Phase transition, magnetic, and electronic properties of CeOInS2

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The magnetic and electronic properties of CeOInS2 and their influence on phase transition were analyzed in this study. High-temperature XRD measurements of CeOInS2 revealed that orthorhombic CeOInS2 transformed into tetragonal CeOInS2 at a high temperature of 636 K. The transport properties of CeOInS2 showed semiconducting behavior, with a larger temperature dependence of electronic resistivity in the tetragonal phase compared to that in the orthorhombic phase. Unlike structurally similar Ce(O,F)BiS2 superconductors that show long-range magnetic ordering, CeOInS2 neither exhibited superconducting transition nor long-range magnetic ordering at temperatures between 2 and 300 K.

Key-words: Oxysulfide, Phase transition, Synchrotron XRD

1. Introduction

LaOMCh2 (M: Bi, In, Sb; Ch: S, Se) compounds consist of alternating stacks of La–O and M–S layers,1–5 and their conduction and valence bands are composed of M and Ch p orbitals in the MCh2 layers.3,4 These layered oxysulfides have drawn attention because of their various functionalities. For example, the oxysulfates exhibit low thermal conductivities suitable for thermoelectric materials.5–9 Additionally, the superconductivity of F-doped La(O,F)BiS2 has been extensively studied,10–17 which has led to theoretical predictions for LaOSbSe2 as a topological material.18,19 The substitution of La with Ce in such layered structures often results in interesting properties. For example, in contrast to non-superconductive LaOBiS2,20,21 CeOBiS2 exhibits superconducting properties below 1.3 K.20,22 Ce(O,F)BiS2 shows both superconducting and long-range magnetic ordering.16–18,23–25 It is likely that the 5d and 4f orbitals of Ce3+ as well as the coexistence of Ce4+ play an important role in the appearance of such exotic properties.

Recent studies have investigated layered LaOlnS2 as a semiconductive photocatalyst for H2 or O2 evolution under visible light from a solution containing a sacrificial agent.4 LaOlnS2 has an orthorhombic structure that is slightly distorted from a tetragonal structure. Large thermal displacements of In, represented by split off-centered positions with half occupancy, are a characteristic feature of LaOlnS2. Correlations between the large displacement of indium and the electronic structure of LaOlnS2 have been experimentally shown by structural analyses of LaOlnS2, CeOInS2, and PrOInS2.26

The dimensionality of the M–Ch plane is an interesting and controversial topic. Considering that the M–Ch layer is along the ab plane, the dimensionality of the layer depends on the crystal system, which can affect its superconducting mechanism.27–29 A study on La(O,F)BiS2 with a monoclinic system featuring a one-dimensional path synthesized by the high-pressure method shows a higher superconducting transition temperature than that of La(O,F)BiS2 with a tetragonal system featuring a two-dimensional path synthesized by ambient pressure.30 By contrast, a higher transition temperature is observed in tetragonal (Ce,Pr)OBiS2. Although these different compounds and their properties have been investigated, the effect of dimensionality on M–S is not yet clear. CeOInS2 is refined as an orthorhombic structure with only a slight distortion from the tetragonal structure and contains ~10 % Ce4+,20 which may afford an electron carrier in the In–S layer. Therefore, the temperature dependence of the crystal structure and electronic properties of CeOInS2 are an interesting motif for investigating the influence of dimensionality of the electron path on the conduction path.

In this work, the crystal structure of CeOInS2 was investigated in this study by heating it to 700 K, and its elec-

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tronic and magnetic properties were subsequently examined. The tetragonal phase of CeOInS$_2$ was found above 640 K with a gap in electronic resistivity, compared to the orthorhombic phase found at a low temperature. Moreover, magnetic properties from 2–300 K were examined.

2. Experimental

CeOInS$_2$ was synthesized using NaInS$_2$ and CeOCl, according to the literature.$^{26}$ A mixture of NaSH·nH$_2$O (Sigma-Aldrich) and In(NO$_3$)$_3$·nH$_2$O (Kanto Chemical) in the weight ratio of 2:1 was heated in a Teflon–coated autoclave at 473 K for 8 h. After washing with distilled water, NaInS$_2$ powder was obtained. CeOCl was synthesized by heating CeCl$_3$·7H$_2$O at 823 K for 34 h in a 4% H$_2$ gas diluted with Ar. Then, NaInS$_2$ and CeOCl were mixed using agate mortar and pestle in an Ar filled glovebox and heated in an evacuated quartz tube at 1123 K for 4 h. After cooling, NaCl was removed by washing several times with distilled water. Synchrotron X-ray diffraction profiles were measured from 300 to 700 K at the BL02B2 beamline at SPring-8 (Proposal No. 2017B1211). The heating rate was 10 K/min, and diffraction patterns were collected in steps of 5 K without waiting for the temperature to stabilize. The X-ray diffraction data were analyzed by the Rietveld method using the RIETAN-FP program,$^{31}$ and the crystal structure was illustrated using the VESTA program.$^{32}$ The resistivity of the CeOInS$_2$ pellet was derived from the slope of the I–V plot in the current range of 1–10 mA by the four-terminal method between 300 and 700 K.

3. Results

Figure 1(a) shows the XRD patterns of the CeOInS$_2$ powder at 300 and 700 K. The crystal structure at 300 K is orthorhombic with $a = 3.98582(6)$ Å, $b = 3.98000(7)$ Å, and $c = 12.69515(10)$ Å, which slightly deviate from tetragonal symmetry.$^{26}$ The 200 and 020 diffraction peaks merge into a sharp peak at a temperature above 636 K, as shown in Fig. 1(b), indicating a phase transition from orthorhombic to tetragonal form. The lattice parameters at 700 K ($a = 4.00248(1)$ Å and $c = 12.70240(9)$ Å) are larger than those at 300 K because of thermal expansion.

The Rietveld refinement of the synchrotron XRD pattern of CeOInS$_2$ at 700 K is shown in Fig. 2. The diffraction data at 700 K were successfully refined using a tetragonal cell in the $P4/nmm$ space group, which is the same as that in superconducting BiS$_2$ compounds such as Ln(O,F)BiS$_2$ (Ln: La, Ce, Pr, Nd, Sm)$^{33,35}$ and CeOBiS$_2$. Tetragonal CeOInS$_2$ has a two-dimensional In–S layer with the same in-plane In–S bonds, in contrast to the one-dimensional In–S chains with different in-plane In–S bonds in the orthorhombic cells. Large displacement parameters of indium were found, especially in the in-plane direction. The crystallographic and refinement data are summarized as a crystal information file (CIF), which is available in the supplementary file.

Figure 3 shows the resistivity of CeOInS$_2$ as a function of temperature. Although the effect of contact resistance between its grains cannot be excluded, the temperature dependence suggests that both the orthorhombic and tetragonal structures of CeOInS$_2$ are semiconductors. An increase in temperature results in an exponential decrease in its resistivity; however, a slight increase is seen at ~630 K, which is the phase transition temperature from orthorhombic to tetragonal form. The slope of tetragonal CeOInS$_2$ in the resistivity curve is steeper than that of zero-field cooling conditions.

![Figure 1](image-url)  
**Figure 1.** (a) Synchrotron X-ray diffraction patterns of CeOInS$_2$ at 300 and 700 K. (b) Expanded profiles of the 200 and 020 peaks. The heating rate is 10 K/min, and each diffraction pattern is measured every 30 s. The thin and bold lines represent orthorhombic and tetragonal phases, respectively.
orthorhombic CeOInS$_2$, suggesting a higher activation energy for electron conduction.

The magnetic susceptibility of orthorhombic CeOInS$_2$ and its reciprocal magnetic susceptibility in the temperature range of 2–300 K are shown in Fig. 4. Neither superconducting transition nor magnetic ordering is observed in orthorhombic CeOInS$_2$. The reciprocal magnetic susceptibility follows the Curie–Weiss law at temperatures above 150 K. The effective magnetic moment for orthorhombic CeOInS$_2$ is determined to be 2.62 $\mu_B$, which is close to that of free Ce$^{3+}$ (2.54 $\mu_B$). This suggests that Ce is mostly trivalent, in agreement with the X-ray absorption results.26)

4. Discussion

At room temperature, CeOBiS$_2$ is composed of both trivalent and tetravalent Ce with a tetragonal structure.36) Additionally, F doping into O sites in LaOBiS$_2$ also results in a tetragonal structure.36) Therefore, carrier doping by mixed-valent Ce or F doping leads to a tetragonal phase. However, at room temperature, CeOInS$_2$ with mostly trivalent Ce has an orthorhombic structure that is slightly distorted from the tetragonal structure, and an increase in temperature causes phase transition to a highly symmetric tetragonal structure. A similar phase transition has been reported in LaOBiSSe, where the phase transition temperature (~340 K) decreases by F doping.38) Therefore, the dimensionality of Bi–S/In–S is likely to be affected by the carrier concentration and temperature.

Figure 5 shows the proposed local structure of In and electron conduction path in the ab plane. Although the average indium position determined by synchrotron XRD in orthorhombic CeOInS$_2$ converges to a centered position with a large displacement factor, the local In position is likely off-centered in the In$_6$ octahedral in the orthorhombic cell; this produces a one-dimensional chain of the In–S network in the ab plane. While relatively short In–S bonds along the c-axis determine the optical bandgap, the conduction path is governed by the relatively long bonds parallel to the ab plane. As a result, the orthorhombic to tetragonal phase transition shifts the local off-centered
indium position into the central position in the InS₆ octahedra. This local shift breaks the one-dimensional conduction path composed of slightly shorter In–S bonds. Therefore, the higher activation energy for electron conduction in the tetragonal structure can be explained by the less overlapped In and S orbitals in the ab plane, which widens the band gap and lowers the mobility of electrons within the InS network in the ab plane. Therefore, these results validate our hypothesis that the dimensionality of CeOInS₂ alters the electron conduction path.

5. Conclusion
A phase transition from orthorhombic to tetragonal form of CeOInS₂ was found above 640 K with a different temperature dependence of electronic resistivity. This structural change included the local structural change in the In–S plane, which altered the dimensionality from one-dimensional to two-dimensional In–S paths. Orthorhombic CeOInS₂ did not show magnetic ordering or superconductive transition at temperatures as low as 2 K.

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Supplementary files
• CIF file of CeOInS₂ at 500 K.
• Summary of Rietveld refinement of CeOInS₂ at 500 K.

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