

- 1995, 36, 7011.
- Lissel, M.; Drechsler, K. *Synthesis* **1983**, 314.
 - Labrouillere, M.; Leroux, C.; Gaspare-Illoughmane, H.; Dubac, J. *Synlett* **1994**, 723.
 - Snyder, D. C. *J. Org. Chem.* **1995**, 60, 2638.
 - Lee, J. G.; Kang, K. K. *J. Org. Chem.* **1988**, 53, 3634.
 - The reaction of benzyl alcohol is representative. A well-dried 100 ml two-necked flask equipped with a reflux condenser and oil bubbler was placed 0.02 mole of chlorotrimethylsilane and 0.01 mole of tellurium dioxide in 15 mL of methylene chloride. After several minutes stirring at room temperature, the mixture changed into a homogeneous pale yellow solution. And 0.01 mole of benzyl alcohol diluted in 5 mL methylene chloride was slowly added dropwise to the above mixture, and the resulting reaction mixture was stirred for 1 hour at room temperature. TLC observation (eluent: methylene chloride/carbon tetrachloride) and NMR spectrum of the crude reaction mixture showed complete conversion to benzyl chloride. The reaction mixture was filtrated through a silica gel (70-230 mesh) column and the solvent was removed using a rotary evaporator. The product was identical in all respects with the authentic benzyl chloride.
 - Khodadad, P. *Bull. Soc. Chim. France* **1965**, 468.
 - Bailar, J. C.; Emeleus, H. J.; Nyholm, S. R.; Trotman-Dickenson, A. F. In *Comprehensive Inorganic Chemistry*, Pergamon Press: Oxford, **1973**; Vol. 2, p 958.
 - Paquette, L. A. In *Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons: New York, **1995**; Vol. 7, p 4712.

XANES Study on the Structural Conformation of Fe Ions

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The XANES (X-ray absorption near-edge structure) gives information on the coordination geometry as well as that of the electronic configuration around the Fermi level of absorbing atoms. Several research groups have reported that the XANES spectra show various features according to the coordination number by study on the XANES spectra of Fe ions existing in various complexes.¹⁻⁴ Though the iron ions exist at various sites with nearly the same local symmetry and in the same valence state, they exhibit significantly different XANES features.

Insofar as both structural and electronic changes are intimately correlated, the origin of the strong XANES modification at the iron K-edge is not obvious. Therefore, to understand the nature of the modifications, we have studied XANES of the Fe ions located at various sites. We present various Fe K-edge XANES features for spinel, perovskite, and K₂NiF₄ type compounds, and try to explain the various XANES features by using multiple scattering.

The crystallographic structures of ZnFe₂O₄ and GeFe₂O₄ are assigned to cubic spinel type structure with the space group of *Fd3m* identified by analysis of XRD patterns. For the spinel structure, the cubic close packed oxygen ions form two different sites such as tetrahedra and octahedra which can be filled by the metal ions.⁵ It is confirmed by the Mössbauer spectroscopic analyses that the valence states of Fe ions in ZnFe₂O₄ and GeFe₂O₄ are 3+ and 2+, respectively, and all of the Fe ions exist in octahedral site.

The LaFeO₃ and LaSrFeO₄ compounds are identified as perovskite and K₂NiF₄ type structures, respectively. The oxidation state of Fe ions for the LaFeO₃ and LaSrFeO₄ is trivalent and the ions are octahedrally coordinated with six ox-

ygens. The representative K₂NiF₄-type compound shows tetragonal system with the *I4/mmm* space group which is composed of rock salt and perovskite layers alternately.^{6,7} The D_{4h} distortion of FeO₆ octahedra takes place due to the relatively weak interplanar interaction along the crystallographic *c* axis between the magnetic ions in K₂NiF₄-type LaSrFeO₄ compounds. Lattice parameters of the LaSrFeO₄ compound are *a*=3.851(2) and *c*=12.65(4) Å and thus the tetragonality (*c/a*) is 3.29. Ca₂Fe₂O₅ is a brownmillerite type structure and its space group is *Pcmm*. Mössbauer spectrum of Ca₂Fe₂O₅ shows that the unit cell consists of alternating sheets of octahedra (FeO₆) and tetrahedra (FeO₄) in the crystallographic *b* direction.⁸ The crystallographic data for the samples in this study are summarized in Table 1.

The Fe K-edge XANES spectra of the compounds have been recorded at the BL-6B of Photon Factory, National Laboratory for the High Energy Physics (KEK-PF) in Japan. Synchrotron radiation from the storage ring has been monochromatized with a Si(1 1 1) channel-cut monochromator. The spectra were calibrated with respect to the first inflection point of a Fe-foil. The data were monitored with a step size of < 0.3 eV in the XANES region.

Figure 1 shows the normalized Fe K-edge XANES spectra for ZnFe₂O₄, GeFe₂O₄, LaFeO₃, LaSrFeO₄, and Ca₂Fe₂O₅. The pre-edge peak denoted as P around 7110 eV is assigned to the formally dipole-forbidden 1s → 3d transition.⁹⁻¹² Since the peak gains its intensity from the quadrupole allowed transition in the octahedral symmetry, the observed pre-edge intensity for the compounds except Ca₂Fe₂O₅ is very weak. However, the pre-edge peak of Ca₂Fe₂O₅ with tetrahedrally coordinated iron ions gains strong intensity due to mix-

Table 1. Crystallographic data for the iron oxide samples prepared in this study

compounds	crystal system (space group)	lattice parameters (Å)	Fe-O bond length (Å) ^a	oxidation state of Fe ions
GeFe ₂ O ₄	cubic (Fd3m)	a=8.356(6)	2.031 (2.117 ^b)	Fe ²⁺ (HS)
ZnFe ₂ O ₄	cubic (Fd3m)	a=8.376(9)	2.063 (2.008 ^b)	Fe ³⁺ (HS)
LaFeO ₃	orthorhombic (Pbnm)	a=5.588(0), b=5.587(7), c=7.892(9)	1.974 ^c	Fe ³⁺ (HS)
LaSrFeO ₄	tetragonal (I4/mmm)	a=3.851(2), c=12.65 (4)	1.925 (in plane) 2.109 (axial)	Fe ³⁺ (HS)
Ca ₂ Fe ₂ O ₅	orthorhombic (Pcmm)	a=5.431(8), b=14.76(3), c=5.606(1)	1.963-1.977 (Oh) 1.884-1.858 (Td)	Fe ³⁺ (HS)

^aThe Fe-O bond lengths are calculated from the lattice parameter. ^bThe Fe-O bond lengths are resulted from the EXAFS analysis for the compounds GeFe₂O₄ and ZnFe₂O₄. ^cThe Fe-O bond lengths in LaFeO₃ is calculated from averaging of $a/2\sqrt{2}$, $b/2\sqrt{2}$, and $c/4$.

ing of p- and d-orbitals in tetrahedra symmetry.

The shoulder near A-position in Fe K-edge XANES spectrum of GeFe₂O₄ is very weak and those of compounds ZnFe₂O₄, LaFeO₃, and LaSrFeO₄ do not appear. However, the A-position shoulder is strong in the spectrum of brownmillerite type Ca₂Fe₂O₅ compound which consists of alternating sheets of FeO₆ and FeO₄. The shoulder is assigned to a 1s → 4p transition with a simultaneous ligand-to-metal charge transfer (LMCT) shakedown process.^{13,14}

We proceed to discuss on the evolution of bands at the top of the absorption edge. The strong resonance B in Figure 1 are attributed to transitions from 1s core level to continuum p states for the Fe ions.¹² The observed variation of the XANES can be investigated by considering the effect of small structural variations. The resonance B on Fe K-edge in the perovskite type LaFeO₃ and the K₂NiF₄ type LaSrFeO₄ is a singlet while the transition peak in the spinel type compounds is split into two. In general, the XANES features depend on the coordination geometry¹² or on the spin states of absorption atoms.^{3,4,15} The local structure around Fe ions can be approximated to octahedra and the Fe ions are high spin states in ZnFe₂O₄, GeFe₂O₄, LaFeO₃, and LaSrFeO₄.

Although the Fe ions in ZnFe₂O₄ and GeFe₂O₄ are different in oxidation states, they are similar in the XANES feature. The peaks of B position for Fe³⁺ ions in ZnFe₂O₄ are shifted by 2.1 ± 0.05 eV to higher energy relative to those for Fe²⁺ in GeFe₂O₄. Bianconi *et al.* have reported that the shift of edge peak from Fe^{II} to Fe^{III} with low spin states is 1 ± 0.2 eV for the Fe K-edge XANES spectra of [Fe(CN)₆]⁴⁻ and [Fe(CN)₆]³⁻ complexes.¹⁶ The shift by 1 ± 0.2 eV is associated with a different binding energy of the 1s core initial state between Fe^{II} and Fe^{III} ions since the Fe-C bond distance are the same in both the Fe^{II} and Fe^{III} complexes. The muffin-tin radii of the ground and excited states are known as 1.152 and 1.152 for low spin state Fe ion and 1.230 and 1.262(Å) for high spin state ones, respectively, which are calculated using the Norman criterium.⁴ If we assume that all the shift of the absorption edge is due to shift of the multiple scattering resonances, the shift of the absorption edge for high spin Fe ion can be affected by the final continuum state due to different muffin-tin radii between ground and excite states as well as the 1s core initial state for the high spin state Fe ions. From the EXAFS analysis of Fe K-edge, the bond distances of Fe-O are 2.117 and 2.008 for GeFe₂O₄ and ZnFe₂O₄, respectively. The shift of peaks B by 2.1 ± 0.05 eV can be due to the elongation Fe-O bond distance in the

Fe³⁺ by 0.109 Å as well as a different binding energy of the 1s core initial state for the spinel type GeFe₂O₄ and ZnFe₂O₄.

The Fe ions coordinate octahedrally with six oxygen ions and the FeO₆ share corners with tetrahedra ZnO₄/GeO₄ in the spinel ZnFe₂O₄ and GeFe₂O₄.¹⁷ In spinel oxides, the separation between the octahedral sites is rather short: $d_{\text{Fe-Fe}} \sim 2.98$ and 2.97 Å resulted from EXAFS analysis of the ZnFe₂O₄ and GeFe₂O₄, respectively. The character of spinels is modulated by the magnitude of Fe_B-Fe_B separation and the valence state of Fe ions on the octahedral site. Two peaks at the top of the absorption edge clearly correspond to the multiple scattering in spinel type structure which consists of the first coordination shell of Fe-O and the second coordination shell of Fe_B-Fe_B with short distance.

In the perovskite type LaFeO₃, the Fe ions are octahedr-

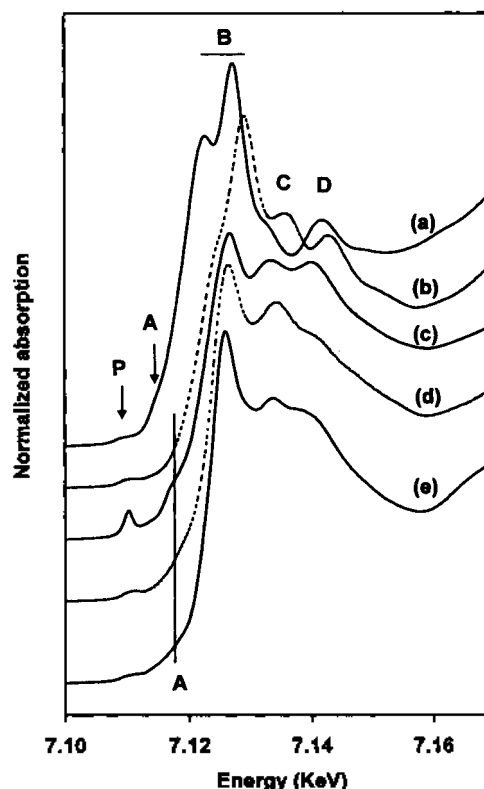


Figure 1. Normalized iron K-edge XANES spectra of (a) GeFe₂O₄, (b) ZnFe₂O₄, (c) Ca₂Fe₂O₅, (d) LaSrFeO₄, and (e) LaFeO₃.

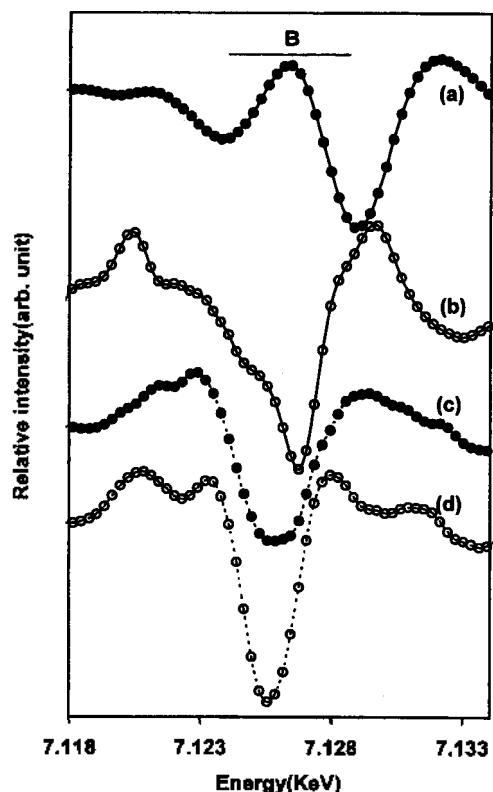


Figure 2. Second derivative of the iron K-edge XANES spectra of (a) ZnFe_2O_4 , (b) $\text{Ca}_2\text{Fe}_2\text{O}_5$, (c) LaSrFeO_4 , and (d) LaFeO_3 .

ally coordinated by six oxygens forming regular octahedra FeO_6 which share corners with the nearest octahedra.⁷ When the FeO_6 in LaFeO_3 forms nearly regular octahedral symmetry, a single and strong $1s \rightarrow 4p \sigma^*$ absorption peak B is observed in XANES region of LaFeO_3 .

In the K_2NiF_4 type LaSrFeO_4 , interplanar interactions are relatively weak and thus FeO_6 are elongated along the crystallographic c axis to form two dimensional structure with the D_{4h} distortion of FeO_6 octahedra.⁶ Actually, the length of axial Fe-O bond is longer about 1.10 times than that of in-plane Fe-O bond in LaSrFeO_4 . The E_0 given by multiple scattering along the axial Fe-O bond shifts to lower energy range than that of in-plane Fe-O bond due to the longer bond length of the axial Fe-O. The second-derivative spectra allow us to confirm that the dipole allowed $1s \rightarrow 4p$ transition of the Fe^{3+} ion in LaSrFeO_4 exhibits broad one by overlapping of two absorption edge which correspond to the multiple scatterings of the axial Fe-O bond and the in plane Fe-O bond as shown in Figure 2.

The second-derivative XANES spectra in Figure 2 show that the absorption edge of the compound $\text{Ca}_2\text{Fe}_2\text{O}_5$ splits into two peak. As for the compound $\text{Ca}_2\text{Fe}_2\text{O}_5$ containing alternating layers of octahedral and tetrahedral Fe^{3+} ions, the Fe-O bond lengths are 1.963-1.977 Å and 1.884-1.858 Å in FeO_6 and FeO_4 , respectively. The E_0 given by the multiple scattering of FeO_6 shifts to higher energy range since the bond Fe-O in FeO_6 is longer than that of FeO_4 . Therefore, the compound $\text{Ca}_2\text{Fe}_2\text{O}_5$ with Fe ions in tetrahedral site and octahedral site shows broad peak in the top of the absorption edge due to overlapping of two absorption resonances.

Finally, the B strong resonance in Figure 1 are attributed to transitions from $1s$ core level to continuum p states for the high spin Fe^{3+} ions. We can assume that the binding energy of $1s$ core electron may be same in the high spin Fe^{3+} ion since the outer $3d$ electron density can not shield the $1s$ electron. Since the muffin-tin radius of excited state is different from that of ground state for high spin state Fe ions, the continuum p states are affected by the bond length when the photo-electron is multiple scattered. If all the shift of the absorption edge is due to shift of the multiple scattering, the shift of the B resonance are associated with both of a different binding energy of the $1s$ core initial state and different distances between the absorbing atom and back-scattering atoms. When the absorbing atoms are surrounded by back-scattering atoms with different bond length due to distortion of local structures around Fe ions, the white line of Fe K-edge XANES is broadened by overlapping of peaks which are induced by shifting the multiple scattering resonances.

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References

- Bianconi, A.; Congiu-Castellano, A.; Durham P. J.; Hasnain, S. S.; Phillips, S. *Nature* **1985**, *318*, 685-687.
- Roe, A. L.; Schneider, D. J.; Mayer, R. J.; Pyrz, J. W.; Widom, J.; Que, L., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 1676-1681.
- Shiro, Y.; Sato, F.; Suzuki, T.; Iizuka, T.; Matsushita, T.; Oyanagi, H. *J. Am. Chem. Soc.* **1990**, *112*, 2921-2924.
- Briois, V.; Cartier dit Moulin, C.; Sainctavit, P.; Brouder, C.; Flank, A.-M. *J. Am. Chem. Soc.* **1995**, *117*, 1019-1026.
- Weller, M. T. *Inorganic Materials Chemistry*; Oxford University Press: Oxford, New York, Tokyo, 1994; pp 44-48.
- Kim, M. G.; Ryu, K. H.; Yo, C. H. *J. Solid State Chem.* **1996**, *123*, 161-167.
- Omata, T.; Ueda, K.; Hosono, H.; Miyazaki, T.; Hasegawa S.; Ueda, N.; Kawazoe, H. *Phys. Rev. B* **1994**, *49*, 10200-10205
- Yo, C. H.; Jung, I. Y.; Ryu, K. H.; Ryu, K. S.; Choy, J. H. *J. Solid State Chem.* **1995**, *114*, 265-270.
- Choy, J. H.; Yoon, J. B.; Kim, D. K.; Hwang, S. H. *Inorg. Chem.* **1995**, *34*, 6524-6531.
- True, A. E.; Scarrow, R. C.; Randall C. R.; Holz, R. C.; Que, L., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 4246-4255.
- Kato, M.; Yamada, Y.; Inagaki, T.; Mori, W.; Sakai, K.; Tsubomura, T.; Sato, M.; Yano, S. *Inorg. Chem.* **1995**, *34*, 2645-2651.
- Kim, S.; Tryk, D. A.; Antonio, M. R.; Carr, R.; Scherson, D. *J. Phys. Chem.* **1994**, *98*, 10269-10276.
- Cartier, C.; Momenteau, M.; Dartyge, E.; Fontaine, A.; Tourillon, G.; Michalowicz, A.; Verdagner, M. *J. Chem. Soc., Dalton Trans.* **1992**, 609-618.
- Shadle, S. E.; Penner-Hahn, J. E.; Schugar, H. J.; Hed-

- man, B.; Hodgson, K. O.; Solomon E. I. *J. Am. Chem. Soc.* 1993, 115, 767-776.
15. Roux, C.; Adams, D. M.; Iti, J. P.; Polian, A.; Hendrickson, D. N.; Verdager, M.; *Inorg. Chem.* 1996, 35, 2846-2852.
16. Bianconi, A.; Dell'Ariceia, M.; Durham P. J.; Pendry, J.

B. Phys. Rev. B 1982, 26, 6502-6508.

17. Gleitzer, C.; Goodenough, J. B. *Structure and Bonding* 61; Clarke, M. J., Goodenough, J. B., Jørgensen, C. K., Neilands, J. B., Reinen, D., Weiss, R., Eds.; Springer-Verlag: Berlin, Heidelberg, New York, 1985; pp 11-12.

Synthesis and Cation Binding Properties of Triester Calix[4]arenes and Calix[4]quinones

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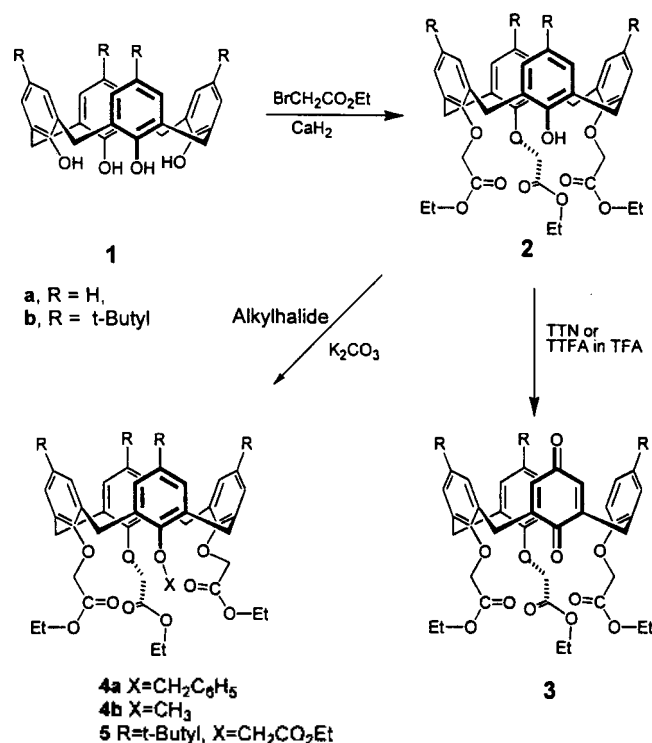
Calixarenes¹ have received much attention recently as a interesting class of cyclophanes possessing ionic and molecular binding properties.² Their potential as enzyme mimics has been suggested and appropriate functionalization of the phenolic units could extend this comparison to redox-switching enzyme.³

Calixarene esters have shown the remarkable ionophoric properties⁴ toward the alkali metals. For example, the tetramer ester display selectivity for the sodium ion, on the other hand the hexamer ester display selectivity for the potassium, rubidium and cesium over sodium ion⁵ and Beer *et al.*⁶ reported the cation binding properties of diester calix[4]quinone. This stimulated us to design a new ester group containing calixquinone. In pursuit of redox switchable receptors we prepared a series of triester calix[4]arene and their corresponding quinone and investigated their cation binding properties.

Triester calix[4]arenes and their corresponding quinones were prepared by the selective trialkylation followed by the oxidation of free phenolic unit (Scheme). Trialkylation was carried out with ethyl bromoacetate in the presence of CaH₂ in DMF according to the reported procedure.⁷ The oxidation of **2a** with thallium(III) nitrate (TTN)⁸ produced the new triester calix[4]quinone **3a** as a pale yellow powder in 34% yields. On the other hand, the oxidation of **2b** was succeeded only with Ti(OCOCF₃)₃ in trifluoroacetic acid solution,⁹ which produced **3b** in 40% yields. For comparison of cation binding properties among the triester calix[4]arenes, their alkyl derivatives **4a** and **4b** were prepared by the reaction of **2** with the corresponding alkyl halides in the presence of K₂CO₃. The methyl derivative **4b** was prepared by the reaction of **2b** and methyl iodide in the presence of NaH because benzylation reaction between **2b** and benzyl bromide in the presence of K₂CO₃ failed probably due to the steric factor of **2b**.

The ¹H NMR spectra of triester calix[4]quinone **3a** showed three doublets at 7.13, 6.81, and 6.20 ppm and two triplets at 6.96 and 6.48 for the nine aromatic protons and a singlet at 6.82 for the two quinone protons. The bridge me-

thylene protons appear as two pair of doublets between 3.2 to 4.6 ppm region and a complicated multiplet at around 4.2 ppm region represents the -OCH₂CO₂- and -OCH₂- protons. The ¹³C NMR spectra **3a** showed two peaks at 32.41 and 31.06 ppm for the bridge methylene carbons, indicating that **3a** exists as a cone conformation.^{10,11} The stepwise addition of a solid NaClO₄ to CD₃CN solution of **3a** resulted in large significant downfield shifts¹⁰ of the ligand protons corresponding to the complexed species as shown in Figure 1. Most notable down field shifts were observed for a doublet at 6.20 ppm and a triplet at 6.48 ppm which represent six aromatic



Scheme