

Impurity Substitution Effect on Magnetoelectric Properties of $\text{CaBaCo}_4\text{O}_7$ Crystals

Ryosuke Oda¹, Ryo Kajihara¹, Kosuke Nishina¹, Mitsuru Akaki²,
Haruhiko Kuroe¹, and Hideki Kuwahara¹

¹ Faculty of Science and Technology, Sophia University, Japan

² Center for Advanced High Magnetic Field Science, Osaka University, Japan
ryosuke-o@sophia.ac.jp

Abstract

We have investigated effects of impurity substitution of Fe for Co sites on magnetic and dielectric properties in $\text{CaBa}(\text{Co}_{1-x}\text{Fe}_x)_4\text{O}_7$ crystals in magnetic fields. The non-doped compound, $\text{CaBaCo}_4\text{O}_7$ with the polar space group $Pbn2_1$, shows a large change of electric polarization ΔP along the c axis below a ferrimagnetic transition temperature. With increasing x , the transition temperatures for the ferrimagnetic and ferroelectric-like phases are shifted towards lower and these phases are completely collapsed above $x=1.56\%$. We have also investigated the magnetic field effects for $\text{CaBa}(\text{Co}_{1-x}\text{Fe}_x)_4\text{O}_7$ crystal with a doping level $x=0.5\%$ where the ferrimagnetic and ferroelectric-like phases sustain. Then a relatively large magnetocapacitance, $\Delta\varepsilon(H)/\varepsilon(0) \equiv [\varepsilon(H) - \varepsilon(0)]/\varepsilon(0)$, of 45% at 58 K was observed, which is not significantly reduced from the parent compound.

Keywords: magnetoelectric effect, multiferroic, cobalt oxides, impurity substitution, ferrimagnetic transition

1 Introduction

Studies of the magnetoelectric (ME) effect, such as control of electric polarization (magnetization) by magnetic (electric) fields, have been attracting revived attention. Many novel multiferroic materials have been found since a gigantic ME effect was discovered in TbMnO_3 [1]. One of such newly-discovered intriguing multiferroic materials is $\text{Ca}_2\text{CoSi}_2\text{O}_7$, which shows spin-driven electric polarization in a “staggered” antiferromagnetic state [2]. In this system, electric polarization is explained not by the well-accepted spin-current model but by the spin-dependent p - d hybridization model [3]. Another example of the remarkable multiferroic materials is a so-called 114 family of compounds focused on in this work, which has been intensively investigated as novel magnetic systems. One of these 114 compounds, $\text{CaBaCo}_4\text{O}_7$ with the polar space group $Pbn2_1$, has recently attracted much interest due to its giant change of electric polarization ΔP , associated with

ferrimagnetic ordering below $T_c=64$ K. One possible origin of ΔP is proposed to be magnetostriction, which is supported by the large change of the lattice parameters at T_c [4]. To further investigate the origin of the large ΔP and the impurity substitution effects, we have systematically studied the ME properties of pristine CaBaCo₄O₇ and its impurity-substituted derivatives CaBa(Co_{1-x}Fe_x)₄O₇ crystals in magnetic fields.

The presently-focused CaBaCo₄O₇ crystal is consisting of a layered structure the CoO₄ tetrahedra (Fig. 1). At room temperature (RT), the space group of CaBaCo₄O₇ is $Pbn2_1$ which breaks inversion symmetry. A spontaneous electric polarization along the c axis is expected from the noncentrosymmetric space group $Pbn2_1$. At 64 K, the magnetization of the CaBaCo₄O₇ crystal sharply rises along the a and b axes [5]. The saturated magnetization is much smaller than fully polarized Co spins, which suggests that magnetization below 64 K is due to the ferrimagnetic (weak ferromagnetic) component [5]. Neutron powder diffraction results indicate that all Co spins lie within the easy ab plane, i.e., parallel to the kagome and triangular layers [6]. In our previous studies, we have found that electric polarization is accompanied by ferrimagnetic transition and emerges along the b and c axes, which were evidenced by measurements of the anisotropic ME properties of CaBaCo₄O₇ crystal [5].

According to the report on the derivatives of CaBaCo₄O₇ [7], electron- or hole-doping by substituting Y for Ca or K for Ba induces a drastic change in the crystal structure and resultant magnetism. In addition, substitution of diamagnetic Zn for Co sites was reported to cause a switch from ferrimagnetism to antiferromagnetism in the ground state [8]. Furthermore, a study of CaBaFe₄O₇ in which Co sites were completely substituted by Fe shows that the crystal structure remains unchanged and magnetic transition temperature rises to 270 K [9]. However, there is no report on the dielectric properties of CaBaFe₄O₇ or CaBa(Co_{1-x}Fe_x)₄O₇. In this study, we aim to clarify the substitution effect on the ferrimagnetic transition temperature and resultant dielectric properties of CaBaCo₄O₇ by introducing Fe to Co sites, corresponding to CaBa(Co_{1-x}Fe_x)₄O₇ crystals. We have also investigated the ME properties of (Ca_{1-x}Sr_x)BaCo₄O₇ and Ca(Ba_{1-x}Sr_x)Co₄O₇ crystals for comparison.

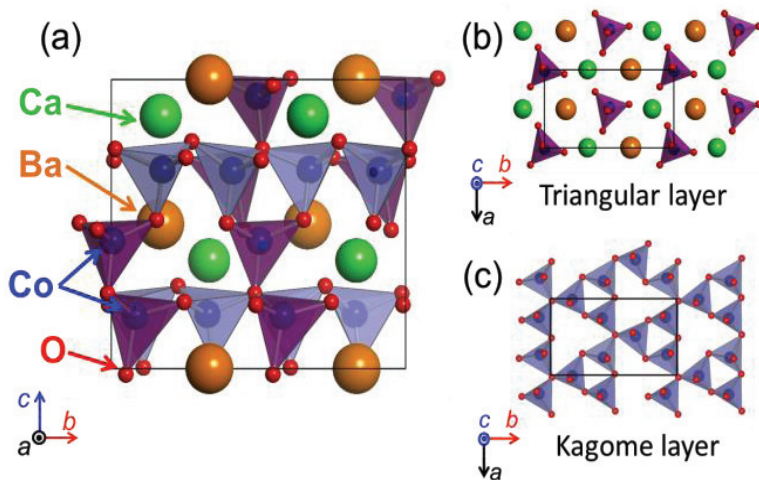


Figure 1. (a) Schematic crystal structure of CaBaCo₄O₇ projected onto the bc plane. (b) Triangular and (c) Kagome layers projected onto the ab plane. Rectangular boxes represent boundaries of the unit cell [5].

2 Experiment

Crystalline samples of CaBa(Co_{1-x}Fe_x)₄O₇, (Ca_{1-x}Sr_x)BaCo₄O₇, and Ca(Ba_{1-x}Sr_x)Co₄O₇ were prepared as follows. We first prepared the polycrystalline samples using CaCO₃, BaCO₃, Co₃O₄, SrCO₃, and Fe₂O₃ as starting materials. The mixed powders with an appropriate molar ratio were calcined at 1173 K for 24 h in air with an intermediate grinding. Then, the calcined powders were pressed into a rod shape (5 mm diameter × 100 mm) and sintered at 1373 K for 12 h in air. The crystalline samples were grown from the sintered rods with a floating zone method at a feed rate of 0.2 mm/h under flowing air of 2.5 atm. We performed powder X-ray diffraction (XRD) measurements for the pulverized crystals. Then we have calculated lattice parameters from the XRD patterns by using the commercial profile-analysis program TOPAS (D8 Advance, Bruker). We confirmed that most of the peaks are well fitted and the lattice parameters and unit cell volume systematically change with impurity concentration. The crystalline samples were randomly cut into a plate-like shape with the size larger than a single crystallographic domain size to average the magnetic and electric anisotropies. Magnetic properties were measured with the Physical Property Measurement System (PPMS, Quantum Design). Magneto-dielectric properties were measured with a conventional two-terminal method using a temperature-controllable cryostat equipped with a superconducting magnet that can provide a magnetic field up to 8 T.

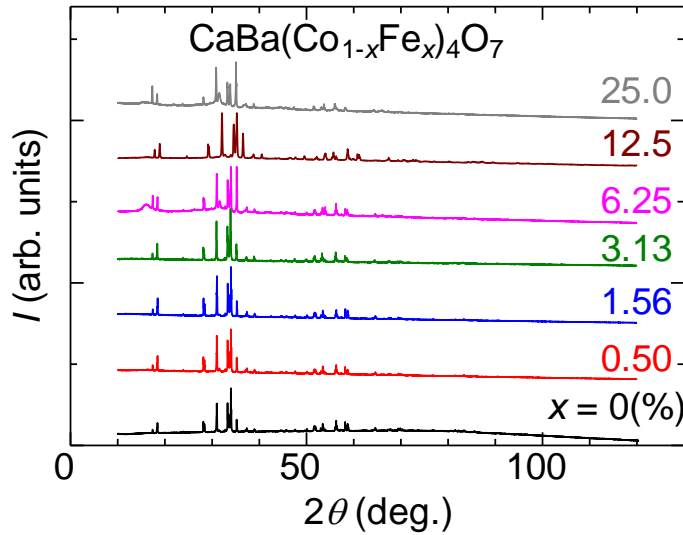


Figure 2. XRD patterns for pulverized CaBa(Co_{1-x}Fe_x)₄O₇ crystals with $0 \leq x \leq 25\%$ at room temperature. The lattice parameters calculated from above XRD patterns for *a* and *c* axes systematically increase, whereas that of *b* axis shrinks with increase of *x*.

3 Results and discussion

In Fig. 3 we show the temperature dependence of the magnetization, specific heat divided by temperature, and dielectric constant of CaBa(Co_{1-x}Fe_x)₄O₇ crystals with $0 \leq x \leq 25.0\%$. The magnetization curve in Fig. 3(a) shows that the magnetic moment sharply rises at 64 K for $x = 0$ and at

54 K for $x = 0.5\%$, while it does not change for $1.56\% \leq x \leq 25.0\%$. This indicates that the ferrimagnetic state disappears for $1.56\% \leq x \leq 25.0\%$. Measurements of specific heats (Fig. 3(b)) and dielectric constants (Fig. 3(c)) show two anomalies for $x = 0$ and 0.5% , while the two dielectric peaks and specific-heat peak at low temperatures do not appear for $1.56\% \leq x \leq 25.0\%$. However, the peak in

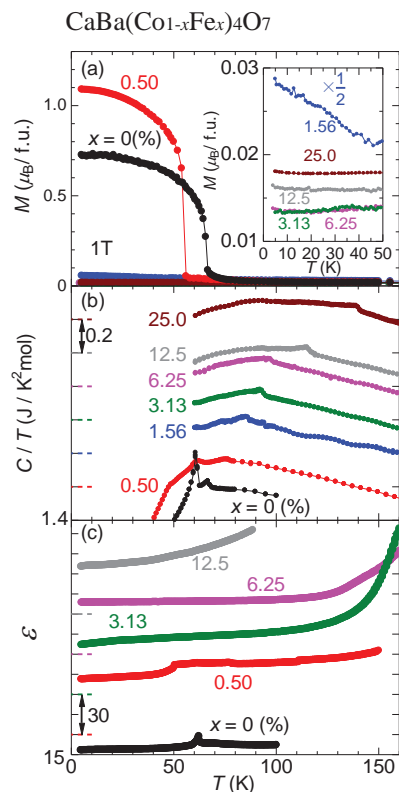


Figure 3. Temperature dependence of (a) magnetization, (b) specific heat divided by temperature, and (c) dielectric constant for CaBa(Co_{1-x}Fe_x)₄O₇ crystals with $0 \leq x \leq 25\%$. Inset in (a) shows a magnification for $1.56 \leq x \leq 25\%$. Vertical axes in (b) and (c) are shifted for clarity.

specific heat at high temperatures remains and rises toward higher temperatures with increasing x . These results indicate that the two dielectric peaks and specific-heat peak at low temperatures correspond to the magnetic transition temperature, while the specific-heat peak at high temperatures is not related to the magnetic transition temperature; the origin of that peak is not yet clarified. The ferrimagnetic and ferroelectric-like phases in low temperatures can be easily destroyed by introducing the very small amounts of magnetic impurity Fe to Co sites. The complicated magnetic structure of the ferrimagnetic order of Co $3d$ spins seems to be fragile for the Co-site substitution. For comparative studies, we have also investigated the substitution of Sr²⁺ for Ca²⁺ or Ba²⁺ sites in CaBaCo₄O₇ with a low substitution level, corresponding to (Ca_{1-x}Sr_x)BaCo₄O₇ and Ca(Ba_{1-x}Sr_x)Co₄O₇ crystals. In these systems, the ferrimagnetic and ferroelectric-like phases can survive by introducing homovalent Sr to Ca or Ba site up to $x = 2\%$ (not shown).

Let us move on to the magnetic-field effect on the magnetic and dielectric properties in CaBa(Co_{1-x}Fe_x)₄O₇. Figure 4 shows the temperature dependence of magnetization, specific heat divided by temperature, and dielectric constant of CaBa(Co_{1-x}Fe_x)₄O₇ for $x = 0$ and 0.5% in a (nearly) zero or several magnetic field(s). In both samples, the magnetic transition temperature, specific-heat

peak, and dielectric-constant anomaly shift toward higher temperatures with increasing magnetic fields. This is due to the stabilization of the weak ferromagnetic component of the ferrimagnetic phase by application of magnetic fields, which also induces the stabilization of the resultant ferroelectric-like phase. In addition, the effect of magnetic field on transition temperatures for $x = 0.5\%$ seems to be more pronounced than that for $x = 0$. Indeed, the relative increase ratio of transition temperature against magnetic fields for $x = 0.5\%$ is larger than that of $x = 0$ when we compare them at the normalized scale of temperature by each phase transition temperature. In addition, we compare both samples in a respect of maximum value of magnetocapacitance near above the ferrimagnetic transition. In the previous study, we observed the magnetocapacitance, defined by $\Delta\varepsilon(H)/\varepsilon(0) \equiv [\varepsilon(H) - \varepsilon(0)]/\varepsilon(0)$, to be over 50% at 68 K for $x = 0$ [5]. In this study, it reaches 45% at 58 K for $x = 0.5\%$, as estimated from Fig. 4(f). We expect that the small impurity substitution induces weakening of the robustness of magnetic and electric domains and the enhancement of the resultant magnetocapacitance. Unfortunately the maximum value of magnetocapacitance in the substituted-sample is nearly the same value as that of the pristine sample in site of our simple expectation. To reveal the substitution effect more deeply, we should measure other parameters such as oxygen contents because it is easy to deviate from ideal oxygen stoichiometry in this 114 compound.

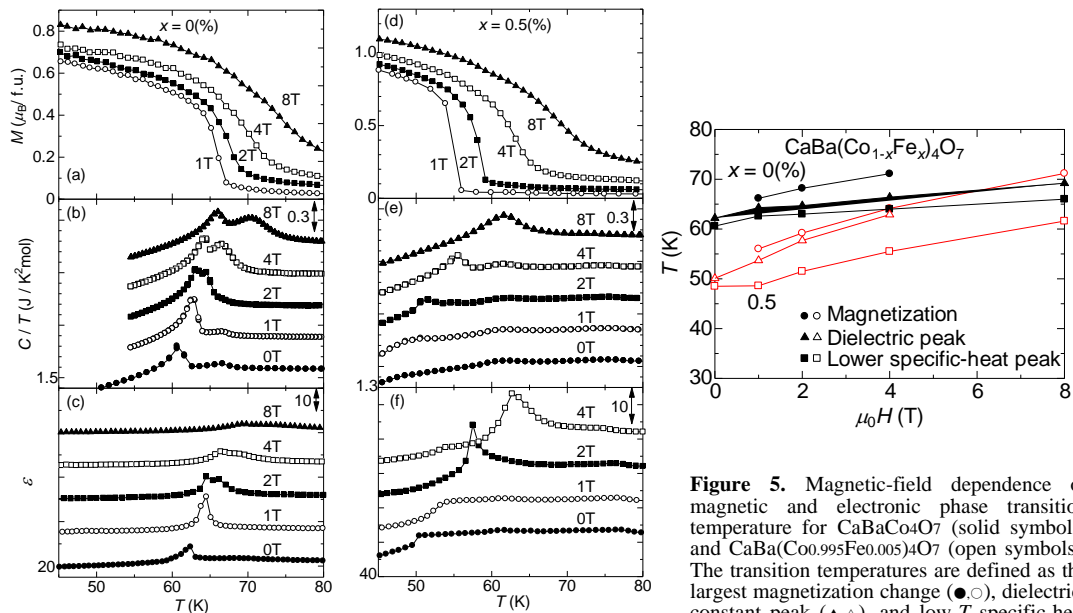


Figure 4. Temperature dependence of (upper panels (a), (d)) magnetization, (middle panels (b), (e)) specific heat, and (bottom panels (c), (f)) dielectric constant of (left) CaBaCo₄O₇ and (right) CaBa(Co_{0.995}Fe_{0.005})₄O₇ in several magnetic fields. Vertical axes in (b), (c), (e), and (f) are shifted for clarity.

Figure 5. Magnetic-field dependence of magnetic and electronic phase transition temperature for CaBaCo₄O₇ (solid symbols) and CaBa(Co_{0.995}Fe_{0.005})₄O₇ (open symbols). The transition temperatures are defined as the largest magnetization change (\bullet , \circ), dielectric-constant peak (\blacktriangle , \triangle), and low- T specific-heat peak (\blacksquare , \square).

4 Summary

We have successfully synthesized the series of high quality crystals of CaBa(Co_{1-x}Fe_x)₄O₇ by the floating zone method. Based on the systematic measurements of magnetization, specific heat, and dielectric constant as a function of temperature and magnetic field, we have found that small substitution level of Fe for Co sites ($x=1.56\%$) drastically collapses the ferrimagnetic and ferroelectric-like phases. Furthermore, the observed magnetocapacitance $\Delta\varepsilon(H)/\varepsilon(0) \equiv [\varepsilon(H) - \varepsilon(0)]/\varepsilon(0)$ of 45% for $x=0.05\%$ is not significantly degraded compared with the parent compound. We could not attain the enhancement of magnetoelectric properties by introducing Fe to Co sites. However, we believe that the end material of CaBaFe₄O₇ would be another candidate for novel multiferroic material showing gigantic ΔP like the parent compound. Therefore we will further investigate the series of 114 compounds to achieve novel magnetoelectric functionalities.

Acknowledgements

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