

XAFS study of copper species stabilized in the interlayer space of layered perovskite oxides

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New intercalation compounds with Cu²⁺ ions in the interlayer of layered perovskite oxides, OA_{1-x}Ca_{2-x}La_xNb₃O₁₀ (OA = *n*-octylammonium ion, 0 ≤ *x* < 1), have been prepared by ion-exchange reaction, and characterized by means of XRD and XAS. For the detail elucidation of the fine structure of the Cu K-edge XANES spectra, polarized XAS was applied for the [Cu(en)₂]²⁺ and Cu²⁺ ions intercalated to the single crystal. According to the XANES and EXAFS spectra measured at Cu K-edge, copper ions are four-coordinated. In addition, XANES spectra have shown that the charge transfer from host layer to intercalated ions influences on the chemical state of copper ion.

Keywords: layered oxide, layer charge, intercalation, polarized XANES, XAFS

1. Introduction

Layered compounds, so called low dimensional materials, have attracting feature in the part of geometrical structure and their physicochemical properties. Recently, several layered metal oxides have been demonstrated to be highly active photocatalysts under bandgap irradiation. (Miyoshi *et al.*, 1989; Ebina *et al.*, 1996) One of the layered oxides is Dion-Jacobson phase with the general formula of M[A_{*n*-1}B_{*n*}O_{3*n*+1}], of which KCa₂Nb₃O₁₀ is a typical *n* = 3 member. (Dion *et al.*, 1981; Jacobson *et al.*, 1985) Characteristics of these layered oxides is that the interlayer alkali metal cations can be exchanged in acid solution to give the protonated forms, H[A_{*n*-1}B_{*n*}O_{3*n*+1}], which readily intercalate alkylamines. These alkylamine intercalated derivatives with large layer expansions can afford to receive various metal ion species into interlayer space by means of ion-exchange reaction, giving opportunity to yield new metastable materials that cannot be obtained by conventional solid state reaction. In addition, the interlayer surface modification of layered compounds by means of intercalation or ion-exchange reaction would be a potential way of preparing a new two-dimensional compound, and the knowledge of its detailed geometric and electronic structures is a prerequisite for understanding its physical and chemical properties (Choy *et al.*, 1995; Choy *et al.*, 1997).

However, it is very difficult to apply diffraction methods for the intercalated or ion-exchanged layered materials in any forms of polycrystal or single crystal because of their low dimensionality and defects such as the elastic deformation of host layer or the imperfection of long-range ordering of guest species. Therefore, many studies have been performed under the assumption that their two-dimensional lattice and/or electronic structures may be unchanged by intercalation or ion-exchange reactions, but this can lead to incorrect interpretations of various physicochemical properties.

In this respect, we have attempted to prepare the ion-exchanged compounds of cupric ion species such as Cu²⁺ or [Cu(en)₂]²⁺ (en = ethylenediamine) ions inbetween the interlayer space of layered oxides with Dion-Jacobson phase, and investigated how their

electronic and geometric structures are influenced by the interaction with the oxide layers by means of x-ray absorption spectroscopy (XAS).

2. Experimental

2.1 Materials

Members of K_{1-x}La_xCa_{2-x}Nb₃O₁₀ (0 ≤ *x* ≤ 1.0) were prepared by reacting appropriate quantities of K₂CO₃, La₂O₃, CaCO₃ and Nb₂O₅ at 1150°C in air for 2 days with one grinding in between. Excess (25 mole %) K₂CO₃ was added to compensate for the loss due to volatilization. The potassium in K_{1-x}La_xCa_{2-x}Nb₃O₁₀ was exchanged with protons by refluxing the solids with continuous stirring in 6N HNO₃ at 60°C for 3 days. Octylamine intercalation compounds (OA_{1-x}La_xCa_{2-x}Nb₃O₁₀) were prepared by refluxing the protonated derivatives with a 15 % amine solution in *n*-heptane around 90°C for several days until the reaction was complete. Single crystal of CsCa₂Nb₃O₁₀ was prepared by the self-flux method with the mixture of stoichiometric CaSO₄, Nb₂O₅ and the 50 mol % excess Cs₂SO₄ at 1500°C. The protonated and amine intercalated derivatives of single crystal were prepared by the same procedure as the polycrystalline samples.

Ion-exchange phase was prepared by refluxing in the aqueous solution of the corresponding transition metal or complex ions with amine intercalated derivatives of polycrystalline and single crystal compounds at 90°C for several days until the reaction was complete.

2.2 Characterization of Materials

Solid phases were confirmed by x-ray powder diffraction (Mac Science MXP3V, Cu K α radiation). X-ray absorption spectra of Cu K-edge were measured at room temperature, using the EXAFS facilities including a Si(311) channel-cut monochromator installed at the beam line BL10B of Photon Factory in the National Laboratory for High Energy Physics (Tsukuba, Japan), operated at 3.0 GeV with ca. 400 mA of stored current. Polarized XANES spectra were recorded in a fluorescence mode by using Lytle detector with Ni filter, and other spectra were recorded in a transmission mode. Photon energies of all spectra were calibrated by the first absorption peak of copper foil which were measured before and after each measurement for the sample. The data analyses for experimental spectra were performed by the standard procedure as previously described. (Rehr *et al.*, 1991) The inherent background in the data was removed by fitting a polynomial to the pre-edge region and extrapolated through the entire spectrum, from which it was subtracted. The absorbance, $\mu(E)$, was normalized to an edge jump of unity. For EXAFS analysis using UWXAFS code, coordination number (C.N.), bond distance (*R*_{*i*}), Debye-Waller factor (σ^2), and threshold energy difference (ΔE_0) were optimized as variables in the course of nonlinear least-squares curve fitting between the experimental EXAFS spectrum and the theoretical one that was calculated by ab-initio FEFF5 code.

3. Results and discussion

3.1 Polarized XANES spectroscopy for single crystal

The intercalation of [Cu(en)₂]²⁺ or Cu²⁺ ions into the interlayer space of layered niobate in the form of single crystal was confirmed by the x-ray powder diffraction. The (00*l*) diffraction peaks give the basal spacing of *d* = 14.4 Å as the [Cu(en)₂]²⁺ ions are incorporated. The thickness of the intercalated layer estimated to be about 3.9 Å by subtracting 11.5 Å of the thickness of the niobate layer from the observed *d*-spacing, suggests that the copper complex

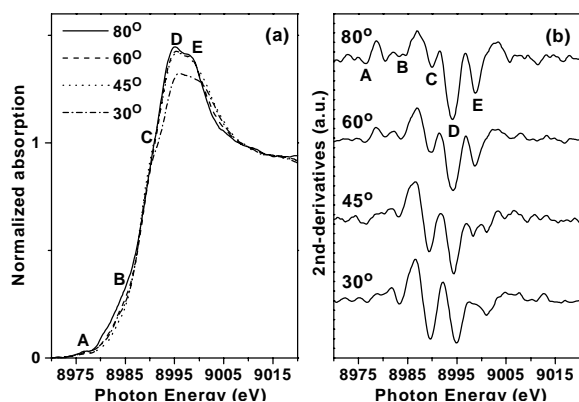


Figure 1

Normalized Cu K-edge XANES spectra (a) and their second-derivatives (b) measured for $[\text{Cu}(\text{en})_2]^{2+}$ ions intercalated to single crystal of $\text{OACa}_2\text{Nb}_3\text{O}_{10}$ (OA=*n*-octylammonium ion). Numeric values in figure are the angle between the incident x-ray beam and *ab*-plane of single crystal.

ions are intercalated as a monolayer. Unfortunately, single crystal structure was not solved, however, because the quality of single crystal made by self-flux method is not enough to apply the single crystal x-ray diffraction method. The plane polarized nature of synchrotron radiation permits the measurement of polarized x-ray absorption near-edge spectra (p-XANES) on the oriented single crystals. The spectral features in the p-XANES regions depend on the orientation of the x-ray beam relative to the molecular principal axes, and thus, can be assigned to molecular orbitals and structures along a particular direction. For the present polarized experiments, the crystallographic *ab*-plane of single crystal was oriented relative to the incident x-ray beam.

Fig. 1 shows the p-XANES spectra and their second derivatives for the single crystal to which $[\text{Cu}(\text{en})_2]^{2+}$ ions are incorporated. The first peak (A) around 8978.5 eV corresponds to the pre-edge due to $1s \rightarrow 3d$ transition, which is predominant in the absent condition of inversion symmetry. The variation of intensity dependency on the incident angles was not clearly observed, which might be due to the somewhat poor spectral quality. The angular dependency of two peaks (B, C) located at 8983 and 8990 eV is opposite to that of two peaks (D, E) located at 8994 and 8999 eV. This tendency indicates that the lower-energy peaks (B, C) and higher-energy ones (D, E) correspond to the transitions to $4p_\pi$ and $4p_\sigma$ orbitals, respectively. (Oyanagi *et al.*, 1990; Kosugi *et al.*, 1990) Based on the above angle dependency of p-XANES, it is concluded that the plane of $[\text{Cu}(\text{en})_2]^{2+}$ ion in the interlayer space is parallel to the niobate layer slab in good agreement with the orientation suggested by the powder XRD. This fact also implies that it is possible to predict the orientation of guest species in intercalation complex if we have p-XANES spectra for the single crystal incorporating guest molecule. And it is noted that the orientation effect must be carefully checked to acquire the some information from peak intensity in XANES spectra for layered materials.

Fig. 2 shows p-XANES spectra for the single crystal to which Cu^{2+} ions are intercalated, which exhibits the same angular dependency as the case of $[\text{Cu}(\text{en})_2]^{2+}$ ion in the interlayer space, except for the absence of B peak corresponding to the $1s \rightarrow 4p_\pi$ transition accompanying shakedown due to the simultaneous ligand-to-metal charge transfer (LMCT). The reason of the absence of B peak is thought to be due to the weak π -bond between Cu^{2+} ion and ligands as well as somewhat poor spectral quality due to the low concentration of intercalated copper species. Combined with the

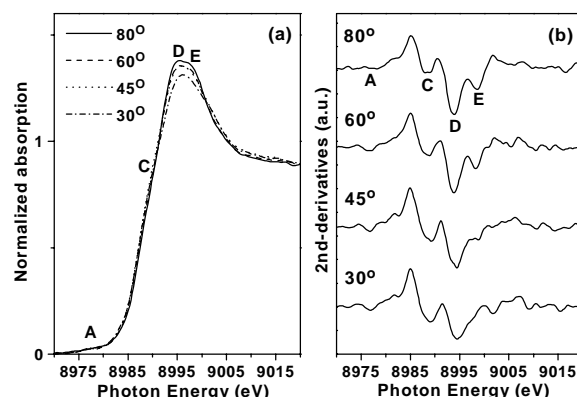


Figure 2

Normalized Cu K-edge XANES spectra (a) and their second-derivatives (b) measured for Cu^{2+} ions intercalated to single crystal of $\text{OACa}_2\text{Nb}_3\text{O}_{10}$ (OA=*n*-octylammonium ion). Numeric values in figure are the angle between the incident x-ray beam and *ab*-plane of single crystal.

thickness of the interlayer space estimated by XRD pattern, the present p-XANES results suggest that Cu^{2+} ions is coordinated with four water molecules, having square planar symmetry parallel to the niobate layer slab.

3.2 Bonding nature of intercalated cupric ion

In order to understand the interaction between the intercalated ion species and the host layer slab, Cu^{2+} ions were incorporated into the interlayer space of layered perovskite oxides with different layer charge density, $\text{OA}_{1-x}\text{La}_x\text{Ca}_{2-x}\text{Nb}_3\text{O}_{10}$ (OA = *n*-octylammonium ion). (Uma *et al.*, 1993) The intercalation of Cu^{2+} ions into the layered niobate was confirmed by the x-ray powder diffraction. Despite the variation of *c*-axis parameter, *a*- and *b*-axis ones were nearly invariant upon the ion exchange, indicating that the intralayer structure of the niobate slab was maintained through the ion-exchange reaction. The (00*l*) diffraction peaks for Cu^{2+} ions-intercalated derivatives give almost the same basal spacing of $d = 14.9 \text{ \AA}$, irrespective of the layer charge density of parent material. The thickness of the intercalated layer is estimated to be about 3.4 \AA by subtracting 11.5 \AA of the thickness of the niobate layer from the observed *d*-spacing, which implies that the copper ions are intercalated as a monolayer.

Fig. 3 shows the XANES spectra at Cu K-edge and their second-derivatives. Based on the above peak assignments for p-XANES, the resolved shoulder peaks C and D corresponds to the $1s \rightarrow 4p_\pi$ and $1s \rightarrow 4p_\sigma$ transition, respectively. But it is clearly seen that both peaks gradually shift to lower energy side as the layer charge density decreases. More interestingly, the change of C peak position is larger than that of D peak. The difference between two peaks is larger for $x = 0.75$ ($\Delta = 6.0 \text{ eV}$) with lower layer charge density than for $x = 0$ ($\Delta = 4.8 \text{ eV}$) with higher one as shown in Fig. 3(b). This fact suggests that the layer charge density of parent material has influence on the bonding nature of the first coordination sphere of intercalated copper ion. That is, there is a charge transfer from negatively charged perovskite layer to positively charged intercalated copper ion, resulting in the bond between copper ion and water to be more covalent upon the lower charge density of parent perovskite layer.

Fig. 4 shows the Fourier transforms (FTs) of EXAFS oscillations for some compounds in the range of $\sim 2.2 \text{ \AA}^{-1} < k < \sim 12.3 \text{ \AA}^{-1}$. As clearly seen in the figure, the sample after ion-exchange reaction

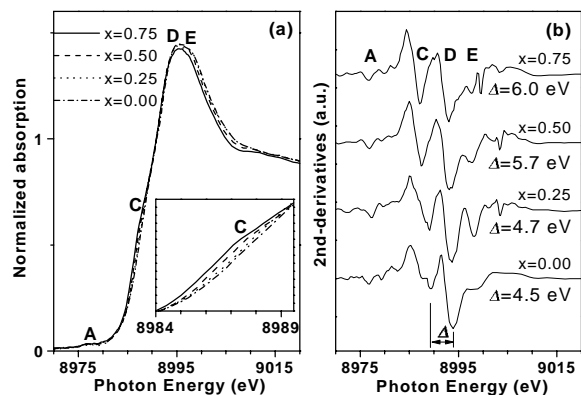


Figure 3
Normalized Cu K-edge XANES spectra (a) and their second-derivatives (b) measured for Cu²⁺ ions intercalated to polycrystalline OAxCa_{2-x}LaxNb₃O₁₀ (OA=*n*-octylammonium ion).

between Cu²⁺(aq) and OAxCa₂Nb₃O₁₀ exhibits different radial distribution function from the others, implying that the Cu²⁺ ions within interlayer space are coordinated to water molecules rather than oxide ion. For the quantitative analysis of the structural data, a non-linear least squares curve fitting has been carried out for the first peak around 1.4 Å with the coordination number(C.N.) as shown in Table 1. For all samples, the Cu-O distance is determined to be 1.93 - 1.96 Å. The fitting results for CuO used as reference shows that each copper has four O neighbors at 1.96 Å, which is in good agreement with the crystallographic data. When the C.N. was fixed to be six for CuO, the resulting Debye-Waller factor was much too high. In the same reason, copper ion intercalated inbetween niobate slab can be reasonably concluded to be four-coordinated to oxygen of water. Even though the three fitting results for heat-treated sample seem to be physically meaningful for any cases, the C.N. of six with the same or almost the same Cu-O bond distance cannot be structurally meaningful when considering the Jahn-Teller effect for Cu²⁺ ion. In this respect, it can be suggested that Cu²⁺ ion is four-coordinated by oxide ions consisting of niobate slab. This occurrence of four-coordinated Cu²⁺ ions in oxide lattice is not usual, and suggests that the ion-exchange reaction with layered oxides can be usefully used to form metastable compounds to be impossible by means of usual solid state reaction.

4. Conclusions

In the present study, we could obtain the new materials by the ion-exchange reaction of Cu²⁺ and [Cu(en)₂]²⁺ ions with layered

Table 1
Structural parameters obtained from the fittings for the Cu K-edge EXAFS spectra

compound	C.N.*	R (Å)	σ ² (×10 ⁻³ Å ²)	ΔE ₀ (eV)
Cu ²⁺ -intercalated niobate	3.7	1.94	5.0	-8.0
	4 (fixed)	1.94	5.7	-7.5
	6 (fixed)	1.93	9.1	-9.0
heat-treated Cu ²⁺ -intercalated niobate	4.5	1.95	3.1	-8.7
	4 (fixed)	1.95	2.4	-8.1
	6 (fixed)	1.94	5.1	-9.2
CuO (reference)	3.8	1.96	4.7	-5.4
	4 (fixed)	1.96	5.0	-5.6
	6 (fixed)	1.95	8.2	-8.4

* Amplitude reduction factor was set to 0.9 in the entire course of fitting procedure.

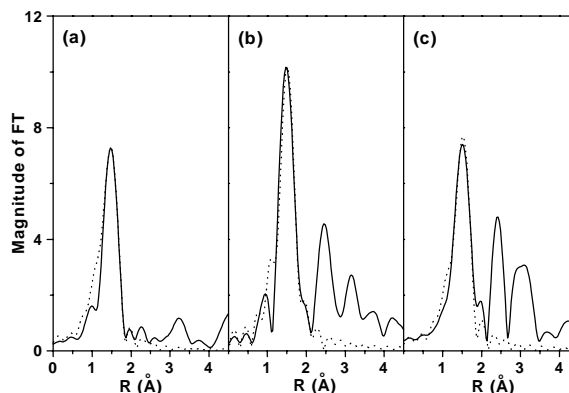


Figure 4
The experimental FTs (full line) and their first-shell fits (dotted line) for the samples of Cu²⁺ ion intercalated niobate (a) and its heat-treated (600°C) sample (b) in comparison with the reference of CuO (c).

niobate oxides in the forms of polycrystal or single crystal. According to powder XRD, while the *d* spacing of the (00l) reflections varied for different products depending on the interlayer species, the peaks corresponding to (*hk*0) reflections remain unchanged. This suggests that the observed changes were only due to the changes in the interlayer spacings.

This study has shown the utility of x-ray absorption spectroscopy to probe the chemical environment of metal ions in the interlayer space. It was confirmed that the plane of [Cu(en)₂]²⁺ ions in the interlayer space is parallel to the niobate layer by means of p-XANES spectra at Cu K-Edge. The charge transfer from host oxide layer influences the chemical states of Cu²⁺ ions in the interlayer space. EXAFS also provided that the Cu²⁺ ions in the heat-treated sample are four-coordinated to oxide ions of lattice, which is rare in compounds prepared by conventional solid state reaction.

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