Creation of Novel Material Sr_3OsO_6 with the Highest Ferromagnetic Transition Temperature among Insulators

Yuki K. Wakabayashi, Yoshiharu Krockenberger, Yoshitaka Taniyasu, and Hideki Yamamoto

Abstract

We have synthesized a novel material, Sr_3OsO_6 (Sr: strontium, Os: osmium, O: oxygen) using a unique oxide thin-film growth technique that has been developed over many years at NTT Basic Research Laboratories. The Curie temperature (T_C) value of this material, estimated from the magnetic measurements, is above 780°C, surpassing the T_C record among insulators for the first time in 88 years by more than 100°C. As Sr_3OsO_6 has been synthesized in a single-crystalline thin film form, this brand-new material is expected to be readily implemented in high-performance magnetic device applications such as magnetoresistive random access memories and magnetic sensors that work above room temperature.

Keywords: molecular beam epitaxy, magnetic oxide, spin-orbit coupling

1. Introduction

Ferromagnetism is a magnetic state in a material that gives it the properties of a magnet. In the ferromagnetic state, the net magnetic moment is large since the magnetic moments of the constituent atoms are aligned (**Fig. 1**). A ferromagnetic insulator is a magnet in which electric current cannot flow due to its high resistivity. Ferromagnetic insulators include maghemite, the first magnet that humans discovered and used as a compass. Today, ferromagnetic insulators are widely used as permanent magnets and in the microwave devices incorporated into, for instance, smartphones, cars, and computers—and such technology could not have been developed without ferromagnetic insulators. Spintronic devices, in which both the electrical and magnetic properties of electrons are utilized simultaneously, are now being extensively investigated to achieve high-speed devices with low power consumption. Ferromagnetic insulators will also serve as essential constituents that make such spintronic devices viable.

In conjunction with trends in computerization, there has been a steadily growing demand for practical devices with higher performance. In terms of temperature, stable operation even above 200°C is required. However, the record Curie temperature (T_C), which is the crucial factor determining the temperature range in which any ferri/ferromagnetic system remains stable, has stood in insulators ever since ferrite magnets[*1] were first developed over eight decades ago in the 1930s. Therefore, researchers have sought to develop the next generation of ferromagnetic insulators with high T_C values as well as to establish guiding principles to search for such materials.

*1 Ferrite magnets: Ferrite magnets are ferromagnetic insulators developed in the 1930s in Japan. They have been the most widely used magnets in the world. The major components are iron oxides, and many ferrite magnets also contain Co (cobalt), Ni (nickel), Mn (manganese), and other elements.

Fig. 1. Schematic diagram of ferromagnetism and paramagnetism.

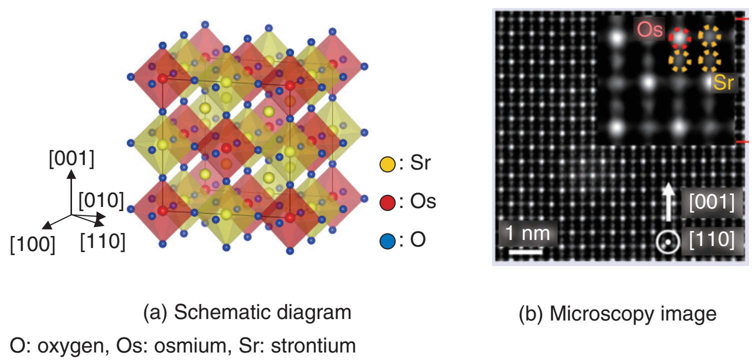


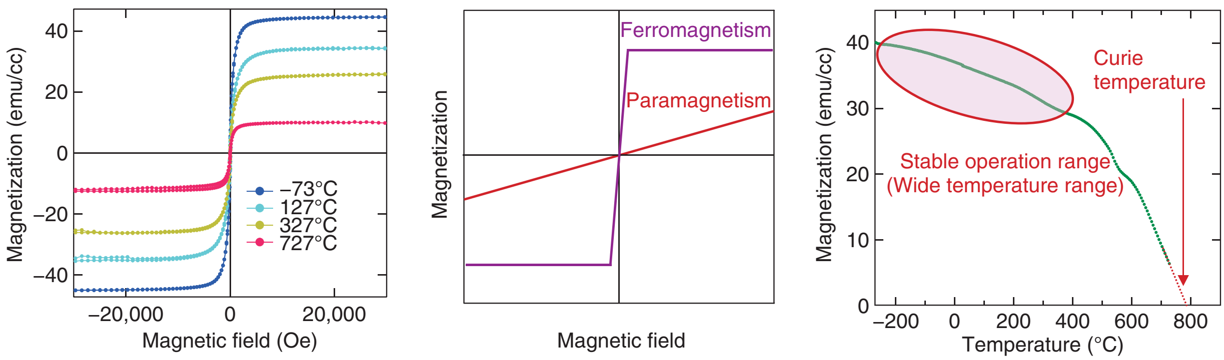
Fig. 2. Crystal structure of Sr_3OsO_6 (double perovskite).

2. Preparation of high-quality Sr_3OsO_6 thin films

Solids in which atoms are periodically and orderly arranged and thus form lattices are called crystals. Crystals that have only a single atomic arrangement over an entire volume are known as single crystals. Samples whose thicknesses range from one atomic layer to about several tens of micrometers (1 μm = 1×10^{-6} m) are called thin films. Single-crystalline thin films are synthesized on single-crystalline substrates. For microfabrication of high-performance devices, it is necessary to prepare samples in the form of single-crystalline thin films with submicrometer thicknesses. In this study, single-crystalline Sr_3OsO_6 thin films with a thickness of 300 nm (1 nm = 1×10^{-9} m) were synthesized on single-crystalline $SrTiO_3$ (strontium titanate) substrates [1].

A schematic diagram of the double perovskite structure of Sr_3OsO_6 is shown in **Fig. 2(a)**. The yellow, red, and blue spheres respectively indicate Sr (strontium), Os (osmium), and O (oxygen) atoms. Sr_3OsO_6 is a novel material synthesized in this study for the first time. In crystals, atoms are regularly ordered and form lattices. There are many kinds of atomic arrangements (crystal structures), and representative ones have specific names. One such arrangement is known as double perovskite, in which the lattice is twice as large as the perovskite structure. Many complex oxides are known to have the perovskite structure. Iodides and chlorides that have the perovskite structure have also been extensively studied recently to develop the next generation of solar cells [2].

To grow high-quality Sr_3OsO_6 thin films, precise control of the flux rate of each constituent cation (Sr, Os) is mandatory. Generally, controlling the flux of Os is a challenge because of its high melting point (3033°C). Nevertheless, we have succeeded in precisely controlling both the Sr and Os flux rates. We accomplished this by monitoring the flux rates with an atomic emission spectrometer and feeding them back to the evaporation source power supplies in real time, which enabled the synthesis of Sr_3OsO_6 thin films with the Sr and Os atoms arranged in a highly ordered structure. An atomic resolution microscopy (scanning transmission electron microscopy) image of an Sr_3OsO_6 film viewed along the [110] direction



(a) Magnetization versus magnetic field

(b) Schematic diagram of ferromagnetism

(c) Magnetization versus temperature

Fig. 3. Magnetic properties of Sr_3OsO_6.

is shown in **Fig. 2(b)**. We can clearly see the atomic ordering depicted in Fig. 2(a).

3. Ferromagnetism above 780°C in Sr_3OsO_6

As described above, we have synthesized the novel material Sr_3OsO_6 having the highest T_C among insulators by using a unique oxide thin-film growth technique that we have developed over many years. First, we measured the electrical and optical properties of the Sr_3OsO_6 thin films. The resistivity at room temperature was 75 Ω·cm, which is about 10^9 times as large as typical metals such as Au (gold) and Cu (copper). Also, resistivity increased exponentially as the temperature decreased. Furthermore, the optical band gap of Sr_3OsO_6 was found to be about 2.65 eV. All these results indicate that Sr_3OsO_6 is an insulator.

Next, we examined magnetic properties. The magnetization versus applied magnetic field curves of an Sr_3OsO_6 film is shown in **Fig. 3(a)**. It shows ferromagnetic behavior (**Fig. 3(b)**) with a finite magnetization even at the high temperature of 727°C. The magnetization versus temperature curve of an Sr_3OsO_6 film is shown in **Fig. 3(c)**. The applied magnetic field was 2000 Oe. The gradual change in the magnetization up to about 400°C is suitable for high-performance magnetic devices that can be stably operated at high temperatures (above room temperature). The T_C value, at which ferromagnetism disappears, is above 780°C, surpassing the T_C record among insulators for the first time in 88 years by more than 100°C.

In addition to the experiments, density functional theory*2 calculations were carried out by the Tsuneyuki Research Group at the University of Tokyo. These calculations revealed that the ferromagnetic insulating state of Sr_3OsO_6 originates from the large spin-orbit coupling of the 5*d* element Os. The spin-orbit coupling consists of interactions between the spin magnetic moment coming from the axial rotation of electrons and the orbital magnetic moment coming from the revolution of the charged particles (electrons) around the nucleus (**Fig. 4**). The elements in the lower rows of the periodic table are heavier than those in the higher rows, and they have a larger spin-orbit coupling. Thus, the spin-orbit coupling in Os is larger than in Fe (iron) and Co (cobalt), which are used in typical magnets. This insight into the mechanism of the emergent high-temperature ferromagnetism will open a new avenue for developing functional materials in which elements having large spin-orbit coupling play a role.

This novel material Sr_3OsO_6 has been synthesized in the form of single-crystalline thin films, which have high compatibility with device fabrication processes. This is in marked contrast to typical new oxides often synthesized in a powder or sintered polycrystalline form. Thus, Sr_3OsO_6 is expected to be readily implemented in high-performance magnetic device applications such as magnetoresistive random

*2 Density functional theory: This theory states that the energies of electrons in solids can be determined by using spatially dependent electron density $n(r)$. The word *functional*, which means the function of another function, is used since the energy is calculated as a function of $n(r)$, which is already a function of r. The electronic states of materials can be calculated and predicted from the fundamental equation that electrons follow based on this theory, without experimental data.

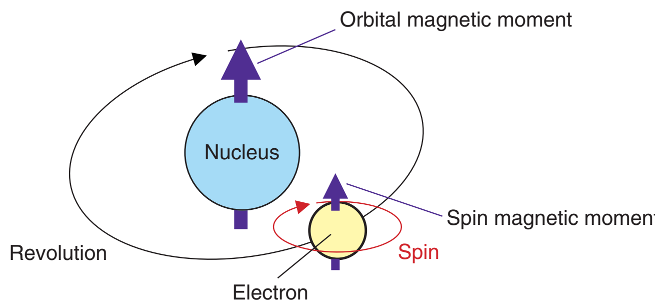


Fig. 4. Spin-orbit coupling.

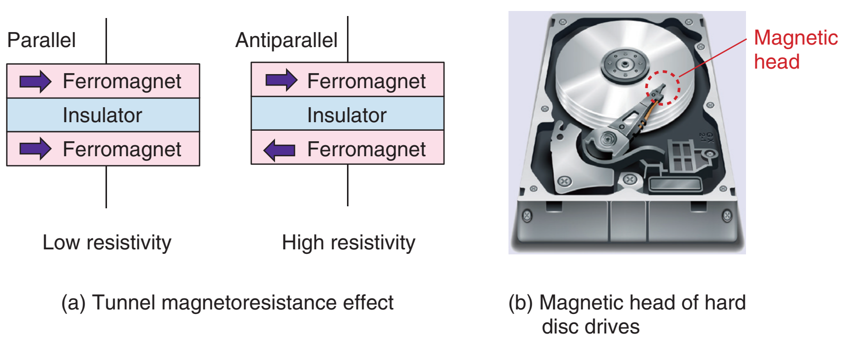


Fig. 5. Tunnel magnetoresistance and its application.

access memories (MRAMs) and magnetic sensors that work above room temperature.

4. Future outlook

In our quest to better understand the fundamentals of ferromagnetism, we will further investigate the electronic structures of Sr_3OsO_6 using advanced spectroscopy techniques provided by synchrotron radiation facilities.*3 As part of efforts to develop high-performance magnetic devices that can be operated at high temperatures, we are working on fabricating some test devices using Sr_3OsO_6 to examine the tunnel magnetoresistance effect. This effect occurs when the tunnel resistance of an insulator sandwiched between two ferromagnets changes depending on the magnetic configuration of the ferromagnets (parallel or antiparallel) (**Fig. 5(a)**). The tunnel magnetoresistance effect has been widely utilized in commercial devices such as hard disc drives (**Fig. 5(b)**), MRAMs, and magnetic sensors. Therefore, demonstration of the tunnel magnetoresistance effect in Sr_3OsO_6 will lead to progress in developing high-performance magnetic devices that work at high temperatures.

References

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[2] M. Liu, M. B. Johnston, and H. J. Snaith, "Efficient Planar Heterojunction Perovskite Solar Cells by Vapour Deposition," Nature, Vol. 501, pp. 395–398, 2013.

*3 Synchrotron radiation facilities: In synchrotron radiation facilities, we can use light with various wavelengths (synchrotron radiation) such as ultraviolet rays and X-rays. Synchrotron radiation is emitted from accelerated electrons that travel in a huge ring in an ultrahigh-vacuum environment. The versatile capabilities of such synchrotron facilities include emissions of intense and variable-wavelength light, and this enables us to perform many kinds of high-resolution spectroscopy to investigate the physical properties of specimens in detail. Therefore, synchrotron radiation facilities are also very useful for materials science research. In Japan, there are several synchrotron facilities in operation, including SPring-8 in Hyogo Prefecture and the Photon Factory in Ibaraki Prefecture.

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He received a B.S. in solid-state physics from Osaka University in 2012, and an M.S. and Ph.D. in electrical engineering from the University of Tokyo in 2014 and 2017. Since joining NTT in 2017, he has been conducting research on thin film growth of ferromagnetic oxides. He received the English Presentation Award by the Spintronics Committee of the Japan Society of Applied Physics (JSAP) at the 62nd Spring Meeting of JSAP in 2015, the Young Researcher Best Poster Award at the 9th International Conference on Physics and Applications of Spin-Related Phenomena in Solids in 2016, and the 45th JSAP Presentation Award at the 66th Spring Meeting of JSAP in 2019.

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