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Electric polarization enhancement in multiferroic CoCr$_2$O$_4$ crystals with Cr-site mixing

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Single crystals of multiferroic cobalt chromite Co(Cr$_{2-x}$Co$_x$)O$_4$ have been grown via several methods to have different Co^{3+} doping levels (x=0.0, 0.14, and 0.18). Under magnetic fields, all the crystals display electric polarization reversal below their spiral spin ordering temperatures. We find that both saturated electric polarization and magnetization under magnetic fields increase significantly with the increase in x. This result can be qualitatively explained by a broken balance between at least two electric polarization contributions existing in CoCr$_2$O$_4$ and is expected to be useful in tailoring electric polarization in similar kinds of multiferroics. © *2009 American Institute of Physics.* [DOI: 10.1063/1.3076102]

Recently, multiferroics, which have two or more ferroic orders in a material system, have attracted considerable attention[1] owing to their potential applications in various devices such as multibit memories[2] or sensitive magnetic field sensors.[3] Furthermore, the scientific interest in understanding the origin of multiferroicity and related strong magnetoelectric coupling has triggered a surge of research activities in this field.[4] A newly emerging multiferroic system that exhibits such strong magnetoelectric coupling is the spiral magnet, in which ferroelectricity is induced by the spiral spin ordering.[5,6]

Spinel cobalt chromite CoCr$_2$O$_4$ is a new spiral magnet that has been recently found to exhibit strong magnetoelectric coupling. It shows concomitant long-range spiral (conical-type) spin ordering and ferroelectric transitions at T_S=24–27 K (Refs. 7–10) and a subsequent lock-in transition below T_L=12.5–14 K, where an incommensurate-to-commensurate magnetic transition occurs.[11,12] Thus, a finite electric polarization (P) develops at T_S, accompanied by a sharp decrease in the dielectric constant ε. An additional change in ε is also observed at T_L. More interestingly, P reversal is observed below T_S when a magnetic field of H $\sim$ 0.5 T is applied.[12] This feature can be advantageous for designing novel devices such as H-controlled ferroelectric memories. However, the magnitude of P still needs to be enhanced for practical applications. Due to the intrinsically small P values as often observed in spiral magnets, the saturated value of P at H=0.5 T reaches only $\sim$2 μC/m^2 in CoCr$_2$O$_4$.[12] Thus, it is necessary to increase P value of the spiral magnet by modifying their material properties.

In this letter, we report the observation of enhanced electric polarization in Co(Cr$_{2-x}$Co$_x$)O$_4$ single crystals with Cr-site mixing. By following different crystal growth methods, we control the Co ion content (x) in the Cr-sites to obtain x=0.0, 0.14, and 0.18. We find that with an increase in x,

both magnetization (M) and P increase significantly, while the magnetoelectric coercive field decreases. These observations suggest that Cr-site mixing causes an imbalance between at least two competing P components in the stoichiometric compound.

Single crystalline Co(Cr$_{2-x}$Co$_x$)O$_4$ samples were grown by the flux method and chemical vapor transport method. In the former, CoO and Cr$_2$O$_3$ powders in a 1:1 molar ratio were mixed with PbO, PbO$_2$, and PbF$_2$ flux, heated in a Pt crucible at 1260 °C for 12 h, and then slowly cooled to 900 °C.[13] All of the resultant crystals had octahedral shape with a typical lateral size of $\sim$3–4 mm and were confirmed to be cubic spinels at room temperature by x-ray diffraction.[14] Different amounts of Co (x>0) could be doped into the Cr site by controlling the cooling speed between 2 °C/h (sample F#1) and 1 °C/h (sample F#2). The stoichiometric crystal (C#1; $x\approx0$) could be obtained by the chemical vapor transport method with Cl$_2$ gas as the transport agent.

The valence states of the Co ions in the three different samples were examined by Co $L_{2,3}$-edge x-ray absorption spectroscopy (XAS), as shown in Fig. 1. The XAS measurements were performed at the 2A beamline at Pohang Light Source (PLS). The XAS spectra of C#1 show a multiplet structure observed typically in the Co^{2+} ion in a tetrahedral site symmetry; this pattern agrees well with that of a reference sample.[15] However, in the spectra of F#1 and F#2, an intense additional peak corresponding to the spectral weight from Co^{3+} ions is observed. In particular, the spectral weight of Co^{3+} is greater in F#2 than in F#1. Considering the fact that in a normal spinel structure, Co^{2+} and Co^{3+} ions prefer to reside in the tetrahedral A-site and the octahedral B site, respectively, it is likely that the B-sites in the flux-grown samples are occupied by both Cr^{3+} and Co^{3+} ions, which result in the B-site ionic mixing. The chemical compositions of the obtained crystals were determined by electron probe microanalysis, and the flux-grown crystals were confirmed to contain large excess Co ions. The average values of x in our

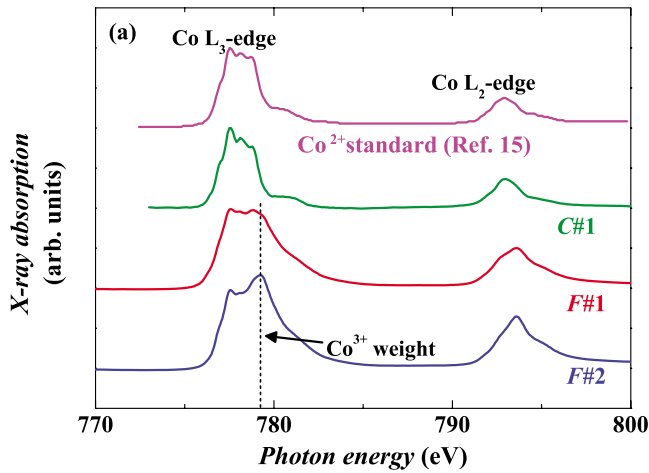a)Author to whom correspondence should be addressed. Electronic mail: khkim@phya.snu.ac.kr.

FIG. 1. (Color online) X-ray absorption near Co *L*-edge for the three kinds of samples Co(Cr$_{2-x}$Co$_x$)O$_4$ [x=0.0 (*C*#1), 0.14 (*F*#1), and 0.18 (*F*#2)] along with the Co^{2+} standard data (Ref. 15). Dashed line at the Co L_3-edge indicates the photon energy corresponding to the Co^{3+} weight.

Co(Cr$_{2-x}$Co$_x$)O$_4$ crystals were estimated to be 0.0 ± 0.02, 0.14 ± 0.02, and 0.18 ± 0.1 for *C*#1, *F*#1, and *F*#2, respectively. In particular, a certain degree of spatial variation in *x* was observed in the case of *F*#2.

B-site mixing brings about marked variations in the physical properties. Figure 2 shows the temperature dependences of *M*, Δ*ε*/*ε*(5 K) {≡[*ε*(*T*)−*ε*(5 K)]/*ε*(5 K)}, and specific heat over temperature (*C*/*T*) for the three samples. At T_S, *M* and Δ*ε* of *C*#1 show the sharpest transition feature, while *F*#1 and *F*#2 show increasingly smeared features. Consistently, the *C*/*T* data for *C*#1 display a highly pronounced peak at T_S, but those for *F*#1 and *F*#2 give systematically suppressed peaks. Moreover, even at T_L, the transition features are well pronounced in *C*#1 but not in *F*#1 and *F*#2. Temperature-dependent *M*/*H* and *C*/*T* measurements were carried out to identify the magnetic transition temperatures of the three samples. It is found that the *B*-site mixing results in suppressions of T_S from 26.5 K (for *C*#1) to 24 K (for *F*#1 and *F*#2) and the ferrimagnetic ordering temperature T_C from 97 K (*C*#1) to 95 K (*F*#1 and *F*#2).
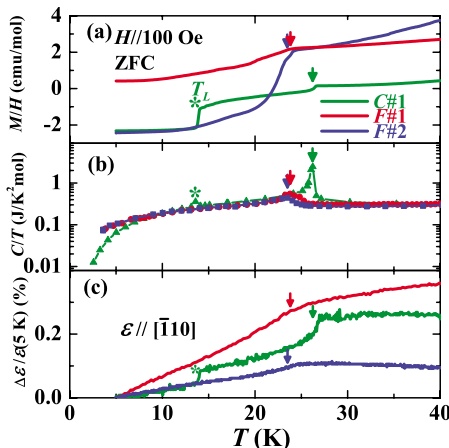

FIG. 2. (Color online) Temperature dependence of (a) *M*/*H* curves measured at *H*=100 Oe after zero-field cooling, (b) *C*/*T*, and (c) Δ*ε*/*ε*(5 K) ≡[*ε*(*T*)−*ε*(5 K)]/*ε*(5 K). In each curve, colored arrows and asterisks represent the spiral ordering temperature T_S and the lock-in transition temperature T_L, respectively.
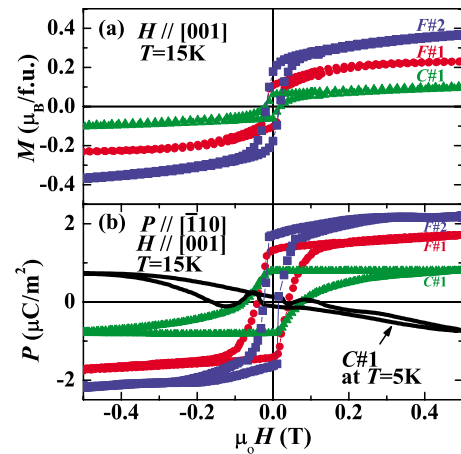

FIG. 3. (Color online) Magnetic field dependence of (a) *M*∥[001] and (b) *P*∥[$\bar{1}$10] measured at *T*=15 K for *C*#1, *F*#1, and *F*#2. In (b), a *P* vs *H* loop of *C*#1 at *T*=5 K is also plotted.

Despite the apparent decrease in T_S and T_C, we find that below T_S, both *P* and *M* are greater in the flux-grown crystals than those in *C*#1. This unexpected behavior is summarized in the magnetic (*M* versus *H*∥[001]) and magnetoelectric (*P*∥[$\bar{1}$10] versus *H*∥[001]) hysteresis loops shown in Fig. 3. The saturation values of *M* (M_S) and *P* (P_S) of *C*#1 at *H*∼0.5 T are as small as 0.09 μ_B/f.u. and 0.80 μC/m^2, respectively. However, M_S and P_S of *F*#2 (*F*#1) are enhanced up to 0.47 μ_B/f.u. (0.37 μ_B/f.u.) and 2.16 μC/m^2 (1.72 μC/m^2), respectively. The remnant *M* and *P* values at *H*=0 T also show similar trends. Through temperature-dependent measurements at *H*=0 T (data not shown), we have confirmed the increase in *M* and *P* in the flux-grown samples. Furthermore, we find that the coercive field in the *P* versus *H* curve decreases with an increase in *x*; the coercive field of *P* changes from 720 Oe for *C*#1 (smallest *x*) to 400 Oe for *F*#1 and 240 Oe for *F*#2 (largest *x*). Thus the *B*-site mixing is effective in achieving the soft *P*-switching with magnetic fields. From independent studies in the polycrystalline samples with controlled values of *x*, we also confirm the same trends; the *x*≈0 sample has the smallest P_S and the largest coercive field. Based on all these observations, we conclude that crystals with excess Co ions in the *B*-site indeed have increased P_S and M_S values and decreased magnetoelectric coercive fields.

To qualitatively understand the origin for the enhanced M_S and P_S, we first consider the spin configuration of the stoichiometric CoCr$_2$O$_4$. Taking into account the spin-only values, we estimate the magnetic moments of both Co^{2+} and Cr^{3+} as 3 μ_B. It is noteworthy that the M_S value of this compound is approximately the same (0.1 μ_B/f.u.) below and above T_S. A neutron scattering study[9] on a flux-grown sample has shown that below T_S, the long-range spiral order is stabilized, and the cone angles along the +*z*-axis correspond to 48°, 32°, and 152° for *A*-, *B*1-, and *B*2-sites, respectively [Fig. 4(a)]. The value of M_S calculated using these cone angles is 0.3 μ_B/f.u., which is close to the experimental value observed for *F*#1. This can explain why M_S has a small value below T_S. The similar value of M_S even above T_S (0.1 μ_B/f.u.) indicates that the Co^{2+} ion and the two Cr^{3+} ions continue to maintain a noncollinear spin arrangement above T_S, which can be ascribed to a Yafet–Kittel[16] state or a
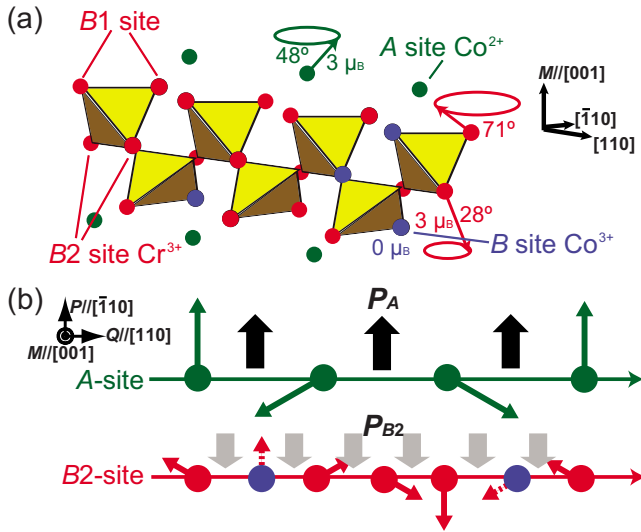
FIG. 4. (Color online) (a) Spiral spin ordering patterns of each Co^{2+} and Cr^{3+} site below T_S, reproduced from Refs. 9 and 12. (b) Suggested spin ordering patterns and directions of P_A and P_{B2}. Co^{3+} in the $B2$-site can reduce the spin moment (dotted arrows) as well as P_{B2}, resulting in a net increase in total $M\|[001]$ and P $(=P_A+P_{B2})\|[\bar{1}10]$.

short-range spiral order.[9] The exact nature of the spin order above T_S remains to be clarified.

The Co^{3+} ions in the Cr-sites are likely to be in a low spin-state at low temperatures, thereby becoming nonmagnetic. If the spin directions are assumed to be rigid even with the Cr-site mixing, substitution of equal amounts of nonmagnetic Co^{3+} into the $B1$- and $B2$-sites is likely to reduce the negative M_z contribution from the B-sites because a sum of the Cr^{3+} spin moments along $[001]$ from the $B1$- and $B2$-sites is negative [Fig. 4(a)]. This, in turn, will result in a net enhancement of the total $M_S\|[001]$, a sum of M_z contributions from the A- and B-sites. The increase in $M_S\|[001]$ is thus understood as the broken balance between the spin moments directing along the $+z$ and $-z$-axes in the sample with $x\approx0$.

It is likely that the competing components exist in the electric polarization as well. Creation of electric polarization in $CoCr_2O_4$ can be understood by the spin-current model,[5,12] in which $P\propto e\times Q$ where e is the spin rotation axis (z, i.e., $[001]$), and Q is the propagation vector of the spiral ordering. From the cation chain directions, Q of $CoCr_2O_4$ is presumably along $[110]$ or $[\bar{1}10]$.[9] As the ions in the A- and $B2$-sites have the same chain direction, i.e., along $[110]$, Q can be along $[110]$ for both sites. If the e vectors of the A- and $B2$-sites can become opposite, i.e., $+z$ and $-z$, respectively [Fig. 4(b)], the induced $P\propto e\times Q$ from the two chains, P_A and P_{B2}, will be $P_A\|[\bar{1}10]$ and $P_{B2}\|[1\bar{1}0]$, respectively. Consequently, within this picture, the net P $(=P_A+P_{B2})\|[\bar{1}10]$ will be determined by the competition between the two antiparallel P_A and P_{B2}. The intriguing finding of the small negative P in $C\#1$ below T_L [Fig. 3(b)] also indicates that a subtle balance existing between the two antiparallel P components can be varied with temperature. In this scenario, replacement of Cr^{3+} (3 μ_B) with Co^{3+} (0 μ_B) in the $B2$-site is naturally expected to reduce the negative P contribution through a decrease in effective spin moments, thus explaining why the total measured P increases in samples with the

Cr-site mixing. Therefore, assumption of at least two competing components in both M and P qualitatively explains the experimental findings in this study. If this assumption is true, $CoCr_2O_4$ might act as a ferrielectric material driven by competing spiral orderings. The characteristic increase in the magnetoelectric coercive field in the stoichiometric $CoCr_2O_4$, as observed in Fig. 3(b), may also be related to the close balance between the two antiparallel P components.

Finally, the mechanism found in this study can also be applicable to similar types of multiferroics such as $FeCr_2O_4$ and $MnCr_2O_4$ or related spinel compounds. If the spin ordering or electric polarization vectors in these multiferroic materials have several competing components, the nonmagnetic dilution or induced disorders may result in unexpected improvements in the value of P or the coercive fields as found in this study.

In conclusion, we have shown that the magnetic and ferroelectric properties of $CoCr_2O_4$ can be significantly improved when the Cr ions in the octahedral sites are substituted with Co ions. We have also qualitatively explained the physical mechanism underlying this improvement, on the basis of the broken balance among competing magnetic moments or electric polarization vectors. Our study directs a possible route to enhance the performance of the multiferroic materials.

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