論 文 の 内 容 の 要 旨

論文題目　Two-dimensional Superconductivity in $BaBiO_3/BaPbO_3$ Heterostructure
（$BaBiO_3/BaPbO_3$ ヘテロ構造における二次元超伝導）

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## Introduction

A perovskite oxide $BaBiO_3$ (BBO) has been studied intensively since the superconductivity related to its charge order state was found. In BBO, the nominal valence state of $Bi^{4+}$ ($6s^1$) is skipped, and the charge order of $Bi^{3+}$ ($6s^2$) and $Bi^{5+}$ ($6s^0$) is realized due to the stability of the closed cells. As a result, BBO shows semiconducting properties with a band gap of 0.2 eV. The chemical substitutions in BBO destroy the charge order and induce a superconducting transition. For instance, the solid solutions $Ba(Pb_{1-x}Bi_x)O_3$ (BPBO) with a semi-metal $BaPbO_3$ (BPO) show superconductivity ($x$ = 0.10 ~ 0.35) with the highest transition temperature $T_c$ of 12 K at $x$ = 0.25. From ionic limit, Pb in BPO forms a valence state of 4+ ($6s^0$), which behaves to remove an electron in 6s orbital of Bi, approaching $6s^1$ state by $Pb^{4+}$ ($6s^0$) + $Bi^{5+}$ ($6s^2$) → $Pb^{3+}$ ($6s^1$) + $Bi^{4+}$ ($6s^1$). K-doped $(Ba_{1-x}K_x)BiO_3$ (BKBO) also undergoes a superconducting transition with $T_c$ = 30 K ($x$ = 0.4) at maximum, indicating that the substitutions by K realize hole-doping on BBO. The difference of $T_c$ is considered to be originated from the disorder by the solid solution, meaning that the substation on Bi is more influential for conduction electrons than that on Ba. Therefore, the enhancement of $T_c$ is expected in BPBO, if disorder due to the solid solution between Pb and Bi is removed.

Charge transfer across the interface is a way to modulate the carrier density without introducing disorder. Recent technical advances in the atomic-scale synthesis of materials have provided the opportunities for investigating their surface or interface states. In particular, the oxide interface is focused on as a field to demonstrate charge transfer, resulting the novel electronic phases, for example, ferromagnetism, superconductivity and the quantum Hall effect.

## Purpose

In this study, we aim at clarifying the relationship between disorder and superconductivity in BPBO system by utilizing heterostructures. The heterojunction of BBO and BPO is expected to occur superconductivity due to the charge transfer, implying the motion of 6s electrons from Bi to Pb at interface. Although BBO/BPO interface has no disorder, the single interface might be hopeless to realize high $T_c$, because the thermal fluctuation with two-dimensional system generally reduces a phase transition temperature. However, in the BBO/BPO superlattice, the overlap of charge transfer regions might recover three-dimensionality and increase the carrier density, inducing the enhancement of $T_c$. In order to achieve these objectives, we fabricated BBO/BPO heterostructures and evaluated its superconducting properties.

## Experimental

The thin films in this work were fabricated on MgO(001) substrate by pulsed laser deposition (PLD) method using a KrF excimer laser ($\lambda$ = 248 nm). In order to realize epitaxial growth of BPO and BBO films, MgO was chosen as the substrate because of the good lattice match between MgO and BBO (BPO). Stoichiometry of thin films was controlled, by changing the composition of target materials in a PLD chamber, and the chemical compositions were analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS). During the deposition, the substrate temperature and oxygen pressure were kept at 650 ~ 675 °C and at 190 mTorr, respectively. The crystal structure and the surface morphology of thin films were evaluated by X-ray diffraction (XRD) and atomic force microscope (AFM) measurement, respectively. The thickness of films was estimated from X-ray reflection measurement. An atomic-resolved EDS mapping of the cross-sectional interface was performed by using a probe forming aberration corrected scanning transmission electron microscope (STEM). Transport properties of thin films were measured by a physical property measurement system (PPMS; Quantum Design) and a home-built apparatus.

## Result and Discussion

### 1. Charge transfer and two-dimensional superconductivity at $BaBiO_3$/$BaPbO_3$ interface

Charge transfer and two-dimensional superconductivity was expected at the atomically flat BBO/BPO interface in epitaxial grown thin films. We fabricated the single crystal thin films of $BPO_m$ and $BBO_n$/$BPO_m$ [$m$ ($n$) unit cells of BPO (BBO)] on MgO(001) substrate. Since a charge order semiconductor BBO has much higher electrical resistance than a semi-metal BPO, the difference of resistance between $BPO_m$/sub and $BBO_n$/$BPO_m$/sub approximately give us the resistance of BBO/BPO interface (sub: MgO(001) substrate). XRD patterns show that $BPO_{25}$/sub and $BBO_{75}$/$BPO_{25}$/sub realize the epitaxial growth along [001] direction, and 002 reflection peaks from BPO and BBO are clearly separated. The lattice constants of BBO and BPO in $BPO_{25}$/sub and $BBO_{75}$/$BPO_{25}$/sub are almost the same length with the bulk values respectively, indicating that the epitaxial strain to BBO and BPO from MgO substrate is negligibly small. The electrical resistance of $BBO_{75}$/$BPO_{25}$/sub is smaller than that of $BPO_{25}$/sub around room temperature, probably because of conducting BBO/BPO interface. The change in temperature dependence of electrical resistance from $BBO_{75}$/$BPO_{25}$/sub to $BPO_{25}$/sub implies semiconducting behavior of BBO/BPO interface. The absolute value of Hall resistance also decreases in $BBO_{75}$/$BPO_{25}$/sub. The amount of carriers seems to be expected to be increased by introducing BBO/BPO interface. These behaviors of transport properties support the charge transfer at BBO/BPO interface.

In spite of clear signature of charge transfer at BBO/BPO interface, superconductivity did not appear in $BBO_{75}/BPO_{25}$/sub. In order to realize superconducting interface by charge transfer, the higher quality of BBO/BPO interface is needed. The roughness of root mean square (RMS) estimated by AFM measurement shows that the surface of $BBO_{75}$ (~ 33 nm)/sub is smoother than that of $BPO_{25}$ (~ 11 nm)/sub. The values of RMS on $BPO_{25}$/sub and $BBO_{75}$/sub are 0.97 nm and 0.34 nm respectively. $BPO_{25}/BBO_{75}$/sub has a possibility to realize higher quality of BBO/BPO interface, which is expected to be superconducting. XRD pattern shows that $BPO_{25}/BBO_{75}$/sub was fabricated as designed. The epitaxial growth along [001] direction is confirmed, and the peaks from BBO and BPO are separated around 004 reflection. $BPO_{25}/BBO_{75}$/sub showed the zero-resistance indicative of a superconducting transition below 3.6 K. Considering that neither $BPO_{25}$/sub nor $BBO_{75}$/sub is a superconductor, superconductivity is realized at BBO/BPO interface. The value of electrical resistance in $BPO_{25}/BBO_{75}$/sub is smaller than that in $BBO_{75}/BPO_{25}$/ sub. This decrease in electrical resistance suggests $BPO_{25}/BBO_{75}$/sub has the higher quality of BBO/BPO interface.

If superconductivity is realized at an interface, two-dimensional character of superconductivity is expected. When the superconductivity is confined in the narrow region, the upper critical field $H_{c2}$ depends on the direction of an applied magnetic field. When the magnetic field is applied parallel to the film, $H_{c2}$ has a maximum value, while $H_{c2}$ become a minimum with an applied magnetic field perpendicular to the film. Especially, in two-dimensional superconductors, the cusp appears around 0 degree in the angular dependence of $H_{c2}$, and this behavior described by Tinkham model. Angular dependence of $H_{c2}$ in $BPO_{25}/BBO_{75}$/sub measured at 2.0 K is reasonably fitted by Tinkham model, which proofs the two-dimensional superconductivity in $BPO_{25}/BBO_{75}$/sub. From Tinkham model, the thickness of superconducting layer and the superconducting coherence length in the plane are estimated to be 8.3 nm (~ 19 unit cells) and 17 nm at 2.0 K, respectively. In two-dimensional superconductor, the transition into the superconducting state would be a Berezinskii-Kosterlitz–Thouless (BKT) transition, characterized by a transition temperature $T_{BKT}$. The formation of the vortex-antivortex pairs realizes the zero-resistance state below $T_{BKT}$ The BKT transition is supported by no-linearity in the current (*I*)-voltage (*V*) characteristics. We observed the no-linearity in the *I*-*V* measurement of $BPO_{25}/BBO_{75}$/sub which agrees with the behavior expected in a BKT transition.

In order to clarify the effect of inter-site mixing, we carried out an atomic-resolved STEM-EDS mapping of the cross-sectional interface, resulting an image of atomically flat BBO/BPO interface. In addition, we investigated the transport properties of solid-solution BPBO thin film. In $BPO_{15}/BPBO_{20}$/sub thin films, the superconductivity disappeared, even though the chemical composition of BPBO is in the range of the superconductor. Therefore, it is difficult to imagine the formation of 8.3 nm (= $d_{Tinkham}$) superconducting layer by inter-site mixing at BPO/BBO interface.

The transport properties of $BPO_{25}$/sub and $BPO_{25}/BBO_{75}$/sub give the information about BBO/BPO interface state quantitatively. BBO thin film was too insulating to measure the transport properties. The carriers are supposed to exist in BPO and at BPO/BBO interface as follows. In both of the electrical resistance and Hall resistance, the absolute value of $BPO_{25}/BBO_{75}$/sub was smaller than that of $BPO_{25}$/sub. Using the parallel resistance model and the two carrier model, the resistivity and the carrier density of BBO/BPO interface were calculated. Here, the interface part is assumed to be equally distributed on BPO and BBO, and $d_{\mathrm{Tinkham}}$, which was estimated from the angular dependence of $H_{c2}$, is used as the total thickness of BBO/BPO interface. The resistivity of BPO/BBO interface is smaller than that of BPO, and the carrier density at BPO/BBO interface is around $1.4 \times 10^{21}$ $cm^{-3}$ which is twice larger than in BPO. These behaviors of transport properties at BBO/BPO interface are not explained within the framework of the solid solution. Therefore, the reduction of resistivity and the enhancement of carrier density at BBO/BPO interface provide the evidence of carrier-doping without introducing disorder. These considerations about transport properties maintain that BBO/BPO interface demonstrates two-dimensional superconductivity due to charge transfer.

### 2. Enhancement of the superconducting transition temperature in $BaBiO_3/BaPbO_3$ superlattices

Superconductivity was induced in a single interface of BBO/BPO by charge transfer. The introduction of the superlattice structure gives rise to a variability of the distance between interfaces. In the limit of a long superlattice period, BBO/BPO interfaces do not interact with each other, and the superconducting properties will be the same as the thin film with a single BBO/BPO interface. However, when the distance between BBO/BPO interfaces is smaller than 8.3 nm ~ $d_{\mathrm{Tinkham}}$, the overlap of interface region might recover three-dimensionality and realize the higher carrier density at the area between interfaces, leading to enhance $T_c$.

In order to increase $T_c$ using superlattice structure, we fabricated $BBO_mBPO_{3m}$ superlattices. The Bi/Pb ratio of superlattices set to be 1/3, which shows the highest $T_c$ in BPBO solid solution systems. In the $BBO_mBPO_{3m}$ superlattice, the total thickness were kept around 50 nm, and the superlattice period was modulated as a parameter of $m$ (the number of BBO layers). XRD patterns of $BBO_mBPO_{3m}$ ($m$ = 2 ~ 7) superlattices indicate that the superlattice peaks, which was never seen in $Ba(Pb_{0.75}Bi_{0.25})O_3$ film, were clearly observed at the expected positions for 4$m$ modulation.

All the superlattices showed superconductivity, and $m$ dependence of $T_c$ changed around $m$ = 5. At $m$ = 5 ~ 7, $T_c$ seemed to be saturated around 4K, implying that BBO/BPO interface dominates superconducting properties. With decreasing $m$ from 5 to 2, $T_c$ enhanced to 6.9 K systematically. One supercell of $m$ = 5 has 20 unit cells, which is comparable to $d_{\mathrm{Tinkham}}$ ~ 19 unit cells. That suggests the overlap of conductive interface area in BBO/BPO superlattices occurs at less than $m$ = 5 and $T_c$ increases due to the recovery of three-dimensionality and the enhancement of the carrier density.

## Conclusion

In this study, we demonstrated charge transfer and two-dimensional superconductivity at BPO/BBO interface. In BBO/BPO superlattices, $T_c$ was enhanced by recovering three-dimensionality and increasing the carrier density due to the overlap of conductive interface region.