XAFS Analysis of Ceria Based Electrolytes Doped with Lanthanide Oxides

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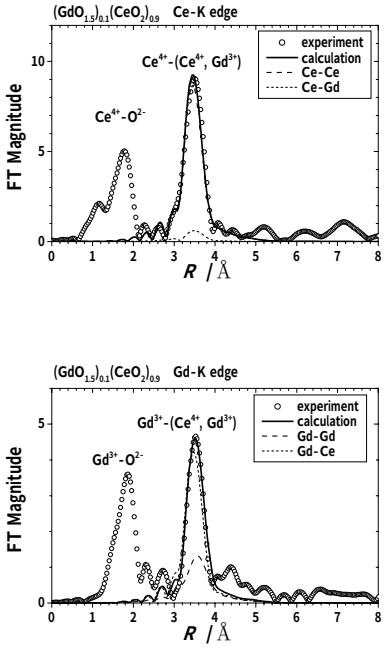
Ceria based compounds doped with lanthanide oxides as dopants are one of the most promising materials for electrolytes of solid oxide fuel cell because of their high ionic conductivity. Although several groups have reported XAFS analysis to investigate the influence of local structure on ionic conductivity, their XAFS analysis are limited to the nearest neighbor around cation (cation-O^{2-} path). Here, we report the XAFS analysis of the second nearest neighbor (cation-cation path) for doped ceria compounds.

The second nearest neighbor around Ce^{4+} in $(GdO_{1.5})_x(CeO_2)_{1-x}$, for example, consists of Ce^{4+} and Gd^{3+}. Similarly that around Gd^{3+} consists of Gd^{3+} and Ce^{4+}. The interatomic distance and Debye-Waller factor of Ce^{4+}-Gd^{3+} path and Gd^{3+}-Ce^{4+} path should have the same value. Therefore, we performed parameter fitting of Ce edge data and Gd edge data simultaneously using the correlations, $R(Ce^{4+}\text{-}Gd^{3+})=R(Gd^{3+}\text{-}Ce^{4+})$ and $\sigma^2(Ce^{4+}\text{-}Gd^{3+})=\sigma^2(Gd^{3+}\text{-}Ce^{4+})$. Figure shows the fitting result of $(GdO_{1.5})_{0.1}(CeO_2)_{0.9}$, which shows good agreement with experimental data. We applied this analysis method to various ceria compounds. The results indicate that the ionic conductivity is influenced by the distortion of the cation network.



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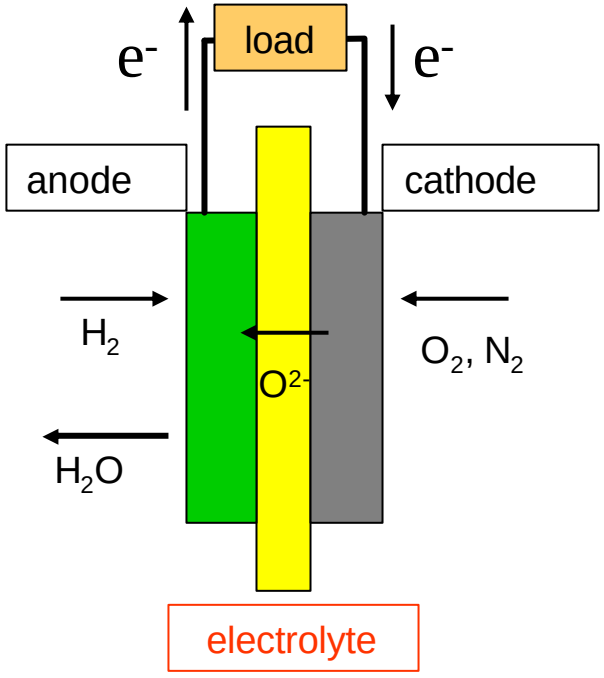
Background

Ceria doped with lanthanide oxides are expected as an electrolyte material for solid state oxide fuel cell because of their high ionic conductivity.

XAFS studies have been reported to understand the relationship between ionic conductivity and structure.

However, their analysis is limited to cation-O^{2-} path (nearest neighbor around cation) .



In this study, we have tried the XAFS analysis of cation-cation path.

Fourier transforms

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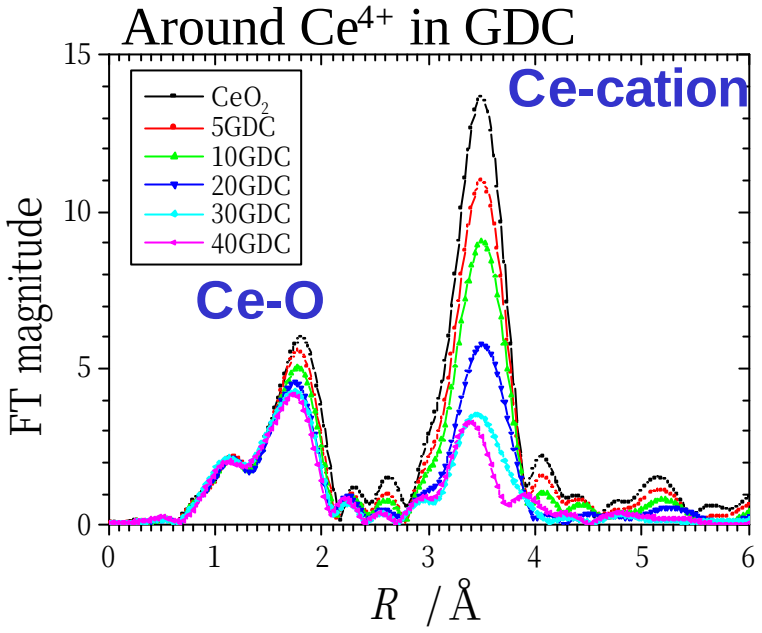

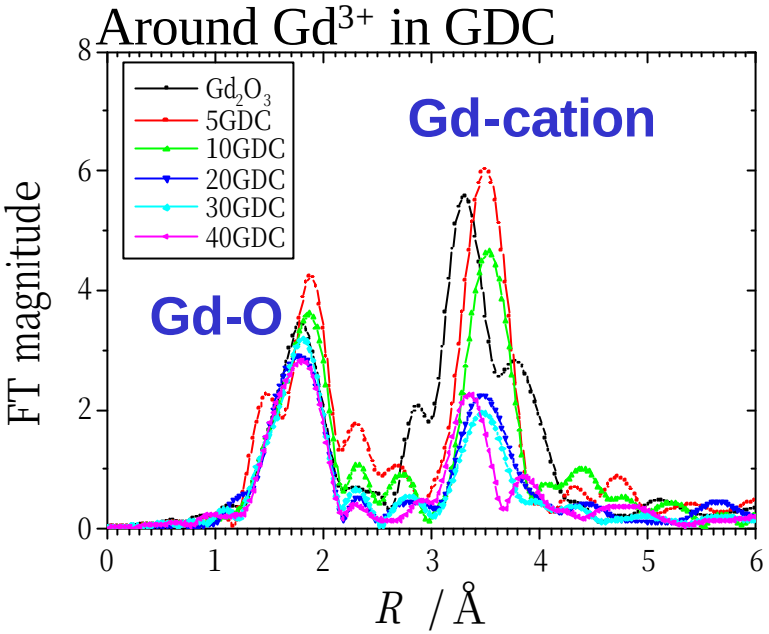

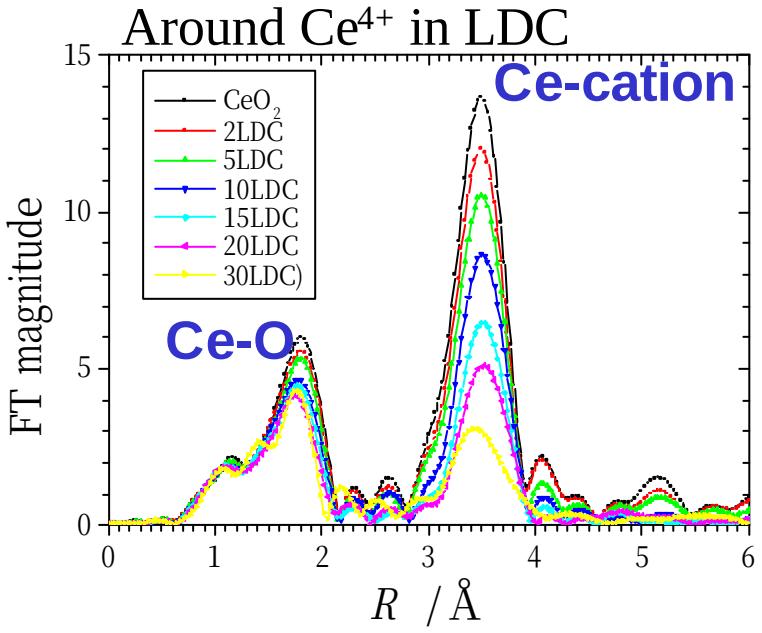

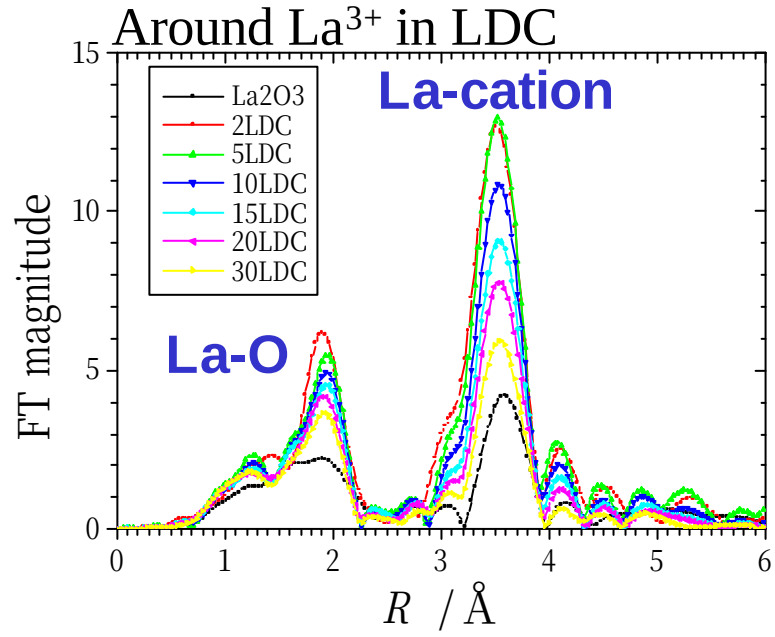

Crystal structure of ceria based electrolyte

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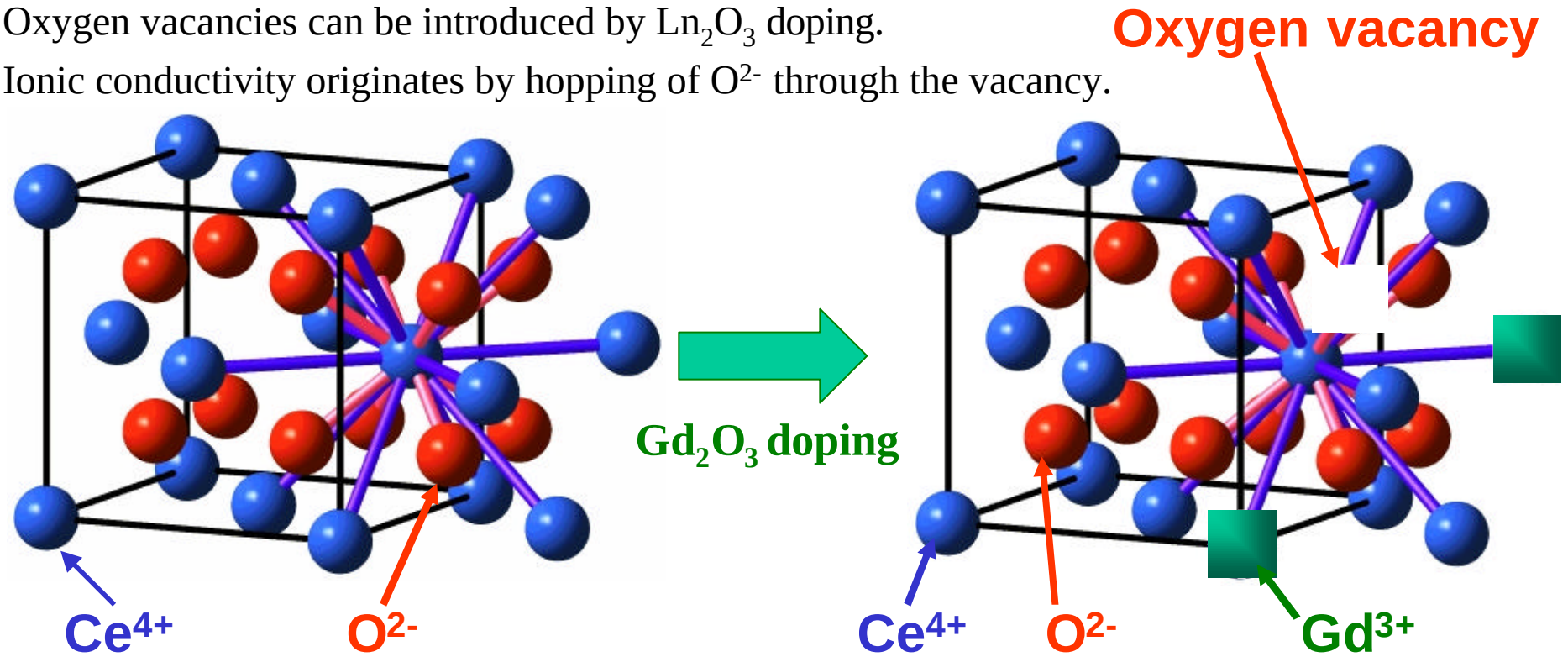
> Oxygen vacancies can be introduced by Ln_2O_3 doping.

> Ionic conductivity originates by hopping of O^{2-} through the vacancy.



	CeO_2	Gadolinia Doped Ceria	
	around Ce	around Ce	around Gd
nearest neighbor	Ce-O (number of path : 8)	Ce-O (number of path : < 8)	Gd-O (number of path : < 8)
second nearest neighbor	Ce-Ce (number of path : 12)	Ce-Ce, Ce-Gd (number of path : 12)	Gd-Gd, Gd-Ce (number of path : 12)

Analysis method

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Ln denotes the dopant cation.

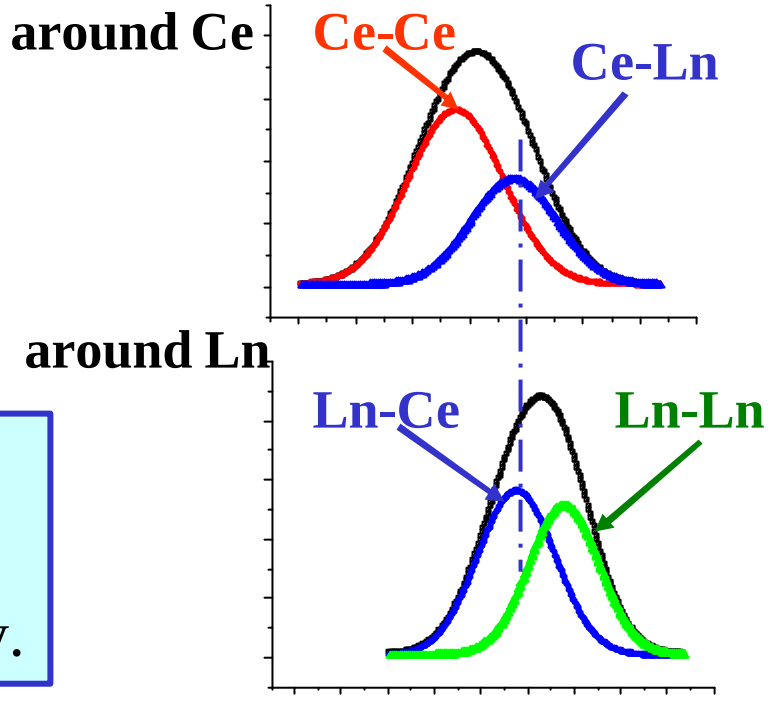
> Using correlation

R(Ce-Ln) = R(Ln-Ce)

σ(Ce-Ln) = σ(Ln-Ce)

> Multiple Data Set Fit

Ce edge data and Ln edge data of the same sample are fitted simultaneously.



Other assumption

Unknown edge energy shifts of Ce-Ln and Ln-Ce were fixed to those of Ce-Ce and Ln-Ln, respectively.

Coordinaton number was fixed to the theoretical value when dopant cations were randomly distributed.

Fitting software feffit

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Samples and Experiments

Samples

$(GdO_{1.5})_x(CeO_2)_{1-x}$	x=0.05, 0.10, 0.20, 0.30, 0.40	→ xGDC
$(YO_{1.5})_x(CeO_2)_{1-x}$	x=0.05, 0.10, 0.15, 0.20, 0.30	→ xYDC
$(LaO_{1.5})_x(CeO_2)_{1-x}$	x= 0.02, 0.05, 0.10, 0.15, 0.20, 0.30	→ xLDC
references	CeO_2, Gd_2O_3, Y_2O_3, La_2O_3	

Experiments

Edges : Ce-K(40.4 keV), Gd-K(50.2 keV), Y-K(17.1 keV), La-K(38.9 keV)

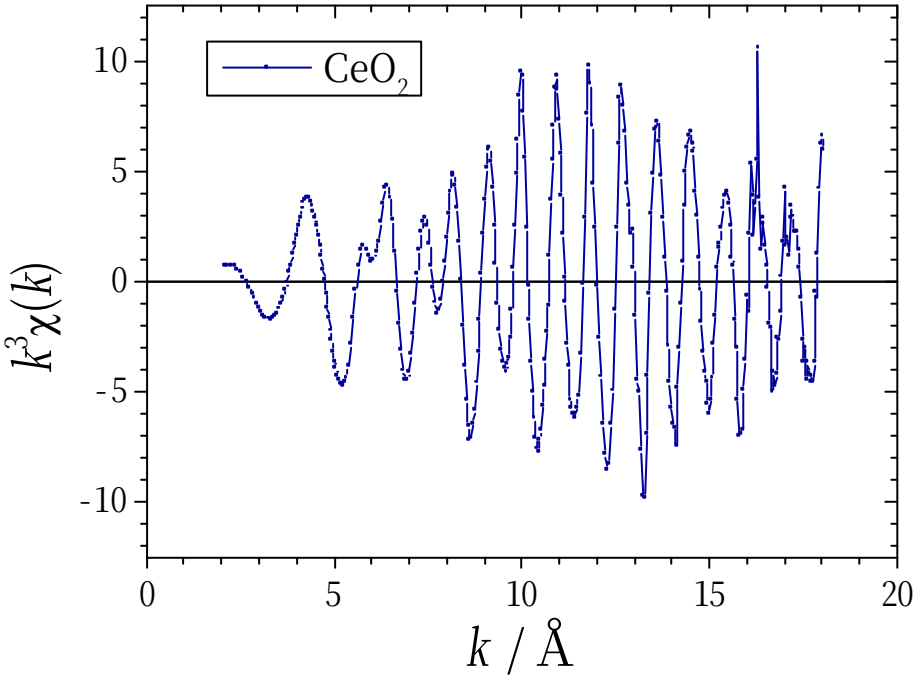
Beamline : SPring-8 BL16B2

Measurements

All samples by transmission mode in air at room temperature.

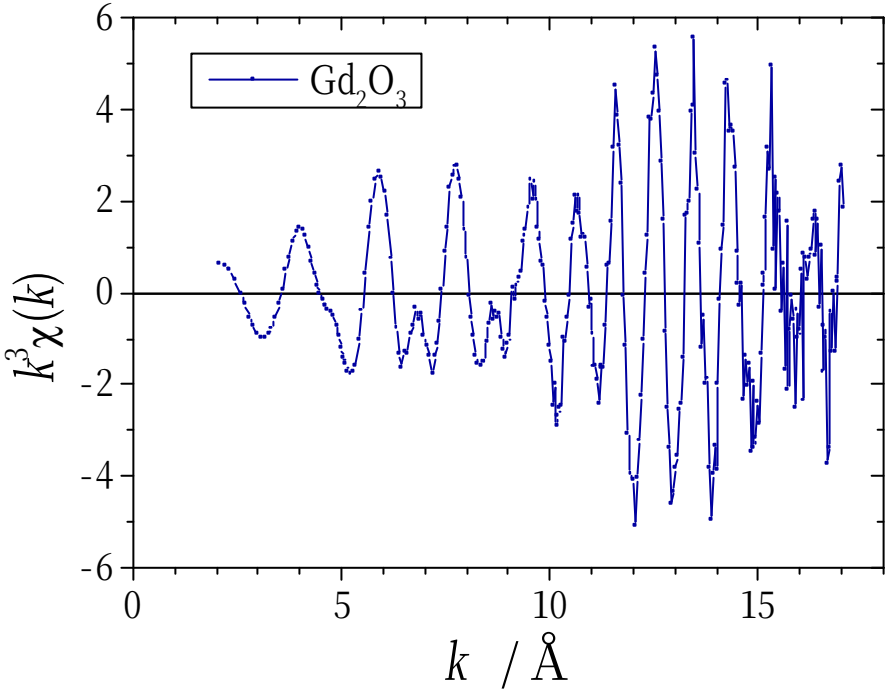
Examples of $\chi(k)$

Ce-K edge : 40.4 keV



CeO_2

Gd-K edge : 50.2 keV

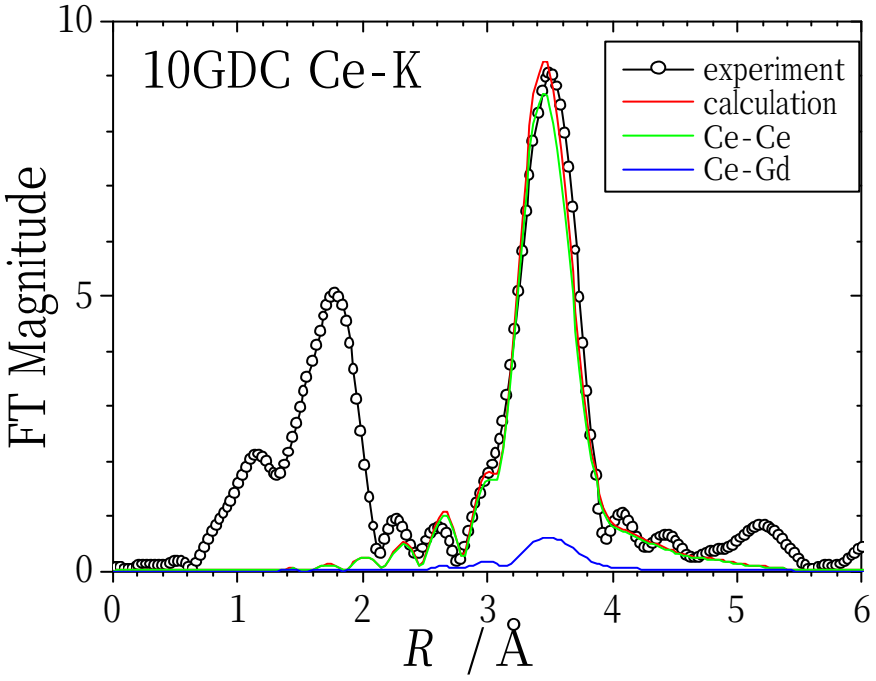


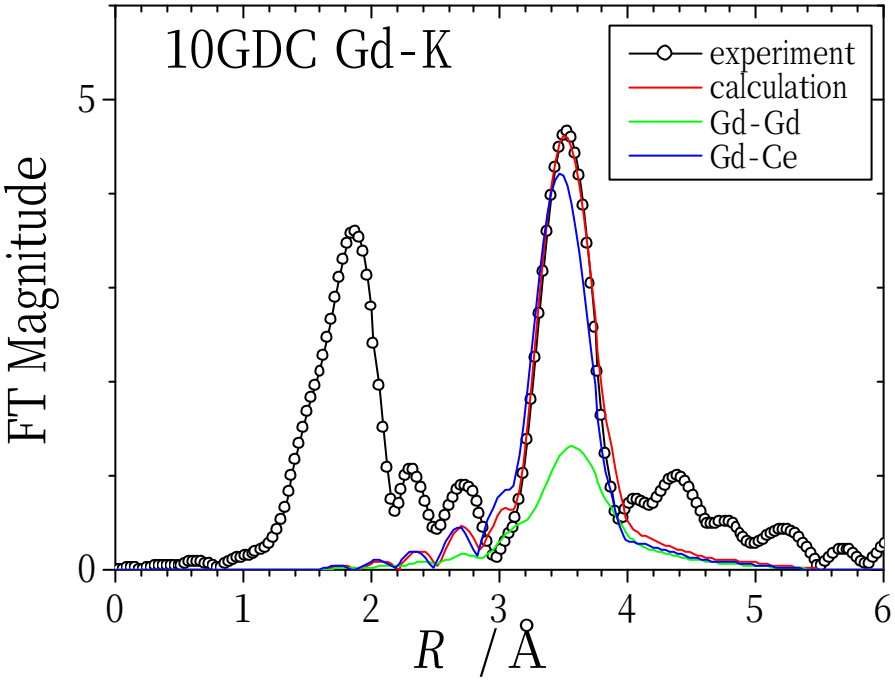
Gd_2O_3

Comparison between experiment and fit

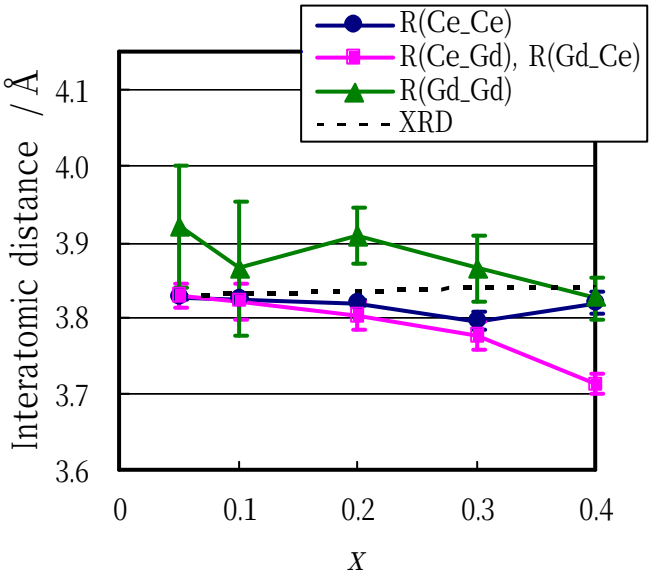
Sample : 10GDC

R factor : 2.76 %

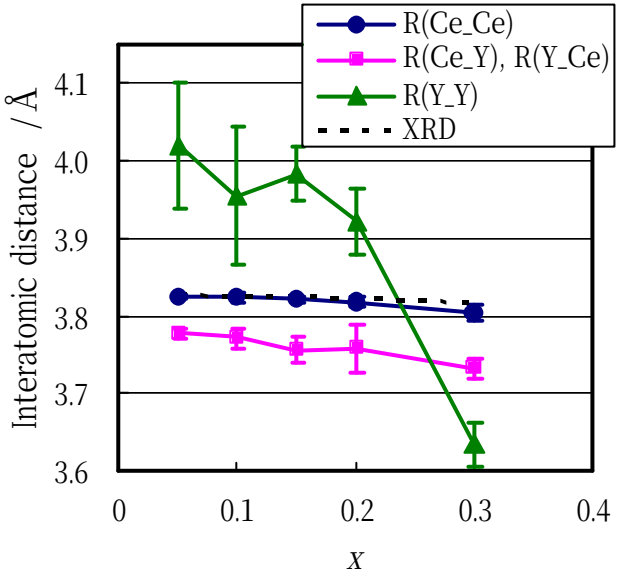




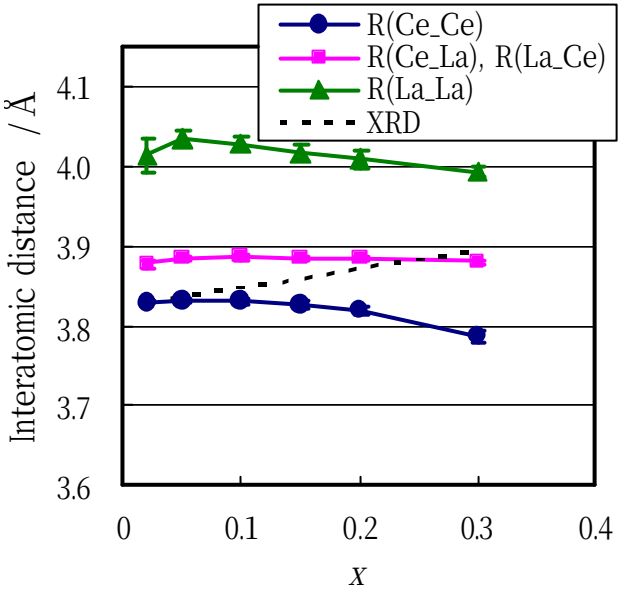
Results : Interatomic distance of cation-cation path



GDC



YDC



LDC

x in $(LnO_{1.5})_x(CeO_2)_{1-x}$

Discussion

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Ln^{3+}-Ln^{3+} path has the longest interatomic distance in every sample.

Especially, though Y^{3+} is smaller than Ce^{4+} in YDC, Y^{3+}-Y^{3+} path length is the longest.

In GDC, Gd^{3+}-Gd^{3+} distance is close to the other paths.

Ce^{4+}-Ln^{3+} distance follows the ionic radius of Ln^{3+}.

In GDC, Ce^{4+}-Gd^{3+} distance is almost the same as Ce^{4+}-Ce^{4+} distance.

↓

Distortion of the cation network is the minimum in GDC.

↓

GDC has the highest ionic conductivity among samples measured in this study.

The conductivity gives the high value with a dopant which brings the small cation network distortion.

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Summary

EXAFS analysis of cation-cation path, the second nearest neighbor, was carried out.

Distortion of the cation network depends on the kind of the dopant.

GDC, which has the highest ionic conductivity among materials measured in this study, has the minimun cation network distortion.

This suggests that the conductivity gives the high value with a dopant which brings the small cation network distortion.

Further analysis is in progress.