#### Low-field Magnetoelectric Effect at Room Temperature

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# Low-field magnetoelectric effect at room temperature

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The discoveries of gigantic ferroelectric polarization in BiFeO3 (ref. 1) and ferroelectricity accompanied by a magnetic order in TbMnO3 (ref. 2) have renewed interest in research on magnetoelectric multiferroics3,4, materials in which magnetic and ferroelectric orders coexist, from both fundamental and technological points of view5-7. Among several different types of magnetoelectric multiferroic<sup>8,9</sup>, magnetically induced ferroelectrics in which ferroelectricity is induced by complex magnetic orders, such as spiral orders, exhibit giant magnetoelectric effects, remarkable changes in electric polarization in response to a magnetic field. Many magnetically induced ferroelectrics showing the magnetoelectric effects have been found in the past several years<sup>10</sup>. From a practical point of view, however, their magnetoelectric effects are useless because they operate only far below room temperature (for example, 28K in TbMnO3 (ref. 2) and 230K in CuO (ref. 11)). Furthermore, in most of them, the operating magnetic field is an order of tesla that is too high for practical applications. Here we report materials, Z-type hexaferrites, overcoming these problems on magnetically induced ferroelectrics. The best magnetoelectric properties were obtained for Sr3Co2Fe24O41 ceramics sintered in oxygen, which exhibit a low-field magnetoelectric effect at room temperature. Our result represents an important step towards practical device applications using the magnetoelectric effects.

Hexaferrites are iron oxides with hexagonal structures and have long been used in technological applications such as permanent magnets and microwave devices because of their room-temperature ferromagnetic and insulating properties. The hexaferrites are classified into several types depending on their chemical formulae and crystal structures<sup>13-14</sup> (for example, M-type (Ba,Sr)Fe<sub>12</sub>O<sub>19</sub> and Y-type (Ba,Sr)2Met2Fe12O22 (Met = divalent metal ion), as shown in Fig. 1a and b, respectively). These hexaferrites' structures can be described as stacking sequences of the basic blocks: S-, Rand T-blocks, as shown in Fig. 1. Recently, it has been reported that some Y-type hexaferrites, such as (Ba,Sr)2Zn2Fe12O22 and Ba2Mg2Fe12O22, show magnetically induced ferroelectricity and resultant magnetoelectric effects related to modifications of spiral magnetic structures by applying a magnetic field<sup>15-18</sup>. Although the magnetic ordering temperatures of these Y-type hexaferrites are above room temperature, their magnetoelectric effects can be observed only up to ~130 K. This is mainly because these hexaferrites are not sufficiently insulating to sustain a substantial macroscopic ferroelectric polarization above ~130 K.

Our target material in the present study is one of the hexaferrites illustrated in Fig. 1c, Z-type (Ba, Sr)3Met2Fe24O41. The structure can be described as the sequence RSTSR\*S\*T\*S\* and regarded as an

alternate stacking of a 1/2 unit cell of M and a 1/3 unit cell of Y. Although most of the Z-type hexaferrites have a uniaxial magnetic anisotropy parallel to the c axis, Ba3Co2Fe24O41 is, exceptionally, a planar ferrimagnet at room temperature<sup>12</sup>. As a result of this planar anisotropy, Ba3Co2Fe24O41 is magnetically soft. In addition, it has a relatively high permeability and ferromagnetic resonance frequency. Owing to these properties, Ba3Co2Fe24O41 has been studied as one of the promising inductor materials for gigahertzrange application. Early studies suggested that Ba3Co2Fe24O41 undergoes a magnetic transition at around 230 K and has a cone of easy magnetization below this temperature12.19. The magnetic properties of Ba3Co2Fe24O41 are affected by replacing Ba with Sr. cording to recent studies on polycrystal room-temperature magnetization curve of Sr3Co2Fe24O41 does not increase monotonically up to a saturation magnetic field, but has a graded increase, which suggests that Sr3Co2Fe24O41 is not a simple rimagnet at room temperature. The shape of the magnetization curve is very similar to that in the magnetoelectric Y-type hexaferrite Ba05Sr15Zn2Fe12O22 (ref. 15). In the Y-type hexaferrite, the partial replacement of Ba with Sr modifies the superexchange interaction of the Fe-O-Fe bonds near (Ba,Sr) sites (surrounded by dashed blue ellipsoids in Fig. 1b) and stabilizes the spiral magnetic ordered state20. As the Z-type structure also contains the same structural components (surrounded by dashed blue ellipsoids in Fig. 1c), we expected that the Z-type Sr<sub>3</sub>Co<sub>2</sub>Fe<sub>24</sub>O<sub>41</sub> would show a similar spiral magnetic ordered state and a resultant magnetoelectric effect at room temperature

It is known that preparation of the pure Z-type phase is extremely difficult because other hexaferrite phases usually coexist with the Z-type during the synthesis process<sup>20–22</sup>. Figure 2a shows powder X-ray diffraction patterns for our polycrystalline samples of Sr3Co2Fe2eO41. The X-ray diffraction patterns coloured by black and red are for a sample sintered in air and for that in oxygen respectively. In both the samples, most peaks can be indexed to the Z-type structure with the space group P63/mmc and lattice parameters a = 5.87 Å, c = 52.07 Å, which demonstrates that the majority phase of these samples is Z-type Sr<sub>3</sub>Co<sub>2</sub>Fe<sub>24</sub>O<sub>41</sub>. However, some peaks (marked with asterisks in Fig. 2a) cannot be indexed to the Z-type structure, but can be indexed to other types of hexaferrite. For the sample sintered in oxygen, the impurity peaks can be indexed by U-type Sr4Co2Fe36O80 (sequence RSR\*S\*TS\*) and W-type SrCo2Fe1sO27 (RS2R\*S2\*), whereas the U-type phase almost disappears for the sample sintered in air.

Figure 2b shows the magnetization measured at 0.01 T as a function of temperature. The temperature dependence of the magnetization exhibits two clear drops at around 510K and 670 K for both the samples. Similar magnetization anomalies were

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# Magnetic Control of Ferroelectricity at Room Temperature

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#### Introduction

In the past decade, magnetoelectric multiferroics, materials that shows both magnetic and ferrolectric orders simultaneouly, have been attracting renewed interest and have been extensively studied in terms of both fundamental and technological points of view [1,2]. Among various types of magnetoelectric multiferroics, studies of magnetically-induced ferroelectrics in which the inversion simmetry breaking and resultant ferroelectricity are induced by complex magnetic orders, have been triggered almost a decade ago by the discovery of multiferroic nature in a perovskite-type rare-earh manganites TbMnO<sub>3</sub> [3]. The magnetically-induced ferroelectrics often show giant magnetoelectric effects (remarkable changes in electric polarization in response to a magnetic field), since the origin of their ferroelectricity is driven by magnetism which sensitively responds to an applied magnetic field. Thus, it is expected that the magneticallyinduced ferroelectrics provide new types of device applications by using the magnetoelectric effect, such as memory devices in which magnetic and/or ferroelectric domains are controlled by an electric and/or magnetic fields. However, their magnetoelectric effects usually occur at temperatures that are too low to be practically useful. The lacks of room-temperature magneticallyinduced ferroelectrics have significantly hampered the promise of this class of multiferroics in developing new devices. Thus, one of the grandest challenges at the present stage in this field is to design or identify room-temperature magnetically-induced ferroelectrics.

#### Hexaferrites as magnetoelectrics

Hexaferrites are iron oxides with hexagonal structures and have long been used in technological applications such as permanent magnets, microwave devices, and absorbers in the gigahertz frequency range because of their room-temperature ferromagnetic and insulating properties [4]. These compounds are classified into several types such as M-type [(Ba,Sr)Fe12O19], Y-type [(Ba,Sr)2Me2Fe12O22], Z-type [(Ba,Sr)3Me2Fe24O41] (Me=divalent metal ion). These hexaferrites' structures can be described as stacking sequences of the basic blocks: S (spinel block), R [(Ba,Sr)Fe<sub>6</sub>O<sub>11</sub>]<sup>2-</sup>, and T (Ba,Sr)<sub>2</sub>Fe<sub>8</sub>O<sub>14</sub>. Recently, it has been reported that some Y-type hexaferrites with the TST'S'T"S" stacked structure [e.g., (Ba,Sr)2Zn2Fe12O22 and Ba2Mg2Fe12O22] show magnetically-induced ferroelectricity and resultant magnetoelectric effects related to modifications of complex spiral magnetic structures by applying a magnetic field [5]. Although spin ordering temperatures of these Y-type hexaferrites are above room temperature, their magnetoelectric effects can be observed

only up to ~130 K. This is mainly because these hexaferrites are not sufficiently insulating to sustain a substantial macroscopic ferroelectric polarization above ~130 K.

### Room-temperature magnetoelectric effect in a Z-type hexaferrite

In this work, we discovered that a Z-type hexaferrite, Sr<sub>3</sub>Co<sub>2</sub>Fe<sub>24</sub> O41, exhibits a low-field magnetoelectric effect at "room temperature" [6]. Figure 1a shows the Z-type hexaferrite structure which can be described as the sequence RSTSR\*S\*T\*S\*. One of the key factors for the achievement of the room-temperature operation is a highly insulating character of polycrystalline Ztype hexaferrites heated in an oxygen atmosphere [ $\sim 10^9 \Omega cm$ ] of electrical resistivity at room temperature]. The high resistivity enables us to measure the ferroelectric polarization at room temperature. Furthermore, a recent powder neutron diffraction study proposed that Sr3Co2Fe24O41 exhibits a complex magnetic order (transverse conical order), as illustrated in Fig. 1b up to about 400 K [7]. According to former theoretical study [8], the magnetic structure can induce finite electric polarization though the so-called spin-current mechanism.



Fig.1 Schematic crystal (a) and proposed magnetic structures [at small magnetic fields (b) and large magnetic fields (c)] of Z-type Sr3Co2Fe24O41

Figures 2a and 2b display the magnetic field dependence of the magnetization and the electric polarization, respectively, at

100, 200, and 300 K for Sr<sub>3</sub>Co<sub>2</sub>Fe<sub>24</sub>O<sub>41</sub> polycrystalline samples sintered in oxygen. As seen in Fig. 2a, the magnetization increases in two steps up to the saturation magnetization. As the magnetic field increases, the magnetization shows a rapid increase from 0 to  $\sim$ 0.1 T, gently increases from  $\sim$ 0.1 T to  $\sim$ 0.7 T, and then is almost saturated at around 1 T. These features can be explained by the transformation from the transverse conical ordered state (Fig. 1b) into the ferromagnetic state (Fig. 1c). These anomalies in the magnetization accompany magnetoelectric effects. As displayed in Fig. 2b, there is almost no spontaneous polarization at zero magnetic fields. By applying a magnetic field, the electric polarization appears and shows a rapid increase up to  $\sim 0.2$  T. With the further increase of the magnetic field, the electric polarization reaches a maximum at  $0.25 \sim 0.3$  T (  $23 \mu$ C/m2 at 100 K) and then starts to decrease. Finally, the electric polarization vanishes at around 1 T where the system becomes a simple ferrimagnet. These results demonstrate that the Z-type Sr<sub>3</sub>Co<sub>2</sub>Fe<sub>24</sub>O<sub>41</sub> exhibits the magnetoelectric effect at a wide range of temperatures including room temperature. The room-temperature ME effect can be understood in terms of the appearance of the electric polarization which is induced by the transverse conical magnetic structure through the spin-current mechanism [8].



Fig.2 Magnetic-field dependence of (a) magnetization and (b) electric polarization at 100. 200, and 300 K for a polycrystalline sample of Sr3Co2Fe24O41 sintered in oxygen.

In the Z-type hexaferrite, a potential use of the magnetoelectric effect in practical device applications is demonstrated, i.e., a sequential switching of the electric polarization by oscillating magnetic fields between 0 and 0.25 T (Fig. 3a) at 300 K. As displayed in Fig. 3b, reproducible variations of the electric polarization were observed without any decays in their magnitudes. In addition, the signs of the magnetoelectric signals are switchable with the polarity of a poling electric field (Compare Figs. 3b and 3d). Thus, the low-field magnetoelectric effect observed in the Z-type hexaferrite ceramics at room temperature has the promise of practical device applications including non-volatile memory where information is stored as electrically-detectable and -controllable spin-helicity, as schematically illustrated in Fig. 3e.



Fig.3 Room-temperature magnetoelectric effect of Sr3Co2Fe24O41 polycrystalline ceramics sintered in oxygen. Oscillating electric polarization responding to periodically varying magnetic fields between 0 and 0.25 T (a,c). The data for (b) and (d) were obtained after poling at plus and minus electric fields, respectively. (e) Schematic illustrations of electrically-detectable and -controllable spin-helicity.

#### Summary

A Z-type hexaferrite Sr3Co2Fe24O41 has been found to exhibit a low-field magnetoelectric effect "at room temperature". The discovery clearly demonstrates the magnetic-field control of ferroelectricity at "room temperature", and represents an important step toward practical applications using the magnetoelectric effect. The results presented here provide the promise of practical magnetoelectric device applications including non-volatile memory where information is stored as electrically-detectable and -controllable spin-helicity.

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### Engineering

Surface-Plasmon Holography with White-Light Illumination Paper in journals: this is the first page of a paper published in *Science*. [Science] 332, 218(2011)

We have constrained the parameters of the BC pair by modeling the short-period eclipses in the Kepler bandlusing the jktebop code (15, 17). The ratio of the radii of the B and C commonents is poorly constrained at present, partly because of A component contributes 99.29% of the system V band, we find  $M_V(B) = 5.6$  and  $M_V(C) = 6.1$ . Such absolute magnitudes indicate spectral types of G8 V and K11 V for stars B and C, respectively (18). Because we do not have independent measurements of Ter for the BC pair, we can only es-0.1 M. each (6

One puzzling feature of the system is the amplitude in all the other phases of the wide similar properties (6). The frequency content of the light curve suggests an intimate link to tidal effects in the triple system, with the first four dominant peaks in the power spectrum identifiable as simple linear combinations of the two orbital frequencies. On the other hand, solarlike oscillations (meaning those excited by nearsurface convection, as in the Sun but also observed in red giants) that are expected to produce an equidistant series of peaks in the power spectrum are not visible, even though all stars with similar parameters in the Kepler database do show clear evidence of these oscillations. in other words, the convectively driven solarlike oscillations that we would expect to see in a giant of this type seem to have been suppressed (5).

In a recent compilation of 724 triple stars 10. R. Hanbury Brown et al., Mon. Not. R. Astron. Siz. 167, (19), there is only one system with an outer orbital period shorter than that of HD 181068 -λ Tau, for which Peut = 33.03 days). Carter et al. (20) reported the discovery of KOI-126 with a similarly the low sampling rate of the Kepler LC data. The short outer pericd (Post = 33.92 days). Extremely compact hierarchical triple systems form a very light in the Keyler passband, and the BC pair small minority of hierarchical triplets, withouly 7 contribute 0.44% and 0.27%, respectively. Taking of the catalogized 724 systems having outer pethe V-band absciute magnitude of HD 181068 A riods shorter than 150 days. Furthermore, HD to be  $M_{\nu}(A) = -0.3$  and assuming that our results 181068 and KDI-126 have the highes: outer for the Kepler passband are representative of the mass ratios [~ 1.1 and 3, defined as mA (mB + m<sub>C</sub>)] among the known systems. In 97% of the known hierarchical triplets before the Kenter era. the mass of the close binary exceeded that of the wider companion, and even the largest outer mass ratio remained under 1.5. It is not yet clear timate their masses based on their spectra, types, whether this rarity of such systems is caused by an This indicates that their masses are about 0.7 ± observational selection effect or has an underlying stellar evolutionary or dynamical explanation.

Its properties make HD 181068 an ideal target short-period fluctuations that have the largest for dynamical evolutionary studies and fortesting amplitudes when the BC pair is behind star A, tidal friction theories. Because of its competeness while remaining apparent with a slowly changing and its massive primary, we can expect shortterm orbital element variations on two different orbit. We have investigated this variability of HD time scales of 46 days (i.e., with period of  $P_{A-BC}$ ) 181068 A with a detailed frequency analysis and and about 6 years ( $P_{A-BC}^{-2}/P_{BC}$ ), the time scale of a comparison to other red giant stars that have the classical apeidal motion and nodal regression (21), which for the triply eclipsing nature could be observed rellatively easily.

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- Surface-Plasmon Holography with White-Light Illumination

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The recently emerging three-dimensional (3 )) displays in the electronic shops imitate depth illusion by rescence sensor (5), solar cell (6), plasmonic laser overlapping two parallax 2D images through either polarized glasses that viewers are required to wear or (7, 8), nanomicroscopy (9, 10), super-lens (11, 12) lenticular lenses fixed directly on the display. Holography, on the other hand, provides real 3D imaging, and photodynamic cancer cell treatment (...3). although usually timiting colors to monochrome. The so-called rainbow holograms-mounted, for example, We report an application of SPP to three on credit cards-are also produced from parallax images that change color with viewing angle. We report dimensional (3D) color holography with whiteon a holographie technique based on surface plasmons that can reconstruct true 3D color images, where the colors are rewonstructed by satisfying resonance conditions of surface plasmon polaritons for individual <sup>1</sup>RIKEN, Wako, Salterna 351-0198, Japan. <sup>2</sup>Department of Ro botics and Mechatranics, Tokyo Denki University, Chayoda ku, Tokyo 101-8457, Japan. <sup>1</sup>Department of Applied Physics and Photonics Advanced Research Center, Osaka University, Suita, wavelengths. Such real 3D color images cam be viewed from any angle, just like the original object oble mutal films, such as silver and gold wave in optical frequency region. The quantum Osaka, 565-0871, Ilipan,

foil, contain free electrons that collective- of this surface wave is called surface p-asmon V ly oscillate and propagate as the surface polariton (SPP)-1). The electromagnetic field gen-

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#### Supporting Online Material

Materials and Methods Tables \$1 to \$3 SOM Data

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enated by SPP can be enhanced and strongly confined spatially in the near field (with the distance less than the wavelength) from the metal surface as a nonirradiative evanescent field (2, 2). The ability to confine and enhance the optical field to the vicinity of the metal surface or nanometal particle has been amplied to immuno-sensor (4), fluo-

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