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Local structures and electronic band states of $\alpha-Fe_2O_3$ polycrystalline particles in the glazes of the HIZEN celadons produced in the Edo period of Japan, by means of X-ray absorption spectra (II)

(Estruturas locais e estados de banda de partículas policristalinas nos esmaltes de celadons Hizen produzidos no período Edo do Japão, por meio de espectros de absorção de raios X (II))

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Abstract

HIZEN celadon glazes produced in 1630's to 1790's (Edo period, Japan) have been investigated by means of X-ray absorption spectra (XAS) near a Fe-K edge by using synchrotron radiation and a Mössbauer spectrum. The XAS suggest that the local structure around Fe_2O_3 fine powders is slightly different between the Izumiyama ceramics of mainly the Quartz-SiO_2 and Ohkawachi ceramics of mainly the feldspar of $(K,Na)Si_3O_8$ (Sanidine), and that the glazes of the HIZEN celadons include the Fe_2O_3 fine powders in the glassy state, though the X-ray diffraction patterns of the glassy celadon glazes do not show any peaks of the Fe_2O_3 structure. The Mössbauer spectrum suggests that the celadon glaze of Seiji (m) includes only Fe^{3+} ions, but not Fe^{2+} ions. This indicates the existence of Fe_2O_3 in the celadon glaze. It is interpreted that the colored brightness of the HIZEN celadons is induced by the structural properties of the used raw celadon ceramics and the other transition-metal ions of Cr, Cu, Zn in the celadon glazes, but not by the chemical reaction from Fe_2O_3 to FeO under the deoxidizing thermal treatment at higher temperature in a kiln.

Keywords: HIZEN celadon glaze, local structure, electronic band states.

Resumo

Esmaltes de celadon Hizen produzidos dos anos 1630 a 1790 (período Edo, Japão) foram investigados por meio de espectros de absorção de raios X (XAS) próximos da linha Fe-K usando radiação síncrotron e espectro Mossbaues. Os resultados de XAS sugerem que a estrutura local em pós finos de Fe_2O_3 é levemente diferente entre as cerâmicas Izumiyama principalmente o quartzo e cerâmicas Ohkawachi principalmente do feldspato $(K,Na)Si_3O_8$ (Sanidine), e que os esmaltes dos celadons Hizen incluem finos pós de Fe_2O_3 no estado vítreo, embora os difratogramas de raios X dos esmaltes celadon não mostrem picos da estrutura do Fe_2O_3. O espectro Mossbauer sugere que os esmaltes celadon de Seiji (m) incluem somente íons Fe^{3+}, mas não Fe^{2+}. Isto indica a existência de Fe_2O_3 no esmalte celadon. É feita a interpretação que o brilho nas cores dos celadons Hizen é induzido pelas propriedades estruturais das cerâmicas básicas de celadon e os outros metais de transição Cr, Cu, Zn nos esmaltes celadon, mas não pela reação química entre Fe_2O_3 para FeO sob tratamento térmico desoxidante em forno a altas temperaturas.

Palavras-chave: *esmalte celadon Hizen, estrutura local, estados eletrônicos.*

INTRODUCTION

It is well known that Kakiemon-style porcelains have very elegant and bright colored overglazes having its original color tone and its characteristic pattern-distribution drawn on their porcelain basic body of white-color. 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, as Chinese porcelains. However, the Kakiemon-style porcelains were one kind of HIZEN colored porcelains produced at Arita and Ohkawachi (Imari) areas, which sited at a Nabeshima domain of HIZEN-Han in the early Edo period (at present, Arita and Ohkawachi are in Saga prefecture of Kyushu island, Japan). The HIZEN colored porcelains are generally classified by four kinds of porcelains: Shoki-Iroe (Kokutani-style), Kakiemon-style, Kinran-style, and Nabeshima ware [1-9]. The Nabeshima wares were as gifts only to the Tokugawa Shogun (Edo period). The raw porcelain ceramics of high-quality ferromagnetic used as the basic body were discovered by Korean potters at a small mountain, called Izumiyama (Arita), in 1610's. The basic porcelain body was consisted of ferromagnetic porcelain ceramics, called Hakujikou.

In the Arita and Ohkawachi areas, the porcelain ceramics including slightly larger content of Fe_2O_3 than that of Hakujikou were collected and used as a raw material of Hizen celadons, where the celadon is called with "Seiji" in Japanese. In 1610~1640's the Shoki-Imari porcelains were produced with a Korea porcelain technique. From 1640~50's, the colored underglazes and overglazes were made by the porcelain technique due to Keitokuchin-kiln (China), while the celadons were due to Ryusen-kiln (China) [10, 11]. The producing technique of the HIZEN celadons at Arita was developed in 1650~1660's and increased its completion in 1670's. After 1700's the technique was gradually declined [12]. In 1630~1650's Mitunomata celadons of elegant and bright were also produced at Mitunomata of Hasami, which is about 10 km away from Arita [13, 14].

It is known that the iron oxides in the celadon glaze show blue-green color under the deoxidizing thermal treatment at high-temperature. However, the celadon glaze changes gradually its color from yellow-brown to black color as increasing the iron oxides, even if under the deoxidizing thermal treatment. J. S. Larid (1918) [15] and R. R. Hunghan (1950) [16] reported that the blue-green color of the celadon glazes results from chemical reaction from Fe_2O_3 to FeO in the celadon glazes under the deoxidizing thermal treatment. At the present, many Japanese celadon potters thought that fine air-bubbles in the celadon glaze contribute to a diffused reflection of blue-green light. Recently, we have studied the correlation between the red-colored brightness and the structural and electronic properties for the overglaze of the HIZEN colored porcelains, which were produced at Arita areas from the 17th to 18th century, by means of X-ray diffraction (XRD) and X-ray absorption spectrum (XAS), using synchrotron radiation [17-19]. In this paper, we study the geographical and historical correlations among the glaze-colors of the HIZEN celadons produced at Aita and Imari areas in the Edo period.

MATERIALS

In order to study the structural deformation localized around Fe ions and the partially electronic band states of Fe ions in the glazes of the HIZEN celadons, we carried out measurements of X-ray absorption spectra (XAS) at the K-edge of Fe ions. Before the present celadon broken pieces, we measured the XAS of the raw ceramics for the Izumiyama celadon ceramics, the Ohkawachi celadon ceramics, and the Izumiyama basic ceramics (Hakujikou), of which the ratios of the oxide components are listed in Table I of Ref. [20]. Three kinds of the raw ceramics contained Fe_2O_3 of about 1.52, 4.21, and 0.56 wt% for the Izumiyama ceramics, the Ohkawachi ceramics, and Hakujikou, respectively. All of their X-ray diffraction patterns showed very small peaks of the Fe_2O_3 structure. The component ratio in the raw ceramics at Izumiyama (Arita) and Ohkawachi (Imari) were not so large difference, as shown in Table I [20]. However, we found from X-ray diffraction that the Izumiyama ceramics are mainly the quartz (SiO_2), while the Ohkawachi ones are mainly the feldspar of $(K,Na)Si_3O_8$ (sanidine). This suggests that both materials are grown in the different mechanism from the earth crust, though Izumiyama and Ohkawachi areas are about 10 km away each other. As described later, their different structural properties are partially related to the characteristic colored brightness of the celadon glazes in the HIZEN celadons produced at Arita and Ohkawachi areas, as shown in photo 1 in Ref. [20].

EXPERIMENTAL

In the present investigations the XAS near the Fe–K edge were measured for the raw ceramics, the HIZEN celadons, and the modern Nabeshima celadons (Choshun celadon) in photo 1 in Ref. [20], by using synchrotron radiation at the Pohang Light Source (2.5 GeV). A double crystal monochromator of Si (111) gave a relative energy

Table I - Oxide compositions (wt.%) of the celadon glazes of the HIZEN celadons, Seiji (c), (e), (j), (h), and (ℓ), in addition to the red-colored overglaze of the Kakiemon-style porcelain.
[Tabela I - Composições de óxidos (peso%) dos esmaltes celadon dos celadons Hizen, Seiji (c), (e), (j), (h), e (ℓ), em complemento aos esmaltes de cor vermelha da porcelana estilo Kakiemon.]

	kiln remain	SiO_2	Al_2O_3	CaO	K_2O	Na_2O	MgO	Fe_2O_3	MnO	TiO_2	PbO
c	Hyakuken	62.8	14.9	11.8	5.39	0.78	0.86	2.73	0.32	0.18	—
e	Nagayoshidani	64.5	15.8	10.8	4.06	0.57	1.39	2.85	0.28	0.26	—
h	Shimoshirakawa	67.3	15.2	9.42	3.91	0.35	1.44	2.02	0.26	—	—
j	Nabeshima kiln	69.3	16.2	5.79	5.61	1.32	—	1.59	0.07	—	—
ℓ	Higuchi	66.6	15.4	8.13	5.74	2.02	—	1.89	0.07	—	—
	Kakiemon	40.1	0.84	10.2	4.59	—	—	19.1	0.33	—	24.2

resolution ΔE to be less than about 0.2 eV at each respective monochromatic incident X-ray beam for the XAS near the Fe-K edge. The incident X-ray photons (I_o) were detected with an ionic chamber set in front of the specimen holder, 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 3 mm in horizontal and 1 mm in vertical on the specimen surface to the electron orbital of the accelerator. The ratio $\mu(I)$ ($=I_F / I_o$) gives the XAS near the Fe-K edge. We normalized the measured raw data with software programs of *Artemis* and *Athena*, which was developed by C. H. Booth and F. Bridges (2005) to analysis of the observed XANES and EXAFS spectra [21].

RESULTS AND DISCUSSION

Fig. 1 shows the XAS around Fe-K edge of the raw ceramics; the Izumiyama celadon ceramics, the Ohkawachi celadon ceramics, and Hakujikou, in addition to the HIZEN celadon of Seiji (h). Seiji (h) was taken at the kiln remain of Shimoshirakawa closed to Izumiyama in 1655-1660's [20]. The X-ray diffraction patterns suggested from the very weak intensity of the observed peaks that the Izumiyama and Ohkawachi celadon ceramics, and Hakujikou include the α-Fe_2O_3 fine powders of small amount, as Table I in Ref. [20]. Thus, the XAS of the raw ceramics in Fig.1 results from the α-Fe_2O_3 particles. On the other hand, the celadon glaze of Seiji (h) shows the XAS to be similar to the raw ceramics, though the celadon glaze is in the glassy state. Fig. 2 shows the EXAFS spectra in the energy region of 7150 to 7500 eV, which are expanded the XAS in Fig. 1. The spectra suggest that the local structure around Fe ions reflects on the structural difference between the Izumiyama ceramics of mainly the quartz and the Ohkawachi one of mainly the sanidine of $(K,Na)Si_3O_8$ [20]. The similarity of the EXAFS spectrum between the Izumniyama celadon ceramics and Seiji (h) also suggests that the glaze material of Seiji (h) was based on the Izumniyama celadon ceramics, though an X-ray absorption threshold (E_o) depends on the structural circumstance around Fe ions in the ceramics.

For comparison we measured the XAS around K-edge of the red-colored overglaze of the Kakiemon-style porcelain, which was produced at Arita in 1710's-1740's, and the marketed powders of FeO. The red-colored overglaze includes much amount of α-Fe_2O_3 (19.1 wt.%) and lead oxide PbO (24.2 wt.%). The results are shown in Fig. 3. The left and right spectra in the lower figures are expanded in the EXAFS region of the XAS in the upper figures for the Kakiemon-style overglaze and FeO, respectively. We found the clear difference of the XAS between the α-Fe_2O_3

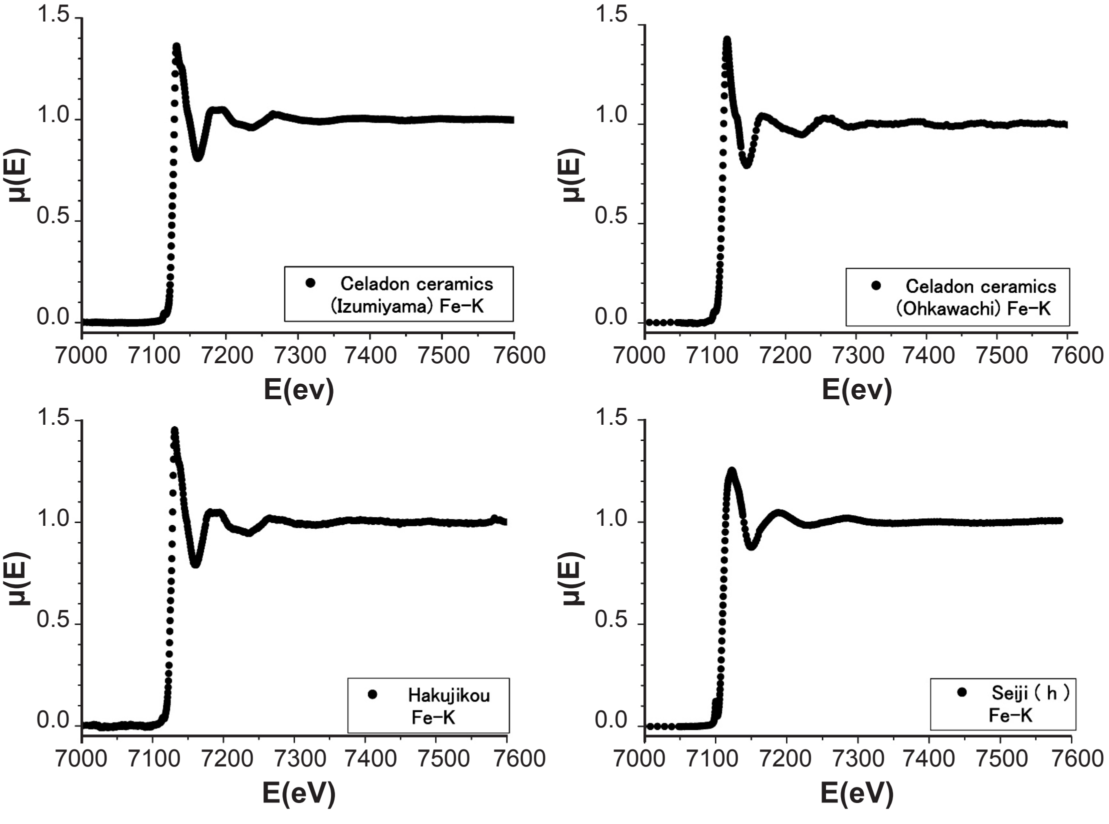

Figure 1: X-ray absorption spectra around Fe-K edge of the Izumiyama celadon ceramics, the Ohkawachi celadon ceramics, the Izumiyama basic ceramics (Hakujikou), and the HIZEN celadon of Seiji (h).

[Figura 1: Espectros de absorção de raios X em torno da borda Fe-K das cerâmicas celadon Izumiyama, cerâmicas celadon Okhawachi, cerâmicas básicas (Kahujikou) Izumiyama e celadon Hizen de Seiji (h).]

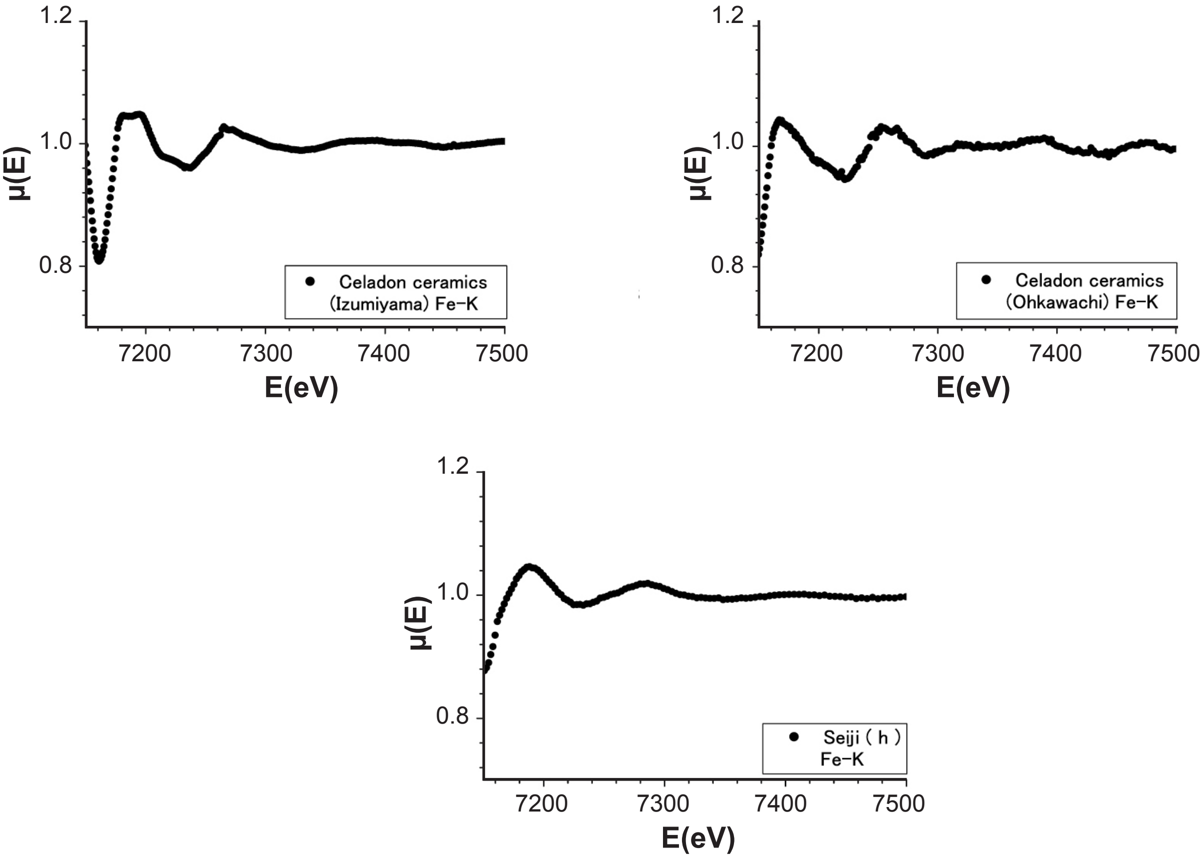

Figure 2: EXAFS spectra around Fe-K edge of the Izumiyama celadon ceramics, the Ohkawachi celadon ceramics, and the HIZEN celadon of Seiji (h) in Figure 1.

[Figura 2: Espectros EXAF em torno da borda Fe-K das cerâmicas celadon Izumiyama, cerâmicas celadon Okhawachi, cerâmicas básicas (Kahujikou) Izumiyama e celadon Hizen de Seiji (h) na Figura 1.]

structure and the FeO one. As described before, the XAS of the raw ceramics also result from Fe ions of the α-Fe_2O_3 structure. Thus, we know from the different oscillated amplitude of the EXAFS spectrum that the XAS also gives structural information of the local circumstance around the Fe_2O_3 fine powders in a material. That is, it is considered that the Fe_2O_3 fine particles make a large cluster of long-range order in the red-colored overglaze and a fine cluster of short-range order or independently co-exist in the raw ceramics. The XAS in Figs. 1 and 2 suggest that Seiji (h) includes the Fe_2O_3 fine particles in its celadon glaze, though the celadon glaze is in the glassy state. The melting temperature of Fe_2O_3 and FeO are 1570 °C and 1370 °C, respectively. In 1630's to 1790's the maximum temperature in the used kilns was about 1200-1250 °C.

In the present investigations the used specimens were 12 broken pieces of the monochromatic HIZEN celadons (photo 1(a) to (ℓ)) produced in 1630's to 1730's at Arita areas (Arita, Yamauchi) and Imari, and 2 ones of the modern Nabeshima celadons (Photo 1(m) and (n)) produced by Choshun kiln sited at Ohkawachi (Imari), as photo 1 in our other paper [20]; (a) Kamanotsuji (Yamauchi, 1630-1640's), (b) Kamanotsuji (Yamauchi, 1630-1640's), (c) Hyakuken (Yamauchi, 1630-1640's), (d) Hyakuken (Yamauchi, 1630-1640's), (e) Chokichidani (Arita, 1655-1660's), (f) Chokichidani (Arita, 1655-1660's), (g) Maruo (Arita, 1650-1660's), (h) Shimoshirakawa (Arita, 1655-1660's), (i) Nabeshima-domain kiln (Imari, 1690-1720's), (j) Nabeshima-damain kiln (Imari, 1690-1720's), (k) Higuchi (Arita, 1760-1790's), (ℓ) Higuchi (Arita, 1760-1790's), (m) Choshun kiln (Imari, 2007), (n) Choshun kiln (Imari, 2007). All of the present kiln remains are famous and historic in the Edo period. It was deduced that the Nabeshima-domain kiln, called Odougu-yama, was transferred from Nangawara (Arita) to Ohkawachi (Imari) in 1673-1681's. Ohkawachi is about 10 km away from Arita, while Yamauchi is about 5 km away from Izumiyama at Arita. The broken pieces of the Nabeshima celadons in Photo 1(i) and (j) were produced at Ohkawachi Odougu-yama. The Nabeshima wares including the celadons show excellently elegance and brightness. Table I lists the ratios of the component oxides in the celadon glazes of the HIZEN celadons, called Seiji (c), (e), (j), and (ℓ), in Photo (c), (e), (j), and (ℓ) of our other paper [20], in addition to those in the red-colored overglaze of the Kakiemon-style porcelain. In that time, Isubai (natural wood ash) including much $CaCO_3$ was traditionally added into the raw ceramics of the HIZEN celadon glazes. $CaCO_3$ is chemically changed to CaO at about 825 °C, and CaO has a catalytic function to

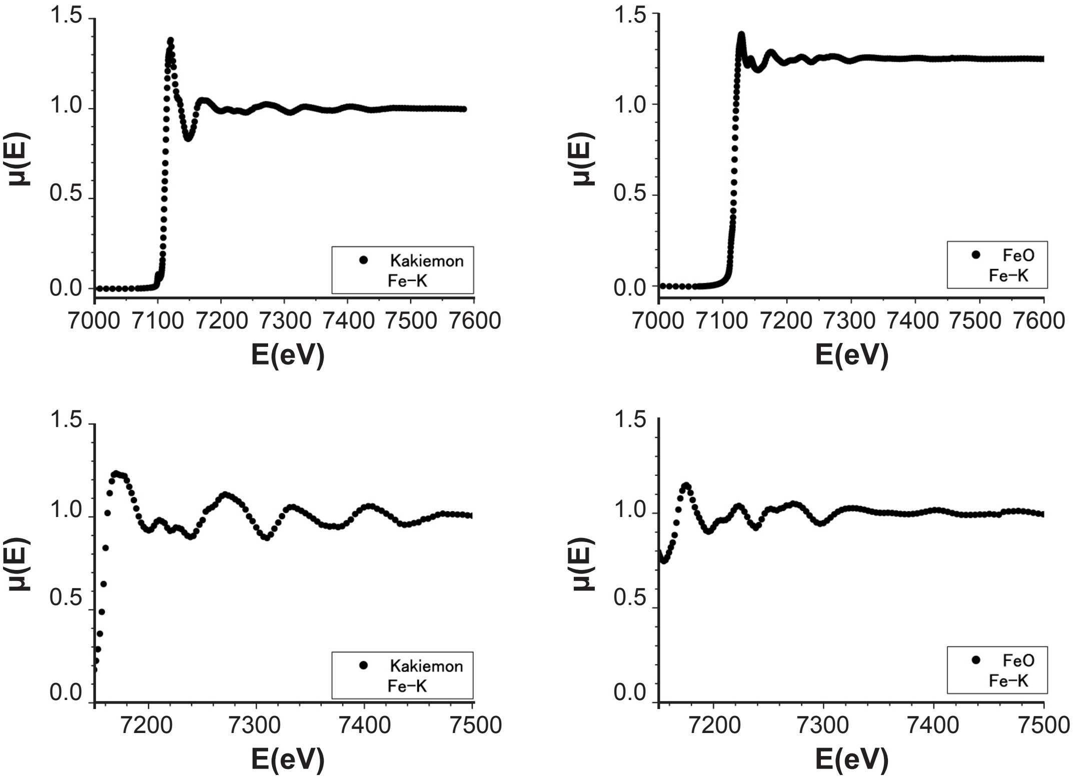

Figure 3: X-ray absorption spectra around the Fe-K edge for the red-colored overglaze of the Kakiemon colored porcelain (Kakiemon) and the marketed powders of FeO.
[Figura 3: Espectros de absorção de raios X em torno da borda Fe-K para os esmaltes de cor vermelha das porcelanas coloridas (Kakiemon) e de pó comercial de FeO.]

reduce the glassy temperature of the raw celadon ceramics.

Fig. 4 shows the Hizen celadon glazes, called Seiji (a), (c), (e), and (f), as in Photo 1(a), (c), (e), and (f) in Ref. [20], respectively. In this paper, all of the figures related to the XAS data were drawn by using only the data points at specific intervals from a lot of observed data points for figure easiness to see. The XAS of the present celadon glazes are very similar each other. E_o slightly shifted from 7111 eV (a free Fe ion) to about 7114 eV. E_o depends on the crystallographic structure. Since the X-ray diffraction patterns in Figs. 3 and 4 of Ref. [20] show the halo-like pattern, it is considered that the XAS data in Fig. 4 reflect the short-range order of the ionic arrangements in the celadon glazes. The XAS spectra do not result from Fe metallic particles in the glazes, because of the largely different spectrum of the Fe particles. However, at a moment, it can not be determined whether all of the component oxides are melted or resolved to make the glassy glaze. As will be described later, we should refine the observed EXAFS spectrum of the present celadon glazes to determine whether the glazes include the fine particles of Fe_2O_3 or FeO. Fig. 5 shows the XAS of the HIZEN celadon glazes, called Seiji (h), (j), (ℓ), and (m), as in Photo 1(h), (j), (ℓ), and (m) in Ref. [20], respectively. The spectra in Fig. 5 are very similar to those in Fig. 4. Thus, it is found that the HIZEN celadons and the modern Nabeshima celadon (Choshun kiln) have the similar local structure and the electronic band states to the Fe ions in the glazes, where the local structure around X-ray absorbing atoms and the band states of the absorbing atoms are obtained from the EXAFS spectrum and the XANES one, respectively. It is usually known that the XANES spectrum is in the region of about –100 to + 50~80 eV, while the EXAFS one is in the higher region of about 50~80 to 700 eV above its X-ray absorption thresholds E_o, when E_o= 0.0 eV.

In order to study the local structure around Fe ions in the celadon glaze, we carried out tthe analysis of the EXAFS spectra of the HIZEN celadons and the modern Nabeshima celadon (Choshun kiln), more quantitatively. We obtained an observed Fourier transformation spectrum $|F(R)|$ to the observed oscillating EXAFS spectrum X_{obs}(E), after representing an energy of X-ray photons with a wave-number $k\{= 8\pi^2 m_e(E-E_o)/h^2\}$, where m_e and h are an effective mass of electron and Planck's constant, respectively. The details of its analysis were already reported in our recent paper [17]. After obtaining the observed oscillating EXAFS spectrum X_{obs}(E), we calculated a theoretical oscillating EXAFS spectrum X_{cal}(E) by using the optical interference theory between the X-ray photoelectron waves emitted from the X-ray absorbing Fe ions and its back-scattering waves induced by the surrounding ions. In the present investigations, we used software programs of *Artemis* and *Athena* to analysis the XAS data and refine the X_{obs}(K) with the theoretical X_{cal}(K) [21]. We carried out to do a best fit between the X_{obs}(K) and the X_{cal}(K) by mean of a least squares

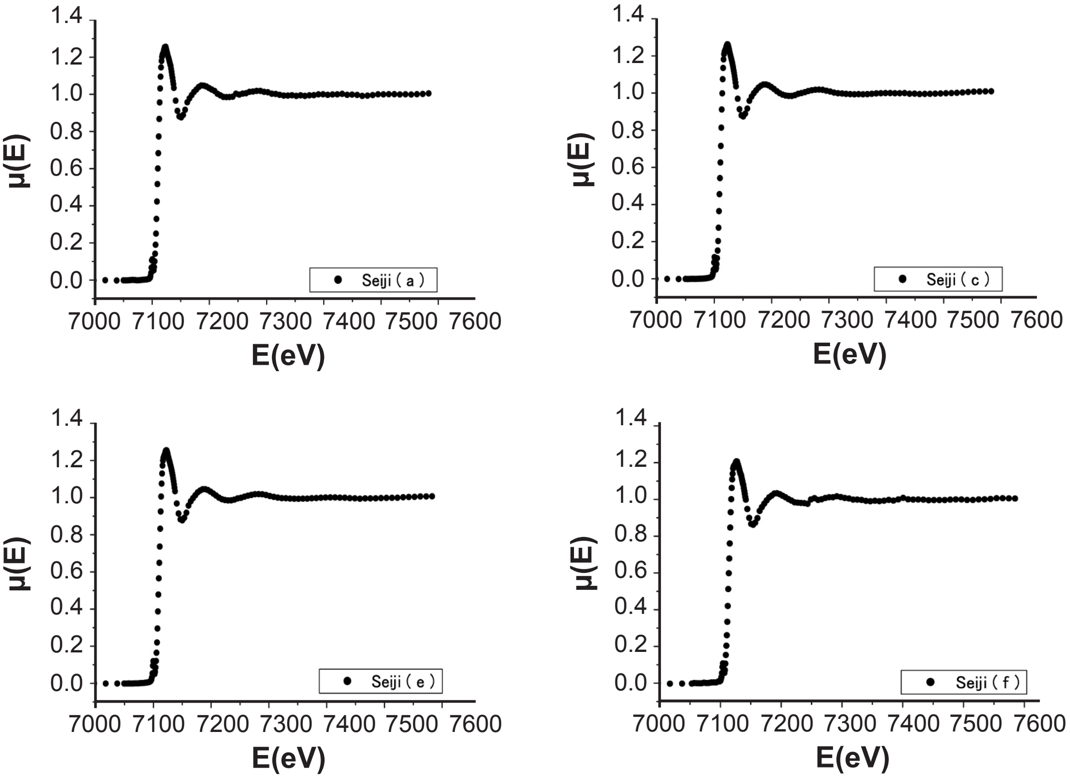

Figura 4: X-ray absorption spectra around Fe-K edge of $\alpha-Fe_2O_3$ in the of HIZEN celadon glazes, Seiji (a), (c), (e), (f).
[Figura 4: Espectros de absorção de raios X em torno da borda Fe-K de α*-*Fe_2O_3 *nos esmaltes celadon Hizen, Seiji (a), (c), (e), (f).]*

method with 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 = $\{\Sigma|X_{obs}(K) - kX_{cal}(K)|^2\}/\Sigma|X_{obs}(K)|^2$, where k is a scale factor. The details were reported in our paper [17]. Fig. 6 shows the refinements of the EXAFS spectra for the Fe ions of the α-Fe_2O_3 structure of Seiji (c), (e) in Fig. 4 and Seiji (j) and (ℓ) in Fig. 5. The abscissa refers to a radial distance (R(Å)) from a X-ray absorbing Fe ion, as a coordinate origin, to its surrounding shells including the cations or anions of the α-Fe_2O_3 structure. The peaks of the observed │F(R)│ approximately represent the shells being away from the X-ray absorbing Fe ions by Rj (Å). Each shell includes the equivalent surrounding ions.

In Fig. 6 the solid lines and the solid circles represent the theoretical and observed Fourier transformation spectrum │F(R)│, respectively. The RF-values were about 0.003, 0.02, 0.03, and 0.04 for Seiji (c), (e), (j), and (ℓ), respectively. The theoretical calculation was based on an ideal α-Fe_2O_3 structure, which has a hexagonal symmetry with its lattice constants of a=5.035 Å and b=13.72 Å. The present spectral analyses were successfully done. Thus, we found from Fig. 5 that the celadon glazes of Seiji (c), (e), (j), and (ℓ) have the α-Fe_2O_3 structure. In the present investigations, we carried out refinements of the EXAFS data for all of the HIZEN celadons and the modern Nabeshima celadons in Photo 1 in Ref. [20]. The results are shown in Table II, except Seiji (a). In Table II, R_{cal} is a radial distance of the ideal α-Fe_2O_3 structure, while the Oj and Fej (j=integer) represent the surrounding oxygen and Fe ion in the shell sited at the radial distance Rj away from the origin of the X-ray absorbing Fe ion, respectively. When studying the local structure by the refinement of the EXAFS spectrum, it is important to regard 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 investigations. The calculated radial distances R_{cal}j are due to the ideal $\alpha-Fe_2O_3$ structure. Thus, a slight difference between Rj and Rcalj results from the effect of the phase parameters. It is found in Table II that the Fe components of the HIZEN celadons and the modern Nabeshima celadon (Choshun kiln) should be the α-Fe_2O_3 structure. However, we could not succeed the refinements of the EXAFS data for the present celadons with the FeO structure.

It is known that the pre-edge XANES spectrum gives information of unoccupied electronic band states in a top region of the valence band just below E_F, while the main XANES spectrum gives empty electronic band states in a bottom region of the conduction band just above E_F. Both XANES spectra sensitively depend on the crystallographic structure. In order to study the structural and electronic properties of Fe ions in the red-colored overglaze of the Kakiemon-style porcelain and the HIZEN celadons, we

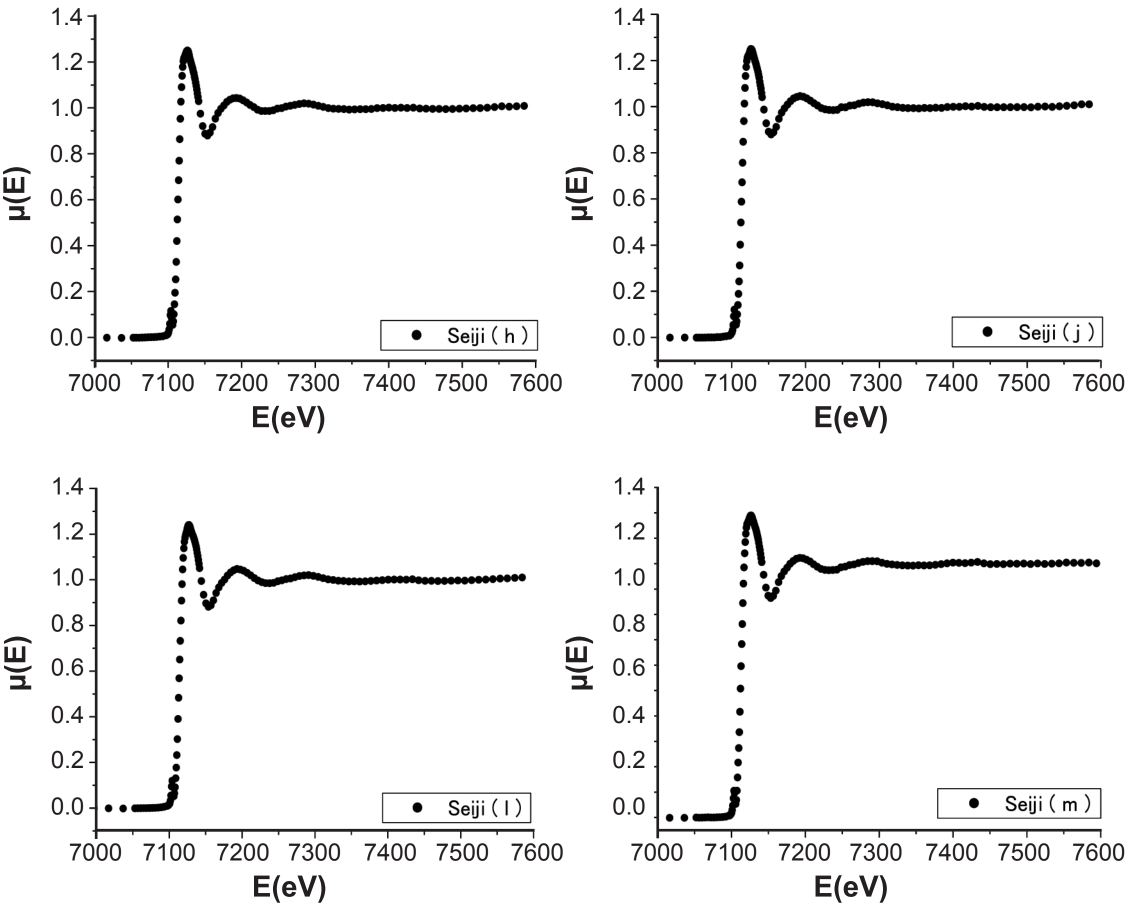

Figure 5: X-ray absorption spectra around Fe-K edge of α-Fe_2O_3 in the HIZEN celadon glazes, Seiji (h), (j), (ℓ), in addition to the modern Nabeshima one (Seiji (m)).
[Figura 5: Espectros de absorção de raios X em torno da borda Fe-K de α-Fe_2O_3 *nos esmaltes celadon Hizen, Seiji (h), (j), (ℓ), alem de um Nabeshima moderno (Seiji (m)).]*

also carried out measurements of XAS around Fe-K edge for marketed FeO powders by using the present XAS spectrometer. Fig. 7 shows a comparison of the pre-edge and main XANES spectra between Fe_2O_3 of the Kakiemon-style porcelain and the HIZEN celadons and FeO in the marketed powders. The sample of the marketed FeO powders was a pellet of 10 mm in diameter and 4 mm in height. As described before, E_o of the Kakiemon-style porcelain and Seiji (h) are about 7114.0 and 7113.5 eV in Fig. 7a, respectively. E_o of FeO is about 7118.8 eV in Fig. 7b. The pre-edge XANES peaks are observed at about 7103.6 eV on Fe_2O_3 (A) and 7113.4eV on FeO (B). The XANES peak in the pre-edge region of the Fe-K absorption edge is induced by an electronic transition between a K-electron band and an unoccupied hybridized valence band of Fe ions in the Fe_2O_3 structure and the FeO one. The electronic hybridization results from an electronic configuration interaction between the unoccupied electronic bands of cations, Fe ions, and the full occupied bands of anions, O ions, in the crystalline solid of Fe_2O_3 and FeO structure [22]. In Fig.7 the relativistic energy difference ΔE ($=E_o-E_p$) between E_o and the pre-edge peak (E_p) are about 10.4 eV and 9.9 eV for the Kakiemon-style porcelain and Seiji (h), respectively, while ΔE of FeO is about 5.4 eV. Thus, the pre-edge XANES peaks suggest that the valence electrons of Fe ions in the celadon glaze is 3+, but not 2+ [22]. This is not consistent with the color emission mechanism of the celadon glaze reported [15, 16]. They suspected that the celadon glaze was colored by the chemical reaction from Fe_2O_3 to FeO under the deoxidizing thermal treatment at higher temperature in a kiln.

As described before, we found that the present celadons have the glazes including the fine particles of Fe_2O_3, but not FeO, by the deoxidizing thermal treatment at about 1200-1250 °C. This means that there is no chemical reaction from Fe_2O_3 to FeO, as reported [15, 16]. In order to re-check the XAS experimental results, we carried out measurement of a Mössbauer spectrum of the celadon glaze. The Mössbauer spectrum gives information of bonding, structural, magnetic, time-dependant and dynamical properties of chemical systems. The Mössbauer effect involves resonant absorption of gamma rays by atoms of the same isotope. The source of gamma rays is a radioactive isotope of an element which decays into an excited state of the isotope, which returns to its ground state by the emission of a gamma ray or electron. In the present investigations, we used a gamma ray emitted from an isotope of ^{57}Co, which undergoes a nuclear decay to ^{57}Fe in its nuclear spin I=5/2 excited state. The decay of this state, which is mainly a 14.4 keV excited state, via gamma

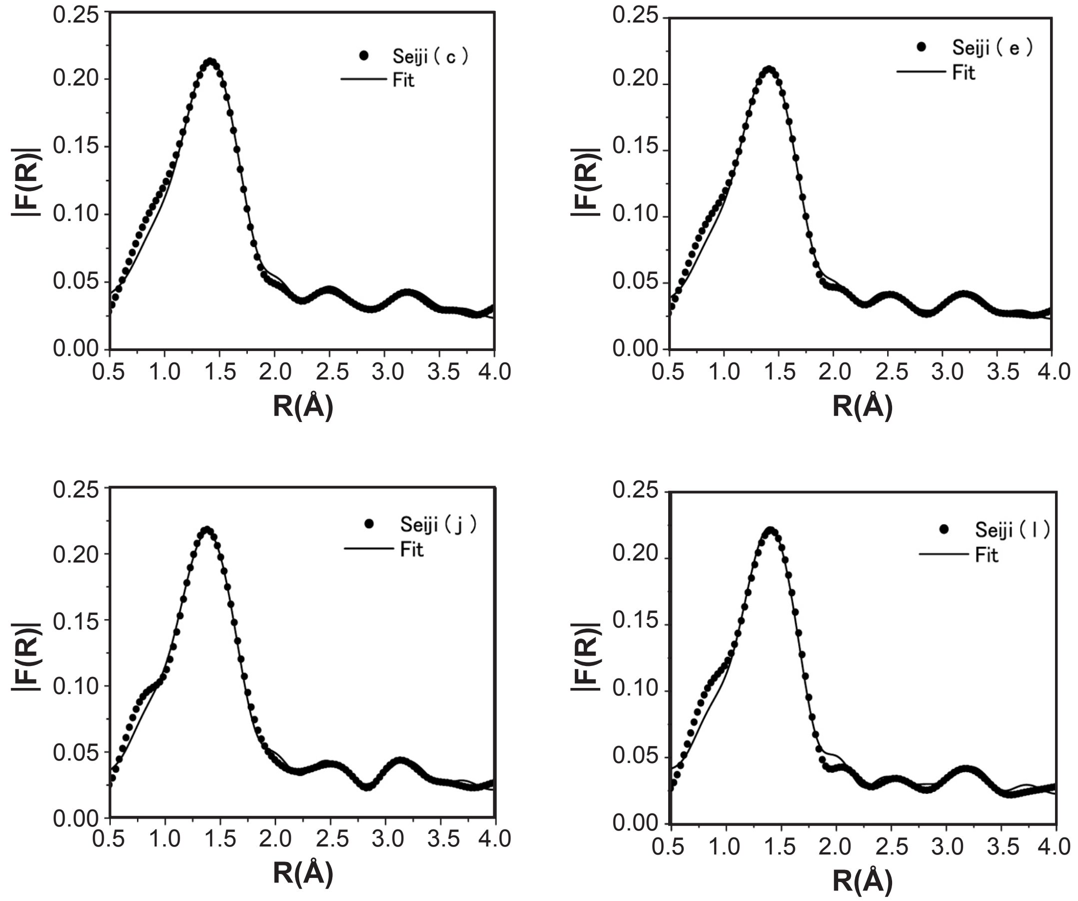

Figure 6: Theoretical |F(R)|(solid line-fit) of the EXAFS spectrum, taken by the least squares refinement to the observed |F(R)| (solid circles) for the Fe ions in the $\alpha-Fe_2O_3$ structure of Seiji (c), (e) in Figure 4 and Seiji (j) and (ℓ) in Figure 5.

[Figura 6: Ajuste teórico |F(R)|(linha sólida-ajuste) do espectro EXAFS, obtido por refinamento por mínimos quadrados do espectro |F(R)| observado (círculos sólidos) dos íons Fe na estrutura $\alpha\text{-}Fe_2O_3$ *de Seiji (c), (e) na Figura 4 e Seiji (j) e (ℓ) na Figura 5.]*

ray or conversion electrons is in the Mössbauer spectrum of iron systems. The Mössbauer spectrum is affected by temperature and three other factors of isomer shift, quadrupole splitting, and magnetic splitting. In the present investigations, we regard only the effects of the isomer shift and the quadrupole splitting because of the measurement at room temperature and no applied magnetic field.

The isomer shift (δ) results from the difference in the electron densities at the nuclear sites in the emitting and absorbing atoms. This difference in density changes the Mössbauer transition-energy and so the Mössbauer spectrum is shifted. The isomer shift is sensitive to the oxidation state and can therefore be used to study valence electrons of Fe ions in the celadon glaze. If the nuclei do not have a charge distribution of spherically symmetric, the nucleus will possess an electric nuclear quadrupole moment. This moment interacts with an asymmetric electronic charge distribution splits the degeneracy of the excited state into two levels, which are separated by the quadrupole splitting (Δ). The Mössbauer spectrum is a doublet. The quadrupole splitting can be broken down into two contributions of a valence contribution from the atom itself and a lattice contribution from neighboring atoms. Fe^{3+} ($3d^5$) ions have no contribution to the electric field gradient from the 3d electron orbitals. This means that Fe^{3+} ions have the relatively low quadrupole splitting. On the hand, Fe^{2+} ($3d^6$) ions have the large electric field gradient contribution from the 6th 3d-electron, and give the large quadrupole splittings of about 1.5-3 mm/s (with a maximum of > 4 mm/s). Thus, the isomer shift and the quadrupole splitting is a useful tool to determine whether Fe ion has the valence electrons of 3+ (Fe_2O_3) or 2+ (FeO). If Fe_2O_3 and FeO particles coexist in the glaze, we can observe a mixed Mössbauer spectrum induced by Fe^{3+} and Fe^{2+} ions.

When measuring the Mössbauer spectrum, the incident gamma rays penetrate a powder specimen in front of its detector. Thus, to make fine powders, we must remove mechanically the celadon glazes of the Hizen celadons from its basic body and crush the broken pieces. However, all of the broken pieces of the Hizen celadons in Photo 1 in Ref. [20] were rented from at the public museum are very important cultural assets in Japan. We were strongly requested to use nondestructive methods for studying the structural and electronic properties of the Hizen celadons. Thus, we measured only the powdered celadon glaze of the modern Nabeshima celadons, Seiji (m), in Photo 1-m

Table II - Refined parameters Rj of the surrounding ions (oxygen ions Oj and Fe ions Fej) around the X-ray absorbing Fe ion to the ideal radial distance $R_{cal}j$(Å) of the α-Fe_2O_3 structure in the glazes of the HIZEN celadons; Seiji (b) to (ℓ) and the modern Nabeshima celadons of Choshun kiln; Seiji (m) and (n).

[Tabela II - Parâmetros refinados Rj dos íons (íons oxigênio Oj e íon Fe Fej) em torno do íon Fe absorvedor de raios X para a distância radial ideal $R_{cal}j$(Å) da estrutura do α-Fe_2O_3 nos esmaltes de celadons Hizen; Seiji (b) a (ℓ) e os celadons modernos Nabeshima de forno Choshun; Seiji (m) and (n).]

	RF	O1	O2	Fe1	Fe2	Fe3	O3	O4	Fe4
N		3	3	1	3	3	3	3	6
R_{cal} (Å)		1.96	2.09	2.88	2.97	3.36	3.38	3.60	3.70
b	0.004	1.88	2.07	2.86	2.94	3.34	3.36	3.57	3.67
c	0.003	1.88	2.08	2.88	2.96	3.36	3.38	3.59	3.69
d	0.002	1.88	2.11	2.91	2.99	3.39	3.41	3.63	3.73
e	0.002	1.87	2.08	2.87	2.95	3.35	3.37	3.58	3.68
f	0.007	1.88	2.10	2.90	2.98	3.38	3.40	3.62	3.72
g	0.003	1.87	2.08	2.87	2.96	3.35	3.37	3.59	3.69
h	0.002	1.87	2.08	2.87	2.95	3.35	3.37	3.58	3.68
i	0.004	1.87	2.07	2.86	2.94	3.34	3.36	3.57	3.67
j	0.003	1.85	2.05	2.84	2.92	3.31	3.33	3.54	3.64
k	0.003	1.87	2.07	2.86	2.94	3.34	3.36	3.57	3.67
ℓ	0.004	1.86	2.09	2.88	2.97	3.36	3.38	3.60	3.70
m	0.005	1.87	2.07	2.86	2.95	3.34	3.36	3.58	3.68
n	0.003	1.88	2.09	2.89	2.96	3.37	3.39	3.61	3.71

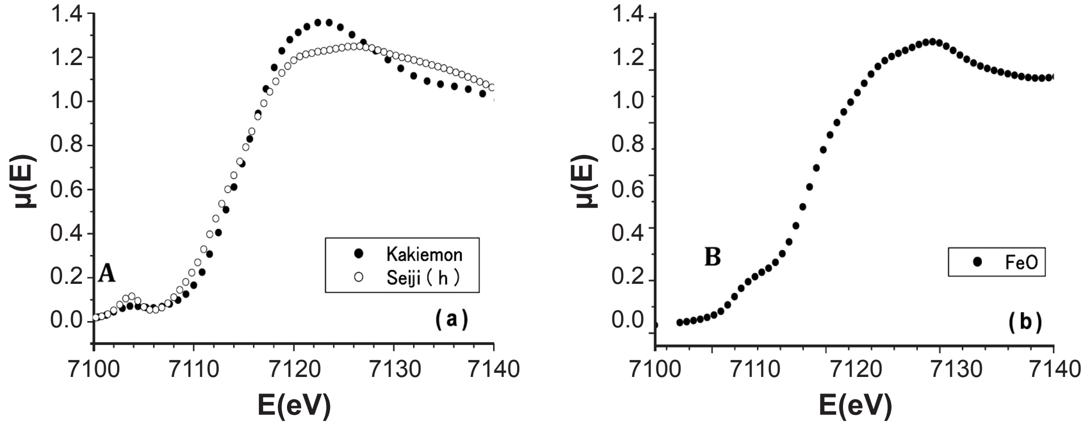

Figure 7: X-ray absorption spectra around Fe-K edge for the red-colored overglaze of the Kakiemon-style porcelain, the HIZEN celadon Seiji (h), and the marketed FeO powders.

[Figura 7: Espectros de absorção de raios X em torno da borda Fe-K para os esmaltes de cor vermelha das porcelanas de estilo Kakiemon, celadon Seiji Hizen (h), e de pó comercial de FeO.]

in Ref. [20]. The Choshun kiln succeeds to produce the Nabeshima celadons traditionally at Ohkawachi (Imari), until now. The Nabeshima-domain kilns, called Odougu-yama, were set up at Ohkawachi, after transferred from Nangawara (Arita) to Okawachi (Imari) in 1673-1681's.

The observed Mössbauer spectrum taken at room temperature is shown in Fig. 8. The abscissa refers to a shift velocity of the incident ^{57}Co gamma ray radiation, while the ordinate to a penetrating ratio of the incident gamma ray to the powder specimen. After refining the Mössbauer spectrum, we obtained that the isomer shift δ and the quadrupole splitting Δ were about 0.57 mm/s and 0.92 mm/s, respectively, while the line width was about 0.31 mm/s. The Mössbauer spectroscopy for Fe oxides and oxyhydroides are reported [23, 24]. From the reported data, δ and Δ of Fe^{3+} are in the region of about 0.1 to 0.5 mm/s and of about 0.1 to 1.5 mm/s, respectively, while those of Fe^{2+} are in the region of about 0.9 to 1.4 mm/s and of about 1.8 to 3.5 mm/s, respectively. Thus, the present Mössbauer spectrum suggests that the celadon glaze of Seiji (m) includes only Fe^{3+} ions, but not Fe^{2+} ions. This indicates the existence of Fe_2O_3 in the celadon glaze.

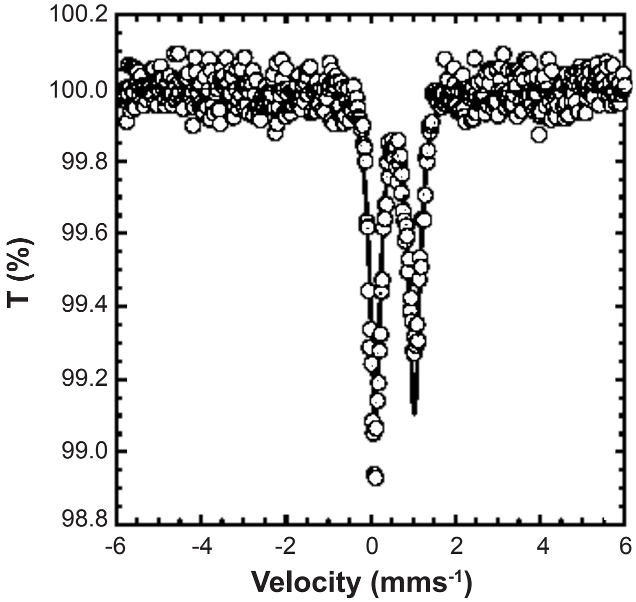

Figure 8: Mössbauer spectrum of the Seiji (m) celadon glaze.
[Figura 8: Espectro Mössbauer do esmalte celadon Seiji (m).]

CONCLUSIONS

In order to study the historical and technical correlation of the Hizen celadon glazes including the modern Nabeshima celadon (Choshun kiln), we carried out the measurements of the X-ray absorption spectra (XAS) near the Fe-K edge by using the synchrotron radiation, and the Mössbauer spectrum. Although the oxide components in the raw ceramics at Izumiyama (Arita) and Ohkawachi (Imari) were not so large difference [20], we found from X-ray diffraction that the Izumiyama ceramics are mainly quartz, while the Ohkawachi one are mainly the feldspar of (K,Na) Si_3O_8 (sanidine). The XAS near the Fe-K edge results also showed that there is the slight difference of the EXAFS spectra between the Izumiyama and Ohkawachi ceramics. As regarding the Fe-XAS of the red-colored overglaze of the Kakiemon-style porcelain and the marketed powders of FeO, this suggested that the α-Fe_2O_3 particles are structurally affected by the surrounding other oxides of the raw ceramics. All of the present celadon glazes show the similar Fe-K XAS to that of the Izumiyama ceramics. The spectrum similarity suggested that the celadon glazes include the Fe_2O_3 fine powders, since the melting temperature of Fe_2O_3 is about 1570 °C, while FeO is about 1370 °C. In 1630's to 1790's, the used kiln temperature was about 1200-1250 °C. After refining the EXAFS spectra, it was found that the celadon glazes include the Fe_2O_3 fine powders, but not FeO, even in the glassy state. The pre-edge XANES peaks also suggested that the valence electrons of Fe ions in the celadon glaze is 3+, but not 2+ [22]. The Mössbauer spectrum suggested that the celadon glaze of Seiji (m) includes only Fe^{3+} ions, but not Fe^{2+} ions. This indicates the existence of Fe_2O_3 in the celadon glaze. Thus, the present investigations are not consistent with that reported [15, 16]. They suspected that the celadon glaze was colored by the chemical reaction from Fe_2O_3 to FeO under the deoxidizing thermal treatment at higher temperature in a kiln. We considered that the colored brightness of the Hizen celadons depends on the structural properties of the used raw celadon ceramics and the other transition-metal ions of Cr, Cu, Zn in the celadon glazes [20]. However, in the present investigations, we could not determine what kinds of the oxides of Cr, Cu, Zn exist in the celadon glaze, because of their very small amounts and the renting condition of the nondestructive methods for studying the structural and electronic properties of the Hizen celadons from the public museum.

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