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Vacuum ultraviolet reflectance and electron energy loss spectra of CaTiO_3

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Abstract. Normal incidence light reflection measurements have been performed for CaTiO_3 single crystals over the wide energy region from 0.4 to 35 eV. The dielectric functions and optical constants are evaluated from the reflectance spectrum by the Kramers–Krönig transformation technique. The experimental electron energy loss spectrum is in reasonable agreement with the energy loss function calculated from the dielectric functions. In comparison of the dielectric functions with joint density of states, the peaks in the energy region from 3 to 8 eV are mainly attributed to the transition from O 2p to Ti 3d orbitals, and those from 8 to 15 eV are assigned to the transitions from O 2p to Ti 3d, Ca 4s and Ti 4s orbitals.

1. Introduction

Reflection measurements in the vacuum ultraviolet (VUV) region and normal/inverse photoemission measurements are effective methods to obtain invaluable information about the electronic structure of materials. In contrast to the photoemission measurements, the reflection measurements have several merits: they are not so sensitive to surface states as photoemission measurements, and samples do not have to be conductive. Dielectric functions and optical constants can be estimated from the reflection spectra by the Kramers–Krönig (KK) transformation technique. Relatively intense and sharp structures in spectra are often obtained because the reflection measurements do not need an energy transfer from photons to electrons. However, the interpretation of the structure is not as straightforward as that in the photoemission spectra, because the structures in the reflectance spectra simultaneously include information about both occupied and unoccupied states. Therefore, theoretical supports such as an energy band calculation will be required for reasonable interpretations. Although the complex structures in the reflection spectra appear to make the analysis of electronic structures difficult, they provide a strict criterion because a good agreement between calculations and spectra can be obtained only when the calculations are reliable in both the occupied and unoccupied states.

CaTiO_3 is one of the alkaline earth titanates with perovskite structure such as SrTiO_3 and BaTiO_3 . These titanates have various attractive properties from the electrical and optical viewpoints. Helped by the simplicity in the crystal structure, in the cases of SrTiO_3 [1–9] and BaTiO_3 [10–12], extensive studies on their electronic structures have been carried out to clarify the origins of the interesting properties. On the other hand, in the case of CaTiO_3 , such investigations are few. This is because the crystal structure of CaTiO_3 is, strictly speaking, GdFeO_3 type derived from distorting the ideal cubic perovskite structure, and the complication in the crystal structure prevents researchers from studying the electronic

structure of the material. However, the investigation concerning the electronic structure of CaTiO_3 is important to comprehend the electrical and optical properties of CaTiO_3 as well as that of the other alkaline earth titanates. The understanding of the electronic structures over these alkaline earth titanates will be essential to pursue the origin of their attractive properties because some factors related to the alkaline earth ions, such as ionic radius and basicity, may influence them.

In the present study, VUV reflectance and electron energy loss spectra of CaTiO_3 are reported along with the dielectric functions and optical constants calculated by the KK transformation technique. The reliability of the results of the KK transformation is examined referring to the refractive indexes reported by Linz and Herrington [13] in the visible region and an experimental electron energy loss spectrum. The imaginary part of the dielectric functions is interpreted by a theoretical calculation, and the peaks in the function are assigned to some transitions between component orbitals.

2. Experiment

Single crystals were prepared by the floating zone (FZ) method using an infrared radiation furnace with a halogen lamp. The single-crystal rods were 4–6 mm in diameter and 30–60 mm in length, and samples were cut out of the rods in the shape of a plate. Only one side of the surfaces was polished using $0.1 \mu\text{m}$ diamond slurry and $0.05 \mu\text{m}$ Al_2O_3 slurry. The other side was rubbed by sandpaper to make it rough. This procedure is important to avoid reflections from the back surface of a sample. A plate shaped single-crystal sample was set so that the incident angle of light was $\sim 10^\circ$ to achieve almost normal incident reflection. The sample was irradiated with the incident light normal to the (100) planes.

Reflection spectra were measured in as wide an energy range as possible to obtain accurate results in the KK transformation. In the energy range from 0.4–6 eV, optical transmission and reflection measurements were carried out using a conventional UV–VIS–NIR spectrometer (Hitachi U-4000). VUV optical reflection spectra were obtained at a pressure of $\sim 10^{-8}$ Torr on the BL-1B of UVSOR in the Institute for Molecular Science (IMS). Using two gratings, the photon energy was scanned from 2.0 to 20 eV and from 8.0 to 35 eV with the resolution ≤ 0.1 eV. Three reflection spectra obtained through the wide energy range from 0.4 to 35 eV were smoothly connected at ~ 3 and ~ 15 eV. The dielectric functions, reflective indexes and extinction coefficients were evaluated by the KK transformation technique.

Electron energy loss spectroscopy (EELS) measurements were carried out on a transmission electron microscope (Hitachi H9000NAR) equipped with a LaB_6 electron source and an electron energy loss spectrometer (Gatan 676). Spectra were recorded in a diffraction mode using a 300 keV electron beam and the energy resolution was estimated to be ~ 1 eV by measuring the energy spread of the electron beam. The electrons spread after passing through the specimen were cut by an aperture in front of the spectrometer and its collection angle was ~ 3 mrad.

An empirical energy band calculation by the tight-binding method was performed in order to interpret the reflectance spectrum. Parametrization by Harrison [14] was adopted in the calculation, which might be a rough approximation but quite convenient for semi-quantitative discussions. Optimization of parameters was carried out referring to the reported parameters adopted in the band calculations of some titanates [1–3, 15, 16], so that they can reproduce fundamental experimental results such as an energy gap. Although a shallow core level of Ti 3p orbitals was not included in the calculation to simplify it, Ca 3p and O 2s levels were included as bases in the linear combination of atomic orbitals (LCAO).

3. Results

Figure 1 shows the reflectance spectrum of CaTiO₃ in the photon energy region from 0.4 to 35 eV. An extrinsic reflection from the back surface of the sample appeared around 3 eV in the reflection spectrum measured with the synchrotron radiation even if the back surface was rough. Since this reflection was not observed in the spectrum measured using the conventional spectrometer with a tungsten lamp, it probably occurred because of the strong brightness of the synchrotron radiation. Therefore, two spectra measured by using the synchrotron radiation and a tungsten lamp were smoothly connected to cancel the extrinsic reflection.

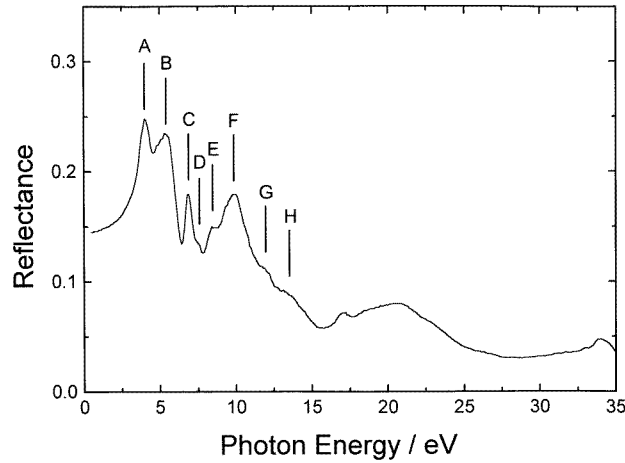


Figure 1. Vacuum reflectance spectrum of CaTiO₃. The prominent peaks observed below 15 eV are indexed.

Table 1. Prominent peaks in the reflectance spectrum of CaTiO₃ up to 15 eV with the comparable peaks in SrTiO₃ and BaTiO₃. Corresponding peaks in the ϵ_2 function are listed in parentheses.

CaTiO ₃	Energy (eV)	SrTiO ₃		BaTiO ₃	
		Cardona	Bäuerle	Cardona	Bäuerle
A	4.0 (4.3)	A ₁	A ₁	A ₁	B ₁
B	5.3 (5.7)	A ₂ , A ₃	A ₂ , A ₃	A ₂	B ₂ –B ₄
C	6.8 (7.0)	B ₁	A ₄	B ₁	B ₅
D	7.5 (7.6)	B ₂	A ₅	B ₂	B ₆
E	8.4 (8.7)	C ₁	A ₆	B ₇	B ₇
F	9.9 (10.1)	C ₂	A ₇	C ₁	B ₈
G	12.0 (12.1)	D	A ₈	C ₂	B ₉
H	13.6 (13.8)	—	A ₉ , A ₁₀	D	B ₁₀

Prominent peaks in the reflectance spectrum below 15 eV are indexed as shown in figure 1 and listed in table 1. Since the structure in the reflectance spectrum of CaTiO₃ is generally similar to that of SrTiO₃ and BaTiO₃ reported by Cardona *et al* [7] and Bäuerle *et al* [9], the comparable peaks in their spectra are also summarized in the table, using their indexes. The analogy in the structure indicates that the type of alkaline earth ion may have little effect on the structure.

The reflectance of CaTiO_3 has a sharp structure near the absorption edge, and the intensity of the reflectance decreases with increasing energy, exhibiting some broad peaks in the high-energy region. A small shoulder was not observed at the fundamental absorption edge in CaTiO_3 as recognized in SrTiO_3 and BaTiO_3 . However, the disappearance of the small shoulder in CaTiO_3 is not definitive yet because the connection of two spectra may make the reflectance around the absorption edge ambiguous. The detailed peak assignments will be demonstrated in the following discussion by comparison of the experimental spectra with theoretical calculations.

The results of the KK transformation are shown in figures 2 and 3: figure 2 shows the real and imaginary parts of the dielectric function, and figure 3 the refractive indexes

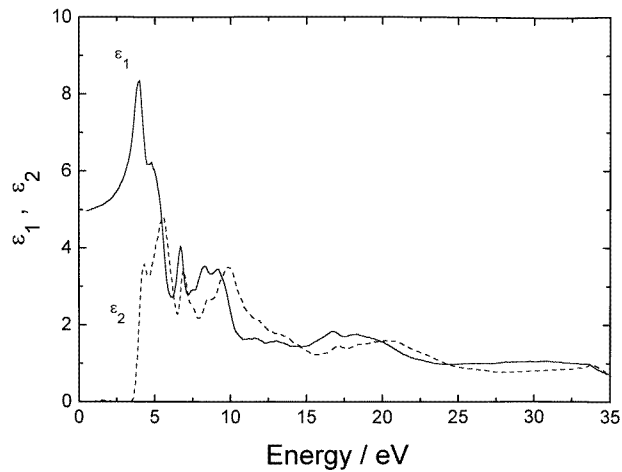


Figure 2. Real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function of CaTiO_3 . ϵ_1 : solid line, ϵ_2 : dashed line.

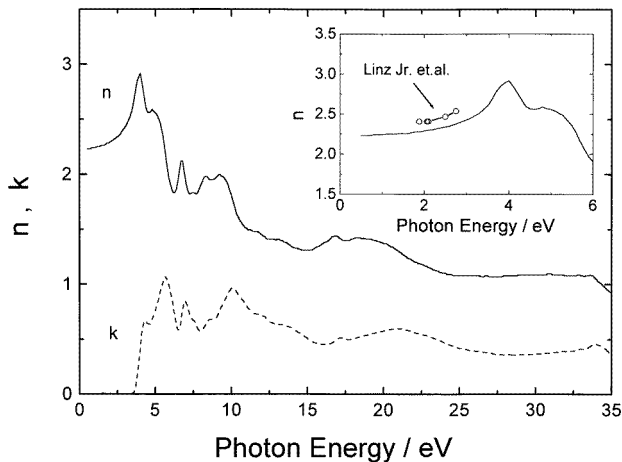


Figure 3. Optical constants of CaTiO_3 : refractive indexes (n : solid line) and extinction coefficients (k : dashed line). The comparison of the spectrum with the data by Linz *et al* is shown in the inset.

and the extinction coefficients of CaTiO₃. Some approximate methods to extrapolate the reflectance spectrum were tried in the KK transformation. All the methods resulted in a similar feature in a higher-energy region than the fundamental absorption edge, while they gave quite different results below the absorption edge. The Roessler method [17] was adopted to obtain a reasonable result in the low-energy region. In the KK transformation by his method, two arbitrary energies are required at which extinction coefficients are already known. The optical transmission measurement on CaTiO₃ demonstrated that no detectable absorptions appear in the energy range between the lower limit of the measurement at 0.4 eV and the fundamental absorption edge at 3.57 eV. Therefore, the two energies of 0.9 and 3.0 eV were selected and the extinction coefficients were assumed to be zero at these energies.

The top of peaks in the imaginary part of the dielectric function (ϵ_2) is generally ~ 0.3 eV higher in energy than those in the reflectance spectrum, as shown in parenthesis in table 1, because of the phase changes of light on reflection. In spite of the energy shift, the structure in the ϵ_2 function is similar to that of the reflectance spectrum except below the fundamental absorption edge. Therefore, the peaks in both spectra are comparable with each other and the peak assignment was carried out referring to the ϵ_2 function instead of the reflection spectrum.

Bäuerle *et al* evaluated the energy loss function ($-\text{Im}(1/\epsilon)$) and found an intense maximum at 29.7 eV for SrTiO₃ and at 27.3 eV for BaTiO₃. On the other hand, no intense band was observed for CaTiO₃ in the present study. It is obvious that the difference originates only from the intensity of the reflectance peak at high energy; 20 eV for CaTiO₃, 28.5 eV for SrTiO₃ and 23.1 eV for BaTiO₃. Therefore, the calculated spectra by the KK transformation technique should be interpreted carefully.

4. Discussion

4.1. Examination of the results of the KK transformation

Although the results obtained by KK transformation are significantly informative for understanding of the electronic structure of materials, deliberative interpretation should be given, especially in the absolute values, because the results are indirectly acquired through two processes; the reflection measurement and the calculation for the transformation. Since no results related to optical coefficients of CaTiO₃ have been reported so far above the fundamental absorption edge, the comparison in the visible region was carried out for the examination of the absolute values in the evaluated spectra by KK transformation. Linz and Herrington [13] reported the refractive indexes of CaTiO₃ in the visible region determined by the angle-of-minimum-deviation method using a prism-shaped single crystal, which is a direct and accurate method to determine the indexes. The comparison of the present evaluated refractive indexes with the reported values by Linz and Herrington are shown in the inset in figure 3. Although the curvatures of the spectra are similar to each other, the average deviation in the absolute values was estimated to be $\sim 7\%$. The cause of the disagreement is not clear at present; however, the small sample used in the present experiment may influence the reflection measurement.

Figure 4 shows the energy loss function calculated by the KK transformation technique and EELS spectrum. The EELS spectrum is a raw spectrum and no corrections were made to it. However, the thickness of the specimen for the EELS measurement was calculated from the area of the spectrum to be less than a total mean free path for all inelastic scattering, which was estimated to be ~ 150 nm for CaTiO₃ by the Lenz model, and the multiple

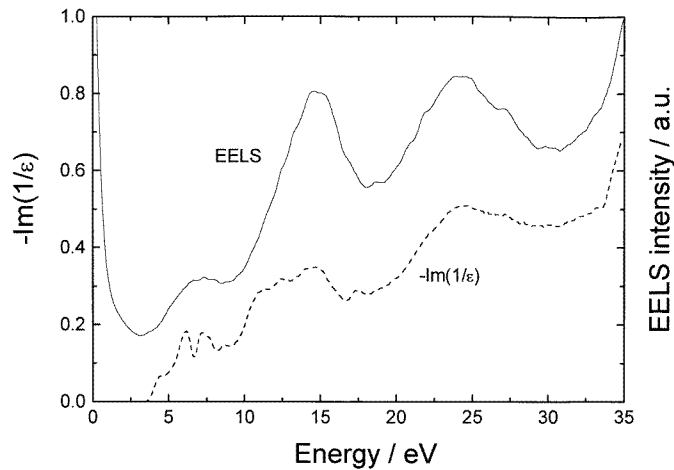


Figure 4. Comparison of the energy loss function with the EELS spectrum. The EELS spectrum: solid line, the energy loss function: dashed line.

scattering would not influence the structure of the spectrum significantly [18]. The energy loss function shows a satisfactory agreement with the EELS spectra in general features. The anisotropy of the energy loss seems to be small and negligible because similar EELS spectra were obtained from several pieces of single crystals with different crystal directions. This observation is consistent with the fact that the remarkable anisotropy was not observed in the polarized-light experiment for the reflection measurements. Although small structures in the low-energy region cannot be observed in the EELS spectrum, this is probably attributable to the low-energy resolution in the present measurement. Since the reflection spectrum and EELS spectrum were acquired independently and they agree well with each other, the dielectric functions are successfully calculated by the KK transformation.

From the discussion above, it can be concluded that the structure in the calculated functions is reliable while the absolute values may include several per cent of deviation in the whole energy range.

4.2. Peak assignments

The peak assignment in the reflection spectra of SrTiO₃ and BaTiO₃ has been carried out mainly referring to the energy band calculation along the symmetrical lines. Although it is a simple method for the assignment, it reflects only one-dimensional interpretation. Since numerous independent k points in the first Brillouin zone contribute to the interband transition, three-dimensional consideration is more favourable. A comparison of the ϵ_2 function with the joint density of states (JDOS) is a better solution for the peak assignment based on the information about k space, because it is known that the ϵ_2 function is proportional to the JDOS under some assumptions (see the appendix).

Figure 5 shows the JDOS of CaTiO₃ and the partial joint densities of states (PJDOS) with the ϵ_2 function. Since shallow core levels of Ca 3p and O 2s orbitals have no PJDOS in the energy range up to 20 eV, their PJDOSs are not shown in the figure. In spite of small energy differences at the top of peaks between JDOS and the ϵ_2 function, the calculated JDOS shows a satisfactory agreement with the ϵ_2 function in regard to its structure except

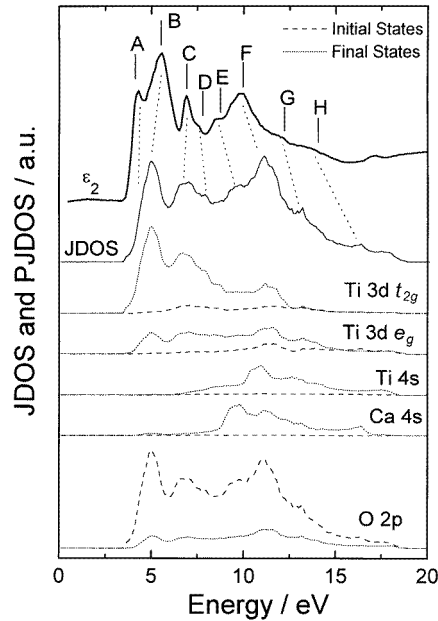


Figure 5. Comparison of the ϵ_2 function with the JDOS and PJDOS of CaTiO₃ calculated by the tight-binding method. ϵ_2 : thick solid line, JDOS: solid line, PJDOS (initial): dashed lines, PJDOS (final): dotted lines.

the peak A. Since the small differences are negligible in a first approximation, the peak assignment will be carried out referring to the JDOS.

The PJDOS clearly demonstrates the contribution of component orbitals to the initial and final states on the transition. Initial states are dominantly composed of O 2p orbitals and final states mainly consist of cation orbitals in this energy region. Since transition frequency is proportional to densities of both initial and final states, transitions occur when both the densities are large. Accordingly, the peaks from A to D are assigned mainly as the transition from O 2p to Ti 3d t_{2g} orbitals. The PJDOS of Ti 3d e_g orbitals spreads so broadly from the fundamental absorption edge to energy about 12 eV that they greatly influence the transition in the energy region. In addition to the transition from O 2p to Ti 3d orbitals, those from O 2p to Ca 4s and Ti 4s orbitals are largely responsible for the peaks E and F, respectively. The peak G is ascribed to the transition from O 2p to Ti 3d e_g , Ti 4s and Ca 4s orbitals, while the contributions of Ti 3d orbitals are not seen in the peak H. The main feature of the ϵ_2 function in the energy range can be understood in that the structure in the function is almost completely determined by the transition from O 2p to cation unoccupied orbitals, namely from valence band to conduction band.

In the energy region above 15 eV, the calculated JDOS does not show a good agreement with the ϵ_2 function as in the energy region below 15 eV. However, the peaks in the higher-energy region are mainly attributed to the transition from shallow core levels to conduction band because the transitions from valence band to conduction band are already assigned as above. Therefore, taking the energy levels of shallow core levels into consideration, the peaks at 17, 22 and 33 eV may be tentatively assigned as the transitions from O 2s, Ca 3p and Ti 3p orbitals, respectively. More precise calculations including excited states would be necessary for more strict assignment in the energy region.

5. Conclusion

Reflection measurements were carried out for CaTiO₃ single crystals over the wide energy region from 0.4 to 35 eV. The dielectric functions, reflective indexes and extinction coefficients were calculated from the reflectance spectrum by the KK transformation technique. From a comparison of the calculated reflective indexes with the experimental ones by Linz and Herrington in the visible region, the possibility of several per cent of deviation in the absolute values is indicated. However, the structure in the dielectric function is accurate enough to reproduce the EELS spectrum. The JDOS obtained by the energy band calculation is in good agreement with the ε_2 function in the energy region up to 15 eV. Referring to the JDOS, all peaks in the energy region were assigned in that the structure in the energy region between 3 and 8 eV mainly originates from the transition from O 2p to Ti 3d orbitals, and the structure between 8 and 15 eV arises from the transitions from O 2p to Ti 3d, Ca 4s and Ti 4s orbitals. Although theoretical interpretation cannot be given by the calculation, the peaks in the energy region above 15 eV were temporarily assigned as the transitions from shallow core levels such as O 2s, Ca 3p and Ti 3p to the conduction band.

Appendix

The imaginary part of the dielectric function, ε_2 , was generally expressed in theory by the following equation [19].

$$\varepsilon_2 = \frac{e^2}{\pi m^2 \omega^2} \int d\mathbf{k} |P_{cv}|^2 \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega) \quad (\text{A1})$$

where c and v denote the final and initial states and P_{cv} is the optical dipole matrix element. If P_{cv} varies slowly in k space and its anisotropy is negligible, P_{cv} can be taken outside the integral and the ε_2 function may be expressed with the joint density of states, J_{cv} , defined as follows

$$\varepsilon_2 = 8 \left(\frac{\pi e}{m\omega} \right)^2 |P_{cv}|^2 J_{cv} \quad (\text{A2})$$

$$J_{cv} = \frac{1}{(2\pi)^3} \int d\mathbf{k} \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega). \quad (\text{A3})$$

Therefore, in this approximation, the ε_2 function is proportional to the joint density of states. Moreover, in the calculation of JDOS, the contribution of the i th atomic orbital to initial or final states can be roughly extracted by multiplying the integral by the LCAO coefficient, c_i .

$$J_{cvi} = \frac{1}{(2\pi)^3} \int d\mathbf{k} |c_i|^2 \delta(E_c(\mathbf{k}) - E_{v_i}(\mathbf{k}) - \hbar\omega). \quad (\text{A4})$$

This density is tentatively called the partial joint density of states (PJDOS) in the present paper.

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