Magnetic and electric properties of triangular lattice antiferromagnets $\text{Ba}_3A\text{Ta}_2\text{O}_9$ ($A = \text{Ni}$ and Co)

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Abstract

We investigated magnetic and electric properties of two triangular lattice antiferromagnets (TLAFs), $\text{Ba}_3A\text{Ta}_2\text{O}_9$ ($A = \text{Ni}$ and Co). $\text{Ba}_3\text{NiTa}_2\text{O}_9$ shows i) a single antiferromagnetic phase transition to 120 degree ordered state at $T_N \sim 3.3$ K, ii) a weak spin-flop-like transition in isothermal magnetization curves around 4 T, and the saturation magnetization about $1.6 \mu_B$ per Ni^{2+} above 9.2 T, and iii) a weak magnetoelectric effect could be removed without ferroelectricity. Comparing to the isostructural TLAF, $\text{Ba}_3\text{NiNb}_2\text{O}_9$ [Phys. Rev. Lett. **109**, 257205 (2012)], which exhibits successive magnetic phase transitions and ferroelectricity, $\text{Ba}_3\text{NiTa}_2\text{O}_9$ shows lower T_N , smaller saturation magnetization, no successive phase transition, and no ferroelectricity. These differences indicate that the higher order superexchange interaction involving Ta atomic orbitals in $\text{Ba}_3\text{NiTa}_2\text{O}_9$ disrupts not only the exotic magnetic phases, also ferroelectricity. We show that this scenario can be also applied to explain the differences between $\text{Ba}_3\text{CoTa}_2\text{O}_9$ and $\text{Ba}_3\text{CoNb}_2\text{O}_9$ [Phys. Rev. B **89**, 104420 (2014)].

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1. Introduction

The magnetoelectric coupling in a single-phase material has been an important issue in the research of condensed matter for a long time. In particular, a strong magnetoelectric coupling is desired to realize new paradigmatic devices that exploit both magnetic and electric properties [1]. It has been proved, however, that such a task is exceptionally challenging in oxides due to the mutually exclusive conditions for magnetic and electric orderings [2]. As a result, many multiferroics occasionally undergo magnetic and electric phase transitions at widely different temperatures, which is suggestive of weakly coupled two order parameters [3]. Recently, a new type of materials with unusually large magnetoelectric effect has been discovered in manganites. In these materials, the complex spin structure accompanying ferroelectricity is stabilized by magnetic frustration [4].

Such behavior has been also observed in several triangular lattice antiferromagnets (TLAFs), such as $\text{Ba}_3\text{CoNb}_2\text{O}_9$ (Co^{2+} , $S_{eff}(\text{effective spin}) = 1/2$) [5], $\text{Ba}_3\text{NiNb}_2\text{O}_9$ (Ni^{2+} , $S = 1$) [6], $\text{Ba}_3\text{MnNb}_2\text{O}_9$, (Mn^{2+} , $S = 5/2$) [7], and $\text{RbFe}(\text{MoO}_4)_2$ (Fe^{2+} , $S = 5/2$) [8]. In those systems, a spin structure called 120 degree ordered and Y phase is stabilized by the geometrical frustration at low fields. This state evolves into so-called up-up-down(uud) collinear phase at intermediate magnetic fields with a magnetization as $1/3$ of the saturation magnetization (M_{sat}). At this stage, the materials listed above separate into two classes in terms of the ferroelectric ground state. The small spin systems such as $\text{Ba}_3\text{CoNb}_2\text{O}_9$ (Co^{2+} , $S_{eff} = 1/2$) and $\text{Ba}_3\text{NiNb}_2\text{O}_9$ (Ni^{2+} , $S = 1$) preserve their multiferroicity in the uud phase, but the large spin systems $\text{Ba}_3\text{MnNb}_2\text{O}_9$, (Mn^{2+} , $S = 5/2$) and $\text{RbFe}(\text{MoO}_4)_2$ (Fe^{2+} , $S = 5/2$) do not. The effect of spin fluctuations seemingly diverges such behavior.

Three microscopic mechanisms have been put forward to explain the multi-

ferroicity. First, dimerization of two nonequivalent magnetic ions may give rise to a strong magnetoelectric coupling in the magnetostriction model. However, it is not able to explain the multiferroicity in compounds herein because they contain only one magnetic ion. Second, the spin current induced by the geometric frustration is strongly coupled to the ferroelectricity and it has been successful to describe the multiferroicity observed in spiral magnets [4, 9, 11, 12]. However, the spin-current model yields zero ferroelectricity for both noncollinear spin state and collinear spin state in TLAFs. The last scheme is from spin-orbit coupling that modifies p - d hybridization so that the electric polarization occurs along the bond direction [13, 14]. It was proposed that the ferroelectricity of a certain class of TLAFs with a proper screw spin structure emerges by this mechanism [15]. Particularly, it is suggested that different electric ground states may be stabilized depending on the number of electrons in d orbitals in the crystal field.

Meanwhile, it is well known that the p - d orbital hybridization has an effect on the magnetic ground state due to the superexchange interaction. It has been pointed out that the exchange interaction path formed by interlayer atoms via ligand orbitals may weaken the magnetic phase transition [16]. In order to test the idea and to extend our previous studies on the multiferroic TLAFs, here we have prepared two new TLAFs, $\text{Ba}_3A\text{Ta}_2\text{O}_9$, where $A = \text{Co}^{2+}$ (effective spin-1/2) and Ni^{2+} ($S = 1$). Recently, the 120 degree spin structure of $\text{Ba}_3\text{NiTa}_2\text{O}_9$ has been resolved by neutron scattering diffraction [17]. In this paper, we investigate their magnetic and electric ground states using various experimental probes. The comprehensive magnetic and electric phase diagrams of $\text{Ba}_3A\text{Ta}_2\text{O}_9$ are compared to those of isostructural TLAFs, $\text{Ba}_3A\text{Nb}_2\text{O}_9$ [6] to understand how the ground states are affected by the higher order superexchange interaction via the interlayer atoms. Our results suggest that the effect of higher order superexchange interaction should be considered to deepen the understandings of magnetic phase transitions and multiferroicity in TLAFs.

2. Experimental

Polycrystalline samples of $\text{Ba}_3\text{ATa}_2\text{O}_9$ were synthesized by solid state reaction method. Stoichiometric mixtures of BaCO_3 , NiO/CoO and Ta_2O_5 were
60 ground together, and calcined in air at 1230 °C for 24 hours.

The neutron powder diffraction(NPD) experiments was performed to identify the lattice structure of $\text{Ba}_3\text{CoTa}_2\text{O}_9$ at room temperature and the lattice/magnetic structures of $\text{Ba}_3\text{NiTa}_2\text{O}_9$ at 10 K and 2 K (above/below the transition temperature, $T_N \sim 3.2$ K). Around 3 g powders were loaded in an
65 Al-cylinder cans, and mounted in an orange cryostat at the neutron powder diffractometer, HB2A, at the High Flux Isotope Reactor (HFIR) of the Oak Ridge National Laboratory (ORNL). The diffraction data were collected with two different wavelengths $\lambda = 1.54$ and 2.41 Å: the shorter wavelength covers a greater momentum transfer (Q) and is usually used to investigate the crystal
70 structure; the longer wavelength gives a better Q resolution at low Q which is important for investigating the magnetic structure. The collimations were set up as $12'$ -open- $6'$. The diffraction data were analyzed by the Rietveld refinement program FullProf [10].

A high-field vibrating sample magnetometer (VSM) at National High Magnetic Field Laboratory (NHMFL) and a commercial SQUID magnetometer
75 (magnetic property measurement system, Quantum Design) were employed to measure the dc magnetization. A homemade ac susceptometer that utilizes the conventional mutual inductance method were used to measure the ac susceptibility with a few hundred hertz of frequency and a few Oe of ac field [18].

80 For dielectric constant and polarization measurement, the samples were polished into a plate like shape with a typical dimension of $10 \times 5 \times 0.2$ mm². Electrical contacts were made by silver paint on the two large surfaces. A commercial capacitance bridge (Andeen-Hagerling AH-2700A) was used to measure the capacitance and it was converted to the relative dielectric constant using the
85 dimension. To measure the polarization, we performed the pyroelectric current measurement. The detailed procedure of the electric polarization measurement

Figure 1: (color online) (a) NPD pattern taken at 300 K for $\text{Ba}_3\text{CoTa}_2\text{O}_9$. The solid curve is the best fit from the Rietveld refinement by using the program FULLPROF. The refinements were done with the $P-3m1$ space group. The upper and lower vertical marks represent the nuclear reflections of $\text{Ba}_3\text{CoTa}_2\text{O}_9$, and Al-can, respectively.

can be found in Ref. 5.

3. Results and Discussion

The lattice and spin structures of $\text{Ba}_3\text{NiTa}_2\text{O}_9$ refined from our NPD patterns agree with the reported data in Ref. [17]: The space group is $P-3m1$ with $a = b = 5.7468(1)$ and $c = 7.0604(1)$ Å at 10 K and the spin structure is the 120 degree ordering structure with magnetic propagation vector as $k_{\text{mag}} = (1/3, 1/3, 1/2)$ (not shown here). The NPD pattern of $\text{Ba}_3\text{CoTa}_2\text{O}_9$ at 300 K was presented in Figure 1. Except the peaks of Al- sample can, there were no impurity peaks observed and the anti-site disorder between Co and Ta ions was less than 1%. The lattice pattern can be indexed in a hexagonal unit cell with $a = b = 5.7827(1)$ Å, and $c = 7.1020(3)$ Å. The space group is $P-3m1$, and the cobalt atom occupies the $1b$ Wyckoff site $(0, 0, 1/2)$, which formed

triangular lattices parallel to the ab plane. Detailed information of the atomic
100 coordinates are shown in Table 1. The final weighted residual error $R_{wp} =$
5.8. Therefore, the Co sample is isostructural to that of the Ni sample here.
Furthermore, the lattice structure of $Ba_3ATa_2O_9$ is isostructural to another
set of TLAfs, $Ba_3ANb_2O_9$. As shown in Figure 2, the magnetic Ni-triangular
layers of $Ba_3NiTa_2O_9$ are separated by the corner shared bi-octahedra Ta_2O_6
105 (in $Ba_3NiNb_2O_9$, the Ni layers are separated by Nb_2O_6). Between the Ni-
triangle layers, the distances among Ni ions were $5.7610(3)\text{\AA}$ in ab -plane and
 $7.0695(3)\text{\AA}$ along c -axis for $Ba_3NiTa_2O_9$ at 2 K, which were comparable to the
Ni-Ni bond lengths of $Ba_3NiNb_2O_9$, $5.7371(3)\text{\AA}$ and $7.0151(4)\text{\AA}$ at 2 K, respec-
tively.

Table 1: Position parameters($\text{\AA}$) of $Ba_3CoTa_2O_9$ at 300 K determined from the NPD data
with the space group $P-3m1$.

atom	site	x	y	z
Ba(1)	$2d$	0.3333	0.6667	0.6585(9)
Ba(2)	$1a$	0.0000	0.0000	0.0000
Co(1)	$1b$	0.0000	0.0000	0.5000
Ta(1)	$2d$	0.3333	0.6667	0.1691(9)
O(1)	$3e$	0.5000	0.0000	0.0000
O(2)	$6i$	0.1653(7)	0.3306(14)	0.3319(7)

110 The dc susceptibility ($\chi_{dc} = M/H$) and its inverse measured at 0.2 T of
 $Ba_3NiTa_2O_9$ are shown in Figure 3. The inset is an expanded view around Neél
temperatures (T_N) denoted as solid azure circles, which decrease with increasing
magnetic field. The effective magnetic moment of $3.12 \mu_B$ and Curie-Weiss
temperature $\Theta_{CW} = -10.0$ K are estimated by fitting the Curie-Weiss law to
115 the inverse susceptibility shown as a solid red line in Figure 3. The mean-field
theory for the triangular lattice, in which the coordination number is 6, leads to
the antiferromagnetic exchange integral $J = -\Theta_{CW}/4 = 2.5$ K. The effective
magnetic moment is consistent with the typical value of Ni^{2+} ions [19] and with

Figure 2: (Color online) (a) The crystal structure of $\text{Ba}_3\text{NiTa}_2\text{O}_9$. Magnetic layer composed of Ni^{2+} is separated by the two non-magnetic layers composed of Ta^{5+} . The grey, red and azure balls represent Ni, O, and Ta, respectively. The solid line and dashed line show the largest exchange interaction path and the higher order exchange interaction path via the Ta atoms. (b) The f orbitals of Ta splitting under the cubic crystal field. The numbers in parenthesis denote the number of degeneracy. The t_{1g} , t_{2g} , and a_{2g} are the symmetry of the orthogonal groups under cubic crystal field.

Figure 3: (Color online) The temperature dependence of the dc magnetic susceptibility at 0.2 T and its inverse. The solid line is Curie-Weiss fitting. Inset: dc magnetic susceptibility at different magnetic fields at low temperatures.

the value of its sister compound $\text{Ba}_3\text{NiNb}_2\text{O}_9$ [6]. On the other hand, Θ_{CW} and J , which scale the magnetic interaction between spins are smaller than those of $\text{Ba}_3\text{NiNb}_2\text{O}_9$ [6] ($\Theta_{CW} = -16.4$ K and $J = 4.1$ K).

Figure 4 shows the isothermal dc magnetization data ($M(H)$) and its derivative with respect to the magnetic field (dM/dH) at various temperatures from 1.0 K to 4.0 K of $\text{Ba}_3\text{NiTa}_2\text{O}_9$. The spin of Ni^{2+} saturates at $\mu_0 H_{sat} = 9.2$ T and, above the saturation, the magnetization increases linearly due to the Van Vleck paramagnetism at the rate of $0.021 \mu_B/\text{Ni}^{2+}/\text{T}$. The value of saturation magnetization is estimated to be $1.6 \mu_B/\text{Ni}^{2+}$ after extrapolating the magnetization above the saturation field to y -axis. From the saturation magnetization value, the g factor is estimated to be 1.6. Since $\mu_0 H_{sat}$ is solely determined by the nearest neighbor J with fixed spin S in the simplest Hamiltonian model [20], the relation $g\mu_B\mu_0 H_{sat} = 9JS$ with g factor of 1.6 leads to $J \sim 2.2$ K, which is comparable to the J found from the dc susceptibility. A prominent peak denoted as the $\mu_0 H_{c1}$ in dM/dH appears around 4 T and this feature is sup-

Figure 4: (Color online) dc magnetization and its derivative for various temperatures measured using VSM and SQUID magnetometer. The dashed line is from the orbital contribution.

pressed upon increasing temperature. The corresponding magnetization value
 135 to this peak is close to $1/2 M_{sat}$ rather than $1/3 M_{sat}$. The feature completely
 disappears above 3.5 K, above which the system is in paramagnetic state.

Figure 5 shows the field dependent ac susceptibility, which is directly propor-
 tional to dM/dH . Here, the high temperature background at 5 K was subtracted
 from the low temperature data $\Delta\chi' = \chi'(H, T) - \chi'(H, 5 \text{ K})$ to show clearer
 140 anomalies. Consistently, a sharp peak around 4 T and a sharp drop around
 9 T at which μ_0H_{c1} and μ_0H_{sat} appear in Figure 4 are observed. Therefore,
 we assign these two anomalies with μ_0H_{c1} and μ_0H_{sat} , respectively. μ_0H_{c1}
 shifts to lower fields and the height of the peaks become smaller with increasing
 temperature.

145 The electric properties of $\text{Ba}_3\text{NiTa}_2\text{O}_9$ were investigated by measuring di-
 electric constant. Figure 6 (a) and (b) show the temperature dependent and
 field dependent dielectric constant, respectively. In the temperature sweep, a
 weak slope change occurs around 3 K. To determine the position of this weak
 slope change precisely, we define a peak in the first derivative of the dielectric

Figure 5: (Color online) Field dependent ac susceptibility at various temperatures below T_N . Data offset properly.

constant as shown in the inset of Figure 6. The temperatures at which the weak slope change appears are comparable with magnetic phase transition temperatures T_N . We note that the same temperature assignment method also yielded temperatures consistent with T_N 's from the magnetic measurement in its sister compound [6]. With increasing magnetic field, the temperatures shift to lower temperatures. Moreover, the field dependent dielectric constant also shows weak anomalies around 3.5 T, which is also comparable with the fields μ_0H_{cl} at which the slope changes in magnetization curves occur. Therefore, the anomalies in the dielectric constants are associated with the spin ordering. Interestingly, the pyroelectric current measurement shows no spontaneous polarization below T_N as shown in the inset of Figure 6 (b).

Based on the phase transition points observed from dc magnetization, ac susceptibility, and dielectric constant measurements, we draw the phase diagram of $\text{Ba}_3\text{NiTa}_2\text{O}_9$ as shown in Figure 7. There are several conspicuous features. First, a single phase transition appears upon cooling from the paramagnetic state to an antiferromagnetically ordered state at zero field. As mentioned above, a re-

Figure 6: (Color online) (a) temperature dependent dielectric constant. Inset: the first derivative of the dielectric constant with respect to the temperature. (b) magnetic field dependent dielectric constant.

Figure 7: (Color online) The magnetic field vs. temperature phase diagram for $\text{Ba}_3\text{NiTa}_2\text{O}_9$. The dashed line shows the magnetic phase boundaries formed by various experimental probes. Spin structures is indicated with arrows.

Figure 8: (Color online) The scaled magnetic phase diagram of $\text{Ba}_3\text{NiNb}_2\text{O}_9$ (solid line) and $\text{Ba}_3\text{NiTa}_2\text{O}_9$ (color codes from Figure 7). FE I and FE II indicates the two different ferroelectric state of $\text{Ba}_3\text{NiNb}_2\text{O}_9$.

Figure 9: (Color online) (a) Temperature dependence and (b) magnetic field dependence of ac susceptibility of $\text{Ba}_3\text{CoTa}_2\text{O}_9$. (c) Magnetization curve at 1.0 K and 1.6 K of $\text{Ba}_3\text{CoTa}_2\text{O}_9$.

Figure 10: (Color online) (a) Temperature dependent dielectric constant at 0 T and 1.5 T. (b) field dependent of dielectric constant at 0.3 K and 0.5 K.

cent neutron scattering diffraction experiment has proved that the three spins form 120 degree ordered state in plane at zero field [17]. Thus, we assign the magnetic phase at zero field with the 120 degree ordered state and with the canted 120 degree structure below 4 T. The single magnetic phase transition
170 at zero field indicates that the system has an easy-plane type anisotropy [22]. Second, a distinctive magnetic phase is stabilized above $\mu_0 H_{c1} \sim 4$ T with $1/2 M_{sat}$. Even though the spin structure in this magnetic phase is not clear at this moment, it might be the spin flopped conical state along the magnetic field direction [23] or the $1/2 M_{sat}$ state observed in Cs_2CuBr_4 [24]. A detailed spin
175 structure of this phase is presented in Figure 7. Lastly, the ferroelectricity has not been observed in all magnetically ordered states.

The magnetic field vs. temperature phase diagrams of $\text{Ba}_3\text{NiNb}_2\text{O}_9$ and $\text{Ba}_3\text{NiTa}_2\text{O}_9$ are scaled by T_N and $\mu_0 H_{sat}$, and represented together in Figure 8 to show the qualitative differences between them. What we observe are
180 i) $\text{Ba}_3\text{NiTa}_2\text{O}_9$ does not show exotic magnetic phases such as *uud* with $1/3 M_{sat}$ and the oblique spin structure phase with $\sqrt{3}/3 M_{sat}$ but rather a single magnetic phase transition at $1/2 M_{sat}$, ii) two different ferroelectric states (FE I and FE II) that accompany the magnetic orderings with strong dielectric anomalies in $\text{Ba}_3\text{NiNb}_2\text{O}_9$ have not been observed in $\text{Ba}_3\text{NiTa}_2\text{O}_9$, although
185 weak anomalies in dielectric constant through the magnetoelectric effect are

observed. Quantitative differences between them are also observed. The saturation field (9.2 T), exchange integral calculated from dc susceptibility ($J = 2.5$ K), the Curie-Weiss constant ($\Theta_{CW} = -10$ K), and the saturation magnetic moment ($1.6 \mu_B/\text{Ni}^{2+}$) of $\text{Ba}_3\text{NiTa}_2\text{O}_9$ are all considerably smaller than those
190 of $\text{Ba}_3\text{NiNb}_2\text{O}_9$ (22 T, 4.1 K, -16.4 K, and $2.2 \mu_B/\text{Ni}^{2+}$, respectively).

To understand the difference between the ground states of $\text{Ba}_3\text{NiTa}_2\text{O}_9$ and $\text{Ba}_3\text{NiNb}_2\text{O}_9$ requires to consider how the exchange interactions form via the Nb or Ta orbitals. The exchange interaction is mainly due to the superexchange interaction via $\text{Ni } 3d - \text{O } 2p - \text{O } 2p - \text{Ni } 3d$, which is antiferromagnetic (Solid
195 line in Figure 2 (a)). Another contribution, which is higher order exchange interaction so that less effective, is $\text{Ni } 3d - \text{O } 2p - \text{Ta } 4f - \text{O } 2p - \text{Ni } 3d$ (Dashed line in Figure 2 (a)). The cubic crystal field splits the degenerate f orbitals of Ta into three groups as shown in Figure 2 (b). The group of f_{x^3} , f_{y^3} , and f_{z^3} with t_{1g} symmetry mainly participates into the orbital hybridization due to the shape
200 of the orbitals with lobes towards the oxygen orbitals. Since the symmetry of t_{1g} is exactly identical with the symmetry of the p orbitals, the argument found in Ref. 16 can be used in this case as well. Accordingly, the second contribution is expected to be ferromagnetic that lowers the total exchange interaction by compensating the main antiferromagnetic exchange interaction [16, 25, 26]. The
205 reduced $|\Theta_{CW}|$ and $\mu_0 H_{sat}$ for $\text{Ba}_3\text{NiTa}_2\text{O}_9$, indicate a larger contribution from the higher order superexchange interaction via Ta than via Nb.

Moreover, the enhanced higher order exchange path leads to the strong orbital hybridization between $\text{Ni } 3d$ and ligands. As a result, the ground state of $\text{Ba}_3\text{NiTa}_2\text{O}_9$ is a strong mixture of d^8 , $d^9 \underline{L}$ and so on, where $\underline{L}$ denotes a hole in
210 the ligand, resulting in a larger net d -electron number in Ni atoms [27]. The reduction in the saturation magnetization from $2.2 \mu_B$ per Ni^{2+} for $\text{Ba}_3\text{NiNb}_2\text{O}_9$ to $1.6 \mu_B$ per Ni^{2+} for $\text{Ba}_3\text{NiTa}_2\text{O}_9$ is because $e_{g\downarrow}$ orbitals more participate in the orbital hybridization than that of Nb compounds with $e_{g\uparrow}$ orbitals already fully occupied. This interaction along a direction perpendicular to the triangular
215 lattice plane increases effective dimensionality, thus, suppresses the effect of spin frustrations [16]. For this reason, the magnetic phases that are strongly

Figure 11: (Color online) (a) Magnetic phase diagram of Ba₃CoTa₂O₉ and (b) The scaled phase diagrams of Ba₃CoTa₂O₉ and Ba₃CoNb₂O₉.

affected by the spin frustrations, such as the *ud* and oblique phases, cannot be stabilized in Ba₃NiTa₂O₉ although the 120 degree ordered state seems robust.

At this moment, we can say little about why ferroelectricity vanishes in Ba₃NiTa₂O₉ since the microscopic mechanism for the triangular lattice has not been satisfactorily resolved yet. The spin-current model [9] for the system with superexchange interactions predict the polarization proportional to J [9, 28]. The reduced J due to the higher order superexchange interaction, thus, may lead to the much smaller polarization in Ba₃NiTa₂O₉. However, the spin-current model is difficult to explain the polarization in TLAFs. The p - d hybridization scheme predicts no electric polarization for pure e_g systems [14]. In this sense, the polarization persists in all magnetic phase in Ba₃NiNb₂O₉ is more peculiar than no polarization in Ba₃NiTa₂O₉. This strongly suggests that the ferroelectricity in TLAFs may be the result of the strong spin fluctuations due to the lower dimensionality.

To confirm the validity of the effect of higher order exchange path, Ba₃CoTa₂O₉ has also been synthesized and characterized. Its properties were compared to those of Ba₃CoNb₂O₉ [5]. The temperature dependence of the ac susceptibility (Figure 9 (a)) shows the a single peak around $T_N = 0.8$ K at zero field for Ba₃CoTa₂O₉, which indicates easy-plane anisotropy. This is contrasted from two peaks at $T_{N2} = 1.36$ K and $T_{N1} = 1.10$ K for Ba₃CoNb₂O₉, indi-

cating easy axis anisotropy. The suppression of T_N to the lower temperature for $\text{Ba}_3\text{CoTa}_2\text{O}_9$ could be explained due to the enhanced ferromagnetic exchange interaction. Meanwhile, the orbital degeneracy of the singly occupied e_g combined with the modified transfer between orbitals may have changed the magnetic anisotropy between these two samples [27].

In the field dependence of ac susceptibility for $\text{Ba}_3\text{CoTa}_2\text{O}_9$ shown in Figure 9 (b), we observed two different magnetic phase transitions at fields denoted as $\mu_0 H_{c1}$ of 0.41 T and $\mu_0 H_{c2}$ of 1.1 T below 0.8 K before the magnetization saturates around 1.5 T of $\mu_0 H_{sat}$. The saturation field 1.5 T is significantly smaller than 5 T of $\text{Ba}_3\text{CoNb}_2\text{O}_9$ [5]. This also supports that the Ta compound has much smaller total exchange interaction due to the strong ferromagnetic exchange interaction via Ta orbitals. Magnetization curve measured using VSM shows the saturation magnetization of $1.8 \mu_B$ per Co^{2+} around 1.5 T, which is consistent with the ac susceptibility data. This saturation magnetization (Figure 9 (c)) is smaller than that of $\text{Ba}_3\text{CoNb}_2\text{O}_9$ ($2.1 \mu_B$), but the reduction here is somewhat smaller than the case between $\text{Ba}_3\text{NiTa}_2\text{O}_9$ and $\text{Ba}_3\text{NiNb}_2\text{O}_9$ compounds. This is because both $e_{g\uparrow}$ and $e_{g\downarrow}$ orbitals hybridizes more with ligands for the low spin state of Co^{2+} ion with a single electron in e_g state [27] than that of Nb compound. The corresponding magnetization at $\mu_0 H_{c1}$ and $\mu_0 H_{c2}$ in Figure 9 (b) is about $1/4 M_{sat}$ and $0.77 M_{sat}$, respectively, as denoted in Figure 9 (c).

In the temperature dependent dielectric constants for $\text{Ba}_3\text{CoTa}_2\text{O}_9$, they show a clear peak around T_N , as shown in Figure 10 (a). Therefore, magnetic ordering couples to dielectric properties. In addition, the peak feature is more prominent compared to the weak magnetoelectric effect in $\text{Ba}_3\text{NiTa}_2\text{O}_9$. This difference confirms the prediction that the electronic configuration in the d orbitals can change the magnetoelectric effect dramatically [14]. The magnetic field dependent dielectric constants (Figure 10 (b)) also show three clear anomalies at fields similar to $\mu_0 H_{c1}$, $\mu_0 H_{c2}$, and $\mu_0 H_{sat}$, which indicate strong magnetoelectric coupling. However, no ferroelectricity is observed in $\text{Ba}_3\text{CoTa}_2\text{O}_9$, which again is different from the $\text{Ba}_3\text{CoNb}_2\text{O}_9$ where the ferroelectricity accom-

panies all magnetically ordered state.

From the magnetic and electric phase transition points, the magnetic phase diagram of $\text{Ba}_3\text{CoTa}_2\text{O}_9$ and the scaled magnetic phase diagram of the $\text{Ba}_3\text{CoTa}_2\text{O}_9$ incorporated with that of $\text{Ba}_3\text{CoNb}_2\text{O}_9$ are presented in Figure 11 (a) and (b), respectively. Overall shapes and features of magnetic phase diagram of $\text{Ba}_3\text{CoTa}_2\text{O}_9$ are similar to that of $\text{Ba}_3\text{NiTa}_2\text{O}_9$, except one phase (brownish region) at high fields and at low temperatures. Although neutron experiments should be done to resolve the spin structure of each magnetic phase, the spin structure at low fields (reddish region) is likely to be the 120 degree ordered state for two reasons. First, its sister compound $\text{Ba}_3\text{CoNb}_2\text{O}_9$ stabilizes 120 degree ordered state at low fields denoted as A in Figure 11 (b). Second, the 120 degree ordered state is robust to the enhanced higher order exchange interaction as demonstrated in $\text{Ba}_3\text{NiTa}_2\text{O}_9$. Note that the exotic magnetic phase denoted as A' between *ud* phase and 120 degree ordered phase in $\text{Ba}_3\text{CoNb}_2\text{O}_9$ has not been observed in $\text{Ba}_3\text{CoTa}_2\text{O}_9$. Besides, the $1/3 M_{sat}$ state does not seem to exist but a peculiar magnetic phase at between $1/4 M_{sat}$ and $0.77 M_{sat}$ is observed. One more phase (brownish region) exists between $0.77 M_{sat}$ and M_{sat} but it quickly disappears at high temperatures. Therefore, we conclude that the higher order ferromagnetic exchange interaction in $\text{Ba}_3\text{CoTa}_2\text{O}_9$ suppresses several exotic magnetic ground states found in $\text{Ba}_3\text{CoNb}_2\text{O}_9$, as in the case of $\text{Ba}_3\text{NiTa}_2\text{O}_9$ and $\text{Ba}_3\text{NiNb}_2\text{O}_9$. However, $\text{Ba}_3\text{CoTa}_2\text{O}_9$ still possesses curious magnetic phases for which the spin structure is difficult to assign, probably due to the strong quantum fluctuations related to the effective spin-1/2.

4. Conclusion

We studied the effects of the higher order superexchange interaction on magnetic and electric properties of TLAFs $\text{Ba}_3A\text{Ta}_2\text{O}_9$ ($A = \text{Ni}$ and Co) using the various experimental probes. The ferromagnetic exchange interaction formed via Ta atomic orbital hybridization in $\text{Ba}_3A\text{Ta}_2\text{O}_9$ forbids the exotic magnetic states stabilized due to the increased dimensionality. More strikingly, the fer-

roelectric states observed in the all magnetically ordered state in isostructural compounds, $\text{Ba}_3\text{ANb}_2\text{O}_9$, completely disappear in the Ta compounds. The magnetic anisotropy of $\text{Ba}_3\text{CoTa}_2\text{O}_9$ also seems to be affected by the higher order superexchange interaction. Our results suggest that the magnetic phase diagrams of TLAFs depend subtly on the superexchange path except for the 120 degree ordered state. In addition, the higher order superexchange interaction are able to completely suppress the ferroelectricity. It is noteworthy to mention that no ferroelectricity has been observed in single crystalline $\text{Ba}_3\text{CoSb}_2\text{O}_9$ [30]. Therefore, the multiferroic state in TLAFs behaves critically to the intercalated atomic orbitals between two magnetic layers.

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