In the present investigations, we always used software programs of *Artemis* and *Athena* to analysis the observed XANES and EXAFS spectra [26]. The E_o of the α-Fe_2O_3 structure slightly shifts from 7111 eV (a free Fe ion) to 7112-7116 eV for the present porcelains, since E_o depends on the crystallographic structure.

RESULTS AND DISCUSSION

It is known that α-Fe_2O_3 particles were already included in the raw materials of the red-color overglazes and the transparent glazes, in addition to the porcelain body of white-color, when the Kakiemon-style porcelains and the Arita one were mass-produced at the Arita areas from the early 17th century as those in Table I. More recently, we confirmed that the existence of the α-Fe_2O_3 particles were contained in the red-color overglazes and the porcelain body of the present porcelains, but not the transparent glazes, by means of the high-resolution 4-circle X-ray diffraction using synchrotron radiation [24]. Fig. 1 shows the XAS near the Fe-K edge of the red-color floral part in the red-color overglaze (solid circles) and the transparent glaze closed to its floral part (open circles) of the Kakiemon-style porcelains A (ARFE01) and B (ARFE02). The ordinate (I_F/I_o) is a count ratio between the fluorescence X-ray photons (I_F) emitted from the specimen and the incident X-ray photons (Io), while the abscissa is the incident X-ray photon energy E (eV). In Fig.1, the XAS of the transparent glazes are very similar for the Kakiemon-style porcelains A (ARFE01W) and B (ARFE02W).

This means that the local structure surrounding the X-ray absorbing Fe ions are same in both porcelains, though the α-Fe_2O_3 structure is not included in the glazes. From the hallo-like scatterings in the X-ray diffraction patterns, we consider that, in the transparent glazes, Fe ions are in the glass-state with other oxides. On the other hand, the XAS of the red-color overglazes shows a slight difference between both porcelains. This means that the local structure around Fe ions in the α-Fe_2O_3 structure is affected by the surrounding cations (Si^{4+}, Al^{3+}, Ca^{2+}, K^{1+}, Na^{1+}, Mg^{2+}) and anions (O^{2-}), since the X-ray diffractions indicated the α-Fe_2O_3 contain in the red-color overglazes [24].

Figs. 2a and 2b show the XAS near the Fe-K edge of the red-color floral part in the red-color overglaze (solid circles) and the transparent glaze closed to its floral part (open circles) of the Kakiemon-style porcelain C (ARFE03) and F (ARFE08), respectively. In Fig. 2, the XAS of the transparent glazes are very similar for the Kakiemon-style porcelains C (ARFE03W) and F (ARFE08W). As described before, the F porcelain piece was fired in 1703, and the red-color overglazes were chemically changed from red-color to dark-brown. However, the XAS shows the similar spectrum for the red-overglaze and transparent glaze, except the slightly energy shift of the spectra with ΔE about 4 eV each other. And also, the X-ray diffraction showed the disappearance of the α-Fe_2O_3 structure in the fired red-color overglaze of the F porcelain [24]. It is known that α-Fe_2O_3 is changed above about 1350 ºC to a mixed phase of Fe_3O_4 + O_2. However, it was not found any reflections of the Fe_3O_4 structure in the X-ray diffraction pattern of the overglaze [24]. Thus, we suspect that the α-Fe_2O_3 particles were decomposed by high-temperature oxidation of the big fire.

The transparent glazes of the Hizen porcelains; Shoki-Iroe (Kokutani-style), Kakiemon-style, Kinran-style, and

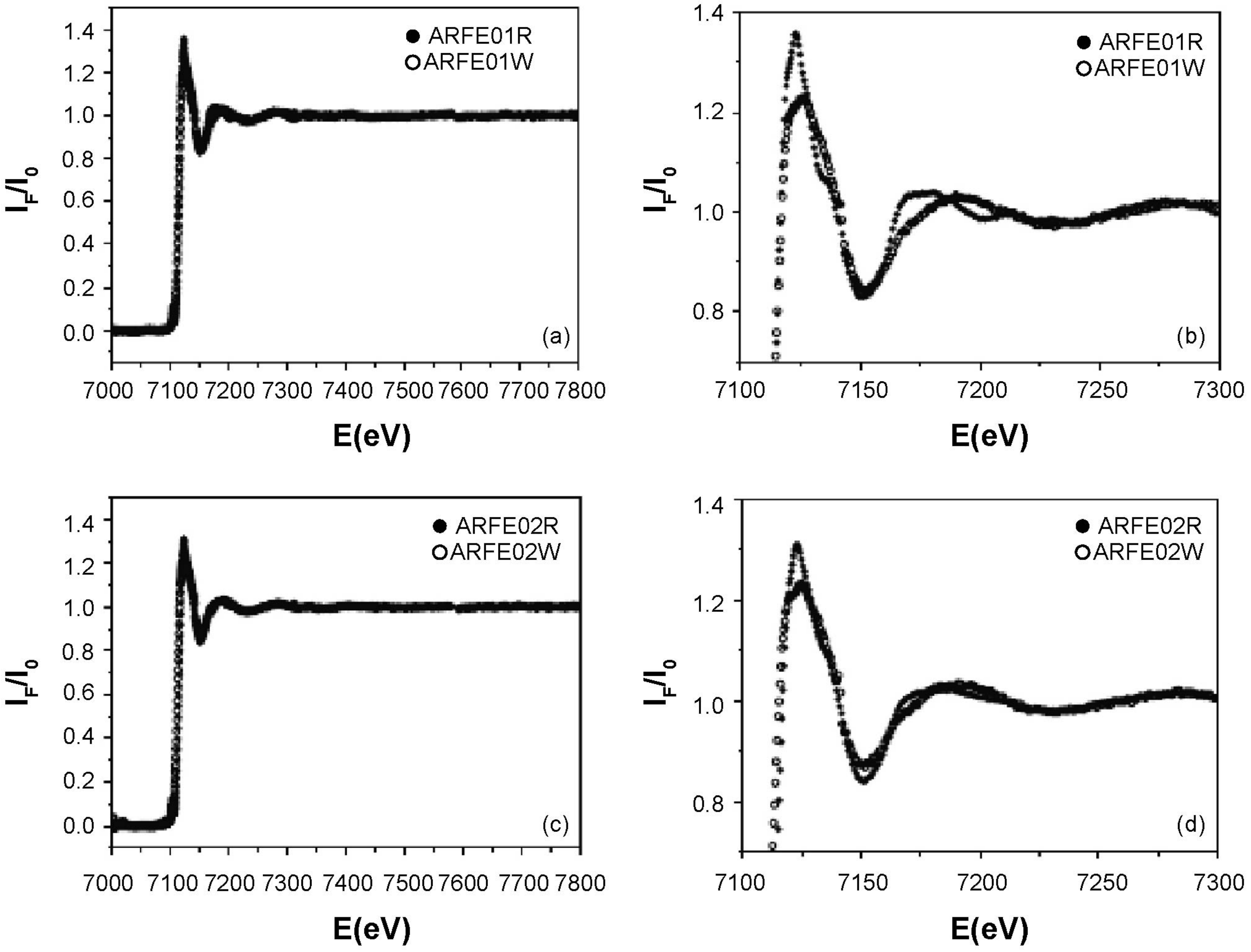

Figure 1: X-ray absorption spectra (XAS) near Fe-K edges of the red-color overglaze (solid circles, R) and the transparent glaze (open circles, W) on the Kakiemon-style porcelains of A and B; (a) and (b) for A (ARFE01), and (c) and (d) for B (ARFE02), where the spectra of (b) and (d) are partially expanded in the XAS of (a) and (c), respectively.

[Figura 1: Espectros de absorção de raios X (XAS) dos esmaltes vermelhos (círculos sólidos, R) e dos esmaltes transparentes (círculos abertos, W) de porcelanas do estilo Kakiemon de A e B; (a) e (b) para A (ARFE01), e (c) e (d) para B (ARFE02), onde os espectros de (b) e (d) são parcialmente expandidos em XAS de (a) e (c), respectivamente.]

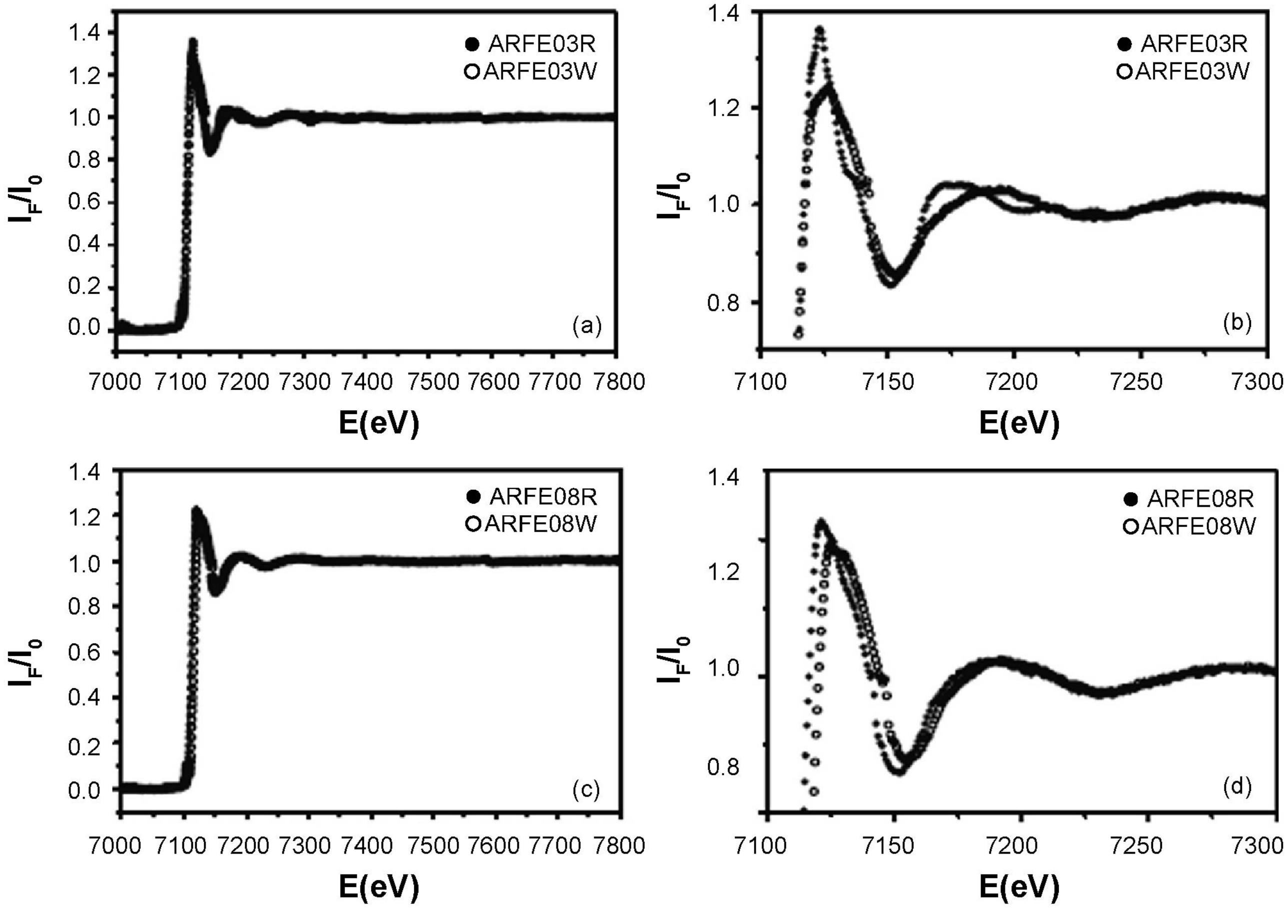

Figure 2: X-ray absorption spectra (XAS) near Fe-K edges of the red-color overglaze (solid circles, R) and the transparent glaze (open circles, W) on the Kakiemon-style porcelains of C and F; (a) and (b) for C (ARFE03), and (c) and (d) for F (ARFE08), where the spectra of (b) and (d) are partially expanded in the XAS of (a) and (c), respectively.

[Figura 2: Espectros de absorção de raios X (XAS) dos esmaltes vermelhos (círculos sólidos, R) e dos esmaltes transparentes (círculos abertos, W) de porcelanas do estilo Kakiemon de C e F; (a) e (b) para C (ARFE03), e (c) e (d) para F (ARFE08), onde os espectros de (b) e (d) são parcialmente expandidos em XAS de (a) e (c), respectivamente.]

Nabeshima ware were usually coated and heated on the porcelain body at about 1300 ºC, before painting the colored overglazes. Thus, it is deduced that the ancient Arita potters empirically found the porcelain techniques for decomposition of the α-Fe_2O_3 structure and the transparent glass-state at its temperature, even if the raw ceramic materials contain the α-Fe_2O_3 fine particles. The glass-state glaze gives its colorless transparent and an observation of the porcelain body of milky-white or white color slightly containing light blue. In the present investigations, we found that the XAS near the Fe-K edge on the present porcelains of A to F show the same short-range order of glass-state in the transparent glazes, mainly constructed by the component ions of SiO_2, Al_2O_3, K_2O, Na_2O, MgO, and PbO, in addition to α-Fe_2O_3.

On the other hand, we found that the XAS near the Fe-K edge of the red-color overglazes on the present porcelains of A to E are slightly different each other, as shown in Figs.1 and 2, except that of F. Thus, we deduce that the deformed α-Fe_2O_3 structure results from structural correlation between Fe ions in α-Fe_2O_3 and the surrounding cations and/or anions of the other oxides or the oxygen complexes grown in the fritted red-color overglaze. It is usually considered that the α-Fe_2O_3 structure is same at room temperature before and after heating up, when only α-Fe_2O_3 particles are heated at high-temperature and cooled down at room temperature. However, if the α-Fe_2O_3 particles structurally and electronically correlate with the other oxide systems or the oxygen complexes, the α-Fe_2O_3 structure is slightly deformed at high temperature of about 900 to 1200 ºC by the surrounding ions. Thus, it is possible to detect the deformation even at room temperature, after cooling down because of the frozen correlation.

In order to quantitatively study the effect of the surrounding ions to the α-Fe_2O_3 structure, we carried out a Fourier transformation $|F_{obs}(R)|$ of the observed oscillating EXAFS spectrum $X_{obs}(k)$, after representing an energy of X-ray photons with a wavenumber k{= $8\pi^2 m_e(E-E_o)/h^2$}, where E_o (about 7115 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. In the present investigations, we used the software programs of *Artemis* and *Athena* to refine the $X_{obs}(K)$ with a theoretical $X_{cal}(K)$ [26]. 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 (Nj) of ions sited on the shell having the same radial distance Rj, Debye-Waller factors (σj), characteristic temperature (Θ_Dj), a passive electron reduction factor(S^2_o). The refinements were always 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.

Fig. 3 shows the theoretical Fourier transformation spectra $|F_{cal}(R)|$ (solid lines) and the observed ones $|F(R)|$ (solid circles) for the observed EXAFS spectra of Fe ions in the red-color overglazes of the present porcelains. In Fig. 3, (a), (b), (c), and (d) indicate the Fourier transformation spectra of the Kakiemon-style porcelains A (ARFE01R), B (ARFE02R), C (ARFE03R), and the Arita porcelain D (ARFE04R) D, respectively. The RF-values at the best refinements were at about 0.04, 0.05, 0.06, and 0.04 for ARFE01R, ARFE02R, ARFE03R, and ARFE04R, respectively. We also carried out the similar refinements for the observed Fourier transformation spectra $|F(R)|$, taken for the red-color overglaze of the Kakiemon-style porcelain E (ARFE06R) and obtained the best value of RF=0.05. Thus, the EXAFS spectral analyses were successfully done.

The results are listed in Table II. The Oj and Fej (j = integer) represent the surrounding shell of oxygen ions and Fe ions on the jth shell sited at the radial distance Rj (Å) away from the origin of the X-ray absorbing Fe ion in the α-Fe_2O_3 structure, respectively, as referred in our other papers [23, 27]. When refining the local structures based on the EXAFS spectra, it is important to consider 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 starting initial vales of the refined parameters Rj were used with ideal radial distances Rcal(j) of the α-Fe_2O_3 hexagonal structure of a=5.035 and c=13.72 Å. In Table I, the Rj values already include the phase sift value of about 0.50 Å, while the abscissa R (Å) in Fig. 3 does not include the phase sift value for comparison between $|F(R)|$ and $|F_{cal}(R)|$.

In order to study the deformation effect of the local structure around the X-ray absorbing Fe ion, we analyzed the Fe4 of the surrounding Fe-shell and O5 of the surrounding O-shell in Table II. The Fe4 and O5 shells site in the third

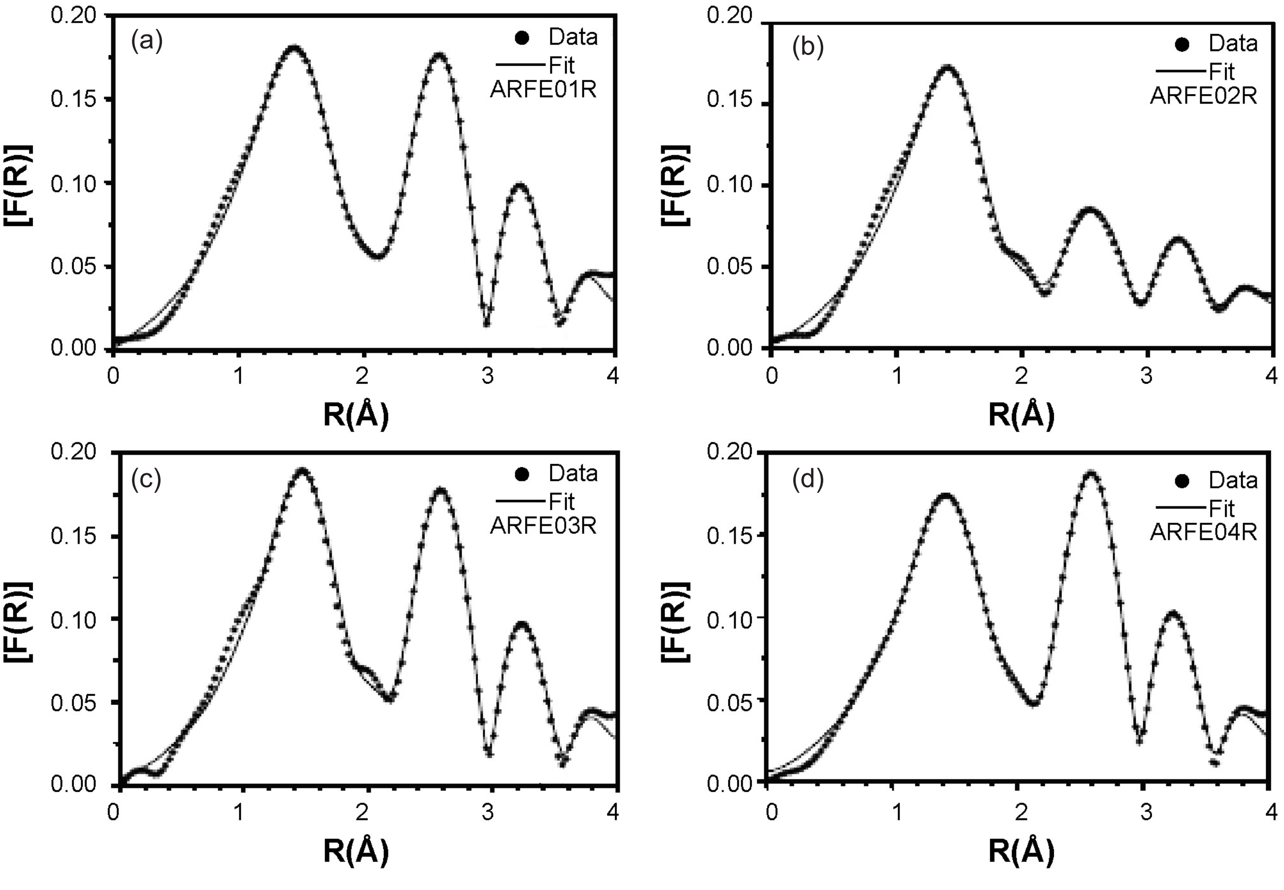

Figure 3: Theoretical $|F_{cal}(R)|$ (solid lines) of the EXAFS spectrum, taken by the least squares refinement to the observed |F(R)| (dotted line) for the Fe ions of the α-Fe_2O_3 structure in the red-color overglazes of the Kakiemon-style porcelains of (a) A (ARFE01R), (b) B (ARFE02R), (c) C (ARFE03R) and (d) the Arita one D (ARFE04R).

[Figura 3: Espectro EXAFS teórico $|F_{cal}(R)|$ (linhas sólidas), obtido pelo ajuste de mínimos quadrados de |F(R)| observado (pontos) para íons Fe da estrutura α-Fe_2O_3 em esmaltes vermelhos de porcelanas do estilo Kakiemon de (a) A (ARFE01R), (b) B (ARFE02R), (c) C (ARFE03R) e (d) Arita, D (ARFE04R).]

Table II - Refined parameters Rj (Å) of the surrounding ions (oxygen Oj and Fe ions Fej) around the X-ray absorber Fe ion to the ideal radial distance Rcalj (Å) in the α-Fe_2O_3 structure for the red-color overglazes of the Kakiemon-style porcelains A (ARFE01R, 1670-90's), B (ARFE02R, 1670-90's), C (ARFE03R, 1670-90's), E (ARFE06R, 1670-90's), and the Arita porcelains D (ARFE04R, 1690-1730's).

[Tabela II - Parâmetros Rj (Å) ajustados dos íons (oxigênio Oj e íons Fe Fej) em torno do Fe absorvedor de raios X para a distância radial ideal Rcalj (Å) na estrutura α-Fe_2O_3 *dos esmaltes vermelhos de porcelanas do estilo Kakiemon A (ARFE01R, anos 1670-90), B (ARFE02R, anos 1670-90), C (ARFE03R, anos 1670-90), E (ARFE06R, anos 1670-90), e porcelanas Arita D (ARFE04R, 1690-1730's).*

	RF	O1	O2	Fe1	Fe2	Fe3	O3	O4	Fe4	O5	Fe5
R_{cal}		1.960	2.087	2.881	2.967	3.364	3.384	3.597	**3.699**	**3.808**	3.979
N		3	3	1	3	3	3	3	6	3	1
A	0.004	1.930	2.092	2.888	2.974	3.371	3.391	3.605	**3.707**	**3.816**	3.988
B	0.005	1.900	2.093	2.889	2.975	3.373	3.393	3.607	**3.709**	**3.818**	3.990
C	0.006	1.940	2.093	2.889	2.976	3.373	3.393	3.608	**3.709**	**3.818**	3.990
D	0.004	1.915	2.094	2.891	2.977	3.375	3.395	3.610	**3.711**	**3.821**	3.992
E	0.005	1.950	2.097	2.894	2.981	3.379	3.399	3.614	**3.716**	**3.824**	3.996

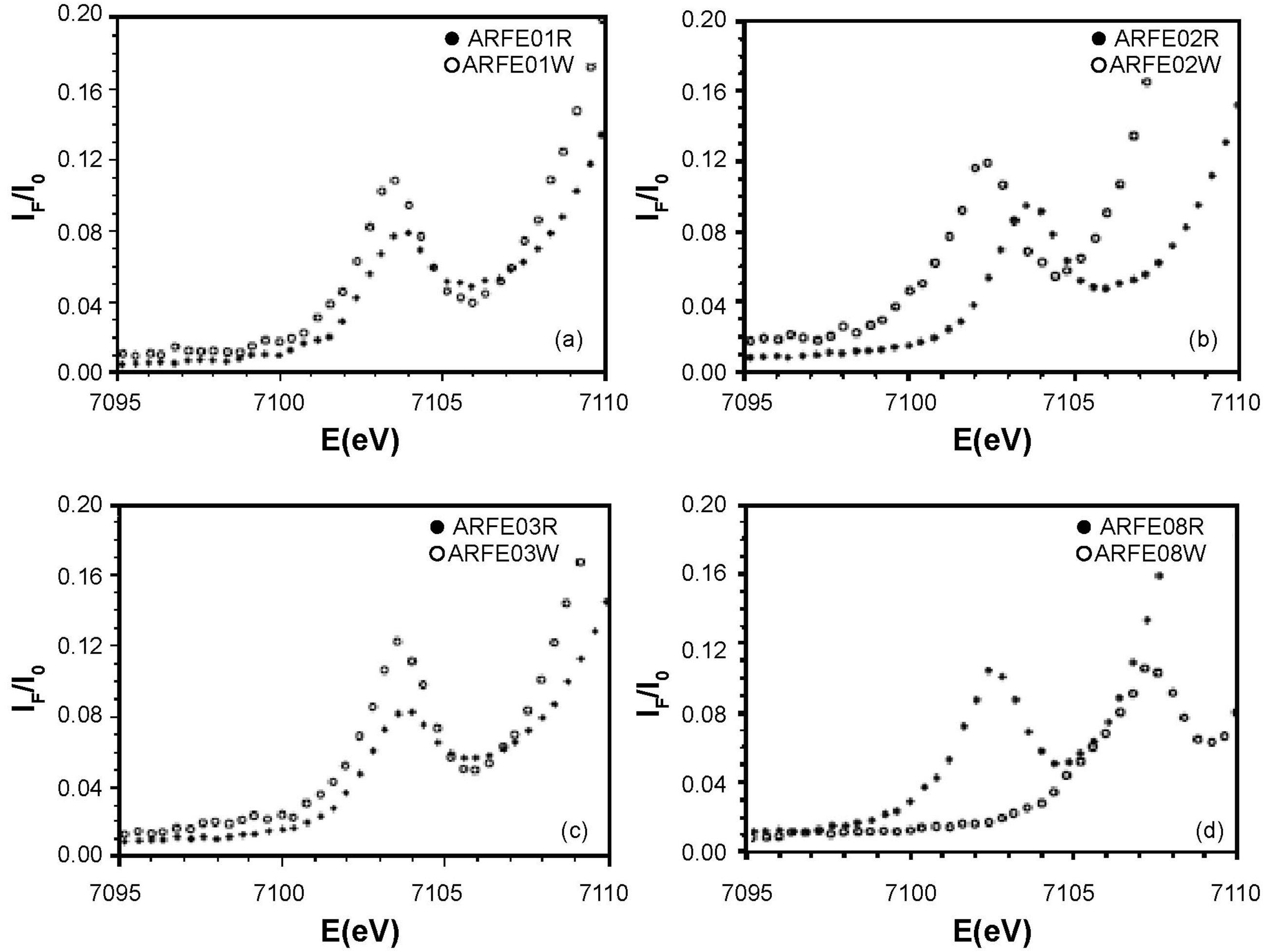

Figure 4: XANES spectra in the pre-edge region just below each X-ray absorption threshold (E_0) of the Fe-K edge for the red-color or dark-brown overglazes (solid circles) and the transparent glazes (open circles) of the Kakiemon-style porcelains; (a) A (ARFE01), (b) B (ARFE02), (c) C (ARFE03), and (d) F (ARFE08) in Figs. 1 and 2.

[Figura 4: Espectros XANES abaixo do limiar de absorção de raios X (E_0*) da linha Fe-K para os esmaltes vermelho ou marron escuro (círculos sólidos) e esmaltes transparentes (círculos abertos) de porcelanas do estilo Kakiemon; (a) A (ARFE01), (b) B (ARFE02), (c) C (ARFE03), e (d) F (ARFE08) nas Figs. 1 e 2.]*

Table III - Energy of the pre-edge XANES peaks (PE1) and the X-ray absorption thresholds (E_o) in the red-color and dark-brown overglazes (R) and the transparent glazes (W) in Fig. 10. $\Delta E(R) = PE1(R) - E_o(R)$, and $\Delta E(W) = PE1(W) - E_o(W)$.

[Tabela III - Energias dos picos XANES (PE1) e limiar de absorção de raios X (E_o) em esmaltes vermelho e marron escuro (R) e em esmaltes transparentes (W) na Fig. 10. $\Delta E(R) = PE1(R) - E_o(R)$, e $\Delta E(W) = PE1(W) - E_o(W)$.]

eV	PE1(R)	PE1(W)	E_o(R)	E_o(W)	ΔE(R)	ΔE (W)
A(ARFE01)	7103.8	7103.5	7114.3	7114.0	10.5	10.5
B(ARFE02)	7103.7	7102.3	7113.9	7111.4	10.2	9.1
C(ARFE03)	7103.8	7103.6	7113.9	7113.5	10.1	9.9
F(ARFE08)	7102.6	7107.3	7112.5	7116.2	9.9	8.9

peak in Fig. 3, in which the curve fittings were quite well. From Table II, Fe4 and O5 suggest that the α-Fe_2O_3 structures of the present porcelains are slightly deformed from its ideal structure by thermal expansion. However, the results suggest that the porcelains were produced by the similar thermal treatment, though the Kakiemon-style porcelain E was produced slightly at higher-temperature in comparison with the other porcelains. On the other hand, Fe4 of the red-color overglazes has the radial distance of Rj (Å) of about 4.021 to 4.023 Å for the Nabeshima wares, produced in 1690-1720's (the prime Nabeshima ware) [27, 28]. Thus, we deduce that the Nabeshima wares of most elegant brightness in Japan were produced by thermal treatment above at higher temperature (above 900 ºC) to the Kakiemon-style porcelains. Since the transparent glazes were heated at about 1300 ºC and were in glass-state, we suspect that the red-overglazes of the Nabeshima wares were heated at about 1000 to 1200 ºC. This means that the elegant brightness of red-color depends on the kiln temperature and the components of the fritted overglazes, in addition to the micro-structural correlation between the fine particles and the other oxides or the oxygen complexes grown in the red-color overglazes.

The Fe-EXAFS analyses suggest that the α-Fe_2O_3 structure is still kept in the red-color overglazes of the Kakiemon-style porcelains A, B, C, E, and the Arita one D, except the Kakiemon-style one F, as reported in the other paper by means of the X-ray diffraction using the synchrotron radiations [24]. On the other hand, the Fe-XAS of the transparent glazes of the present porcelains showed that Fe ions are spatially distributed in the glass-state. However, we are also interested in an electronic valence of Fe ions in the overglazes of red-color and dark-brown color and the transparent glazes of the present porcelains. It is known that the XANES spectrum in the pre-edge regions just below E_o gives information of the electronic band states in the electronic valence bands, that is closed to a Fermi level E_F. Fig. 4 shows the pre-edge XANES spectra of the Kakiemon-style porcelains; (a)A(ARFE01), (b) B(ARFE02), (c) C(ARFE03), and (d) F(ARFE08) in Figs. 1 and 2.

Table III shows the energy values of the pre-edge XANES peaks (PE1) and the X-ray absorption thresholds (E_o) in the red-color overglazes (R) and the transparent glazes (W) for the Kakiemon-style and Arita porcelains in Fig. 4. In Table III, the Kakiemon-style porcelains A, B, and C approximately show the same value for PE1(R) and E_o(R) of the red-color overglazes, but not for PE1(R) and E_o(R) of the transparent glazes. It is known that, in a free Fe ion, a XANES spectrum near a K-edge is induced by an electron transition between K-orbital (1s) and other orbital occupied at higher energy site under quantum physical conditions. While electrons in a solid as crystal make electronic bands or density of states (DOS) due to a periodicity of atomic coordinates. However, the electron transition between two bands is also constrained by the quantum conditions. The electronic transition between 1s and 3d bands is forbidden under the quantum condition. In the α-Fe_2O_3 structure, Fe^{3+} ions usually had five 3d-electrons, that is $3d^5$, though the maximum electron-occupancy of the 3d orbital is 10, that is $3d^{10}$. However, if there is an electronic exchange interaction [29], that is electronic hybridization, between Fe and its neighboring oxygen ions, the electrons will be hopped between the empty 3d orbital of Fe ions and the full-occupied 2p outer-orbital of O^{2-} oxygen ions surrounding the Fe ions. This induces new hybridized bands of $3d^n\underline{L}^m$ near a Fermi level E_F, where $\underline{L}$ means the O-2p bands. Thus, the $3d^n\underline{L}^m$ bands have a p-like character induced by the hybridization between the Fe-3d bands and the O-2p bands. This gives a possibility of the electron transition between the 1s and $3d^n\underline{L}^m$ bands. It is considered that the pre-edge XANES peaks in Fig.4 result from the transition between the 1s band and the hybridized $3d^n\underline{L}^m$ bands of Fe ions [29].

We deduced in Table III that the Fe-3d bands in the α-Fe_2O_3 structure are similarly affected by the surrounding oxides of SiO_2, Al_2O_3, K_2O, Na_2O, MgO, and PbO , for the Kakiemon-style porcelains A, B, and C. On the other hand, the pre-edge XANES peaks of the transparent glazes suggest that the surrounding oxides induce the slight different effect to the 3d bands of Fe ions in the glass-state to the porcelains A, B, and C. However, the porcelain F shows the large different energy of PE and E_o in contrast with those of A, B, and C. The difference results mainly from the large deformation of the local structure around Fe ions in the dark-brown color overglaze and the transparent glaze, which were chemically affected by the big fire in 1703. At that time, the α-Fe_2O_3 structure in the red-color overglazes was decomposed in non-crystalline state as shown in Fig. 2d. The X-ray diffraction patterns showed the existence of the other oxides in the dark-brown color overglaze of the porcelain F [24]. Thus, it is considered that Fe ions should be sited among the particles or clusters constructed by the other oxides, but not in glass-state. In Table III, the energy differences (ΔE(R), ΔE (W)) between the pre-edge XANES peak and E_o are approximately similar for the red-color and dark-brown overglazes and the transparent glaze in Fig. 4. This suggests that all pre-edge XANES peaks of the present porcelains result from Fe ions having the same electronic valence with that of Fe^{3+} ions ($3d^5$) in the α-Fe_2O_3 structure though the partially occupied 3d bands are hybridized with the O-2p bands. Thus, we consider that the transparent glazes in the Kakiemon-style porcelains A, B, C, E, F and the Arita one D have Fe^{3+} ions, even if the natural α-Fe_2O_3 particles are decomposed into the glass-state at high-temperature of about 1300 ºC.

CONCLUSIONS

In order to find an origin of the elegant and brightness for the Kakiemon-style porcelains and the Arita one produced at Arita areas in the early 17th century to the middle 18th century, we carried out the measurements of the X-ray absorption spectra (XAS) near the Fe-K edge, including the EXAFS and XANES spectra for the red-color overglazes and the transparent glaze. It was found that the α-Fe_2O_3 structure in the red-color overglazes of present porcelains A, B, C, D, E are slightly deformed by the other surrounding oxides (SiO_2, Al_2O_3, K_2O, Na_2O, MgO, PbO), and/or the new complexes of (SiO_2-Al_2O_3,) systems constructed by the raw materials. The structural deformation is induced by the thermal treatment of the porcelain kiln at high-temperature of about 900 to 1000 ºC. It was also found that the Fe ions in the transparent glazes of A, B, C, D, E and F are in the glass-state with the other oxides. However, their electronic valence, Fe^{3+}, of Fe ions is the same with that of the α-Fe_2O_3 in the red-color overglazes.

The raw materials of the porcelain ceramics, that is porcelain body of white color, transparent glaze, and the fritted red-color overglazes, includes the α-Fe_2O_3 fine powders, though the containing amount of α-Fe_2O_3 are slightly different each other. We considered that the transparence of the glaze coated on the porcelain body results from the glass-state, which is made by decomposing the α-Fe_2O_3 structure and the other oxygen structures of SiO_2, Al_2O_3, K_2O, Na_2O, MgO at about 1300 ºC. Although the lead oxides (PbO, Pb_3O_4) were used in the Edo period to increase the brightness in the red-color overglazes, the lead oxides (PbO, Pb_3O_4) were perfectly decomposed and Pb ions were in the glass-state because of their low-temperature melting point; PbO:886 ºC and Pb_3O_4:500 ºC.

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. Ohhashi, Old Imari ware, The Sun special issue 63, Autum'88, Heibonsha (1994).
[8] H. Kurita, Collection of Imari and Nabeshima, Kurita Museum (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 Kyushu 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 Powder Metallurgy **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, Ceram. Int. **34**, 7 (2007) 1681.
[24] M. Hidaka, H. Horiuchi, K. Ohashi, R. P. Wijesundera, L. S. R. Kumara, Nark Eon Sung (2008) to be submitted.
[25] S. Kajihara, J. Kakiemon-style Ceramics Art Research Center, ISSN 180-3202 (2006) 227-234.
[26] C. H. Booth, F. Bridges, Physica Scripta **T115** (2005) 202.
[27] M. Hidaka, K. Ohashi, S. Kajihara, R. P. Wijesundera,

L. S. R. Kumara, Jae-Young Choi, Nark Eon Sung, Ceram. Int. **35**, 2 (2009) 875.

[28] M. Hidaka, N. Murakami, R. P. Wijesundera, L. S. R. Kumara, Jae-Young Choi, Nark Eon Sung, Young Jun Park (2008) to be submitted.

[29] J. Zaanen, G. A. Sawatzky, J. W. Allen, Phys. Rev. Lett. **55**, 4 (1985) 418.

(Rec. 01/07/2008, Ac. 05/12/2008)