FERROELECTRIC PROPERTIES OF $BaBi_4Ti_4O_{15}$ DOPED WITH Pb^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Ta^{5+} AURIVILLIUS PHASES

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ABSTRACT

In recent years, the ferroelectric properties of aurivillius oxides have attracted interest and an extensive amount of work has been done toward the realization of their potential application in nonvolatile memories (FeRAM: ferroelectric random access memory). Recently, we have carried out computer simulation in atomic scale in order to predict the energies associated with the accommodation of aliovalent and isovalent dopants (Pb^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Ta^{5+}) in the aurivillius structure of $BaBi_4Ti_4O_{15}$. In this work, the predicted stable phases were synthesized using solid state reactions and their products then were characterized using powder X-ray diffraction method. The cell parameters were determined using Rietveld refinement in orthorhombic system with space group of $A2_1am$. Results from the ferroelectric properties measurement of $BaBi_4Ti_4O_{15}$ were also presented. The cell parameters for $BaBi_4Ti_4O_{15}$ doped with Pb^{2+}, Al^{3+}, Ga^{3+},In^{3+}, Ta^{5+} were a = 5.47116(4) b = 5.45636(5) c = 41.8649(3) Å; a = 5.47104(4) b = 5.45634(4) c = 41.8640(3) Å; a = 5.47112(4) b = 5.45648(4) c = 41.8643(3) Å; a = 5.47111(4) b = 5.45645(5) c = 41.8649(3) Å; and a = 5.47134(4) b = 5.45588(4) c = 41.8639(5) Å. The ferroelectric properties measurement for $BaBi_4Ti_4O_{15}$ doped with Pb^{2+}, Al^{3+}, Ga^{3+},In^{3+}, Ta^{5+} showed that the P_r = 15.225 $\mu C/cm^2$, E_c = 33.96 kV/cm; P_r = 15.925 $\mu C/cm^2$, E_c = 35.724 kV/cm; P_r = 16.625 $\mu C/cm^2$, E_c = 36.504 kV/cm; P_r = 15.57 $\mu C/cm^2$, E_c = 32.925 kV/cm; P_r = 17.2827 $\mu C/cm^2$, E_c = 37.44 kV/cm.

***Keywords**: Aurivillius phase; Rietveld refinement; Ferroelectric properties; $BaBi_4Ti_4O_{15}$*

INTRODUCTION

The bismuth layer-structured ferroelectrics (BLSFs) belong to the oxides family denominated aurivillius, which correspond to compositions with general formula $[Bi_2O_2][A_{m-1}B_mO_{3m+1}]$ [1]. BLSFs have attracted increasing attention because of their high Curie temperature, anisotropic characteristics, and excellent electrical properties for non-volatile ferroelectric random access memory and electro-optic devices applications [2-4].

The aurivillius phases can be described as the combination of regular stacking between the $[Bi_2O_2]^{2+}$ slabs and perovskite-like $[A_{m-1}B_mO_{3m+3}]^{2-}$ blocks. The integer, m, describes the number of sheets of corner-sharing BO_6 octahedra forming the ABO_3-type perovskite blocks. The A could be a monovalent, divalent or trivalent element (or a combination of the three), allowing dodecahedral coordination such as Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Pb^{2+}, Bi^{3+} or Ln^{3+} and the perovskite-like B-site, a transition element suited to octahedral coordination, could be filled by smaller cations such as Fe^{3+}, Cr^{3+}, Ti^{4+}, Nb^{5+} or W^{6+}. Whereas the perovskite blocks offer large possibilities in terms of compositional flexibility due to numerous possible combinations of A and B cations, the cation sites in the $[Bi_2O_2]^{2+}$ layers are almost exclusively occupied by Bi^{3+}. This reflects the fact that there exists a good possibility for mutual dopings within these various elements or with some other ions to BLSFs. These ceramic compounds have potential applications in high-temperature devices, because of their high Curie temperature (T_c), high dielectric breakdown strength, low dielectric dissipation factor, and high anisotropy [5-6].

$BaBi_4Ti_4O_{15}$, as the m = 4 member of the aurivillius family has Ba and Bi ions at the A sites and Ti ions at the B sites of the perovskite $[A_{m-1}B_mO_{3m+3}]^{2-}$ block $\{[Bi_2O_2]^{2+}[(BaBi_2)Ti_4O_{13}]^{2-}\}$. It has a high Curie temperature of 417 °C [7]. One interesting feature of the aurivillius phases resides in the compositional flexibility of the perovskite blocks which allows incorporating various cations. It is thus possible to modify the ferroelectric properties [8] according to the chemical composition. Although this phenomenon was observed since many years, its structural origin not yet clearly elucidated. Dopants are added into a wide

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variety of aurivillius in order to modify their properties. The goals in some cases are to create or enhance desirable properties, while in the other ones are to eliminate or reduce undesirable effects.

Subbarao [2] and Newnham [9] showed that aurivillius phases to be a ferroelectric with the highest known Curie point in the BLSFs family, which is 940 °C. The influence of substituting or doping in the BLSFs was widely reported for improving ferroelectric properties of isotropric perovskite ferroelectrics [10]. However, information about the effect of doping in $BaBi_4Ti_4O_{15}$ material is still limited.

Atomistic simulation methods has been carried out for Bi_3TiNbO_9, $Bi_4Ti_3O_{12}$, $BaBi_4Ti_4O_{15}$ and $Ba_2Bi_4Ti_5O_{18}$ doped with Pb, Al, Ga, In, Ta to determine defect energy in the materials by employing efficient energy minimization procedures [11]. The calculations rest upon the specification of an interatomic potential model, which expresses the total energy of the system as a function of the nuclear coordinates. The Born model framework, which divides the total energy into long-range Coulombic interactions and a short-range term to model the repulsions and van der Waals forces between electron charge clouds, is employed. This is embodied in the GULP simulation code. Dopant solution energy versus ion size trends are found for both isovalent and aliovalent dopant incorporation at Bi and Ta sites. Trivalent dopants (Al, Ga, In) and Pb are more favorable on the Bi site whereas Ta dopants preferentially occupy the Ti site. The predicted stable phases were synthesized using solid state reactions and their products were then characterized by using powder X-ray diffraction method.

This paper will present results of systematic doping in $BaBi_4Ti_4O_{15}$ with the aim that a better understanding of doping effect will be gained. The discussion will be restricted to the substitutional isovalent and aliovalent cations in $BaBi_4Ti_4O_{15}$.

EXPERIMENTAL SECTION

Material

Samples for this investigation were prepared from pure-grade Bi_2O_3, TiO_2, $BaCO_3$, PbO, Al_2O_3, Ga_2O_3, In_2O_3 and Ta_2O_5 (Aldrich Chem. Co.), all with a purity of 99.99%. The starting-mixture compositions were $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (A = Pb, Al, Ga, In), which corresponds to molar ratio, were thoroughly ground with acetone.

Instruments

The purity of the product was monitored by the powder X-ray diffractometer using monochromatized Cu $K\alpha_1$ radiation with λ = 0.1541 nm on Siemens D-500HS and DRON-3 diffractometers. Structure refinements were carried out by using RIETICA program [12]. The ferroelectric properties were evaluated from the P-E hysteresis curves obtained by a high-voltage test system (Model RT-66A, Radiant Technologies, Albuquerque, NM).

Procedure

The aurivillius family of $BaBi_4Ti_4O_{15}$ with aliovalent and isovalent dopants (Pb^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Ta^{5+}) were prepared by the standard solid-state reaction method. Stoichiometric quantities of high purity powders of Bi_2O_3, TiO_2, $BaCO_3$, PbO, Al_2O_3, Ga_2O_3, In_2O_3 and Ta_2O_5 (Aldrich Chem. Co.), all with a purity of 99.99%, were thoroughly ground with acetone and heated in an alumina crucible for 24 h at 700 °C, 24 h at 850 °C, 24 h at 1000 °C, and a further 24 h at 1100 °C with intermediate regrinding between each stage. The samples were slowly cooled to room temperature in air.

After each step, the samples were examined by X-ray diffractometer (XRD) and structure refinements were carried out by using RIETICA program [12]. The ferroelectric properties of $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (A = Pb, Al, Ga, In) and $BaBi_4Ti_{3.95}Ta_{0.05}O_{15}$ were evaluated from the P-E hysteresis curves obtained by a high-voltage test system (Model RT-66A, Radiant Technologies, Albuquerque, NM).

RESULT AND DISCUSSION

The X-ray diffraction patterns of the as-prepared powders showed that structures of $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (A = Pb, Al, Ga, In) and $BaBi_4Ti_{3.95}Ta_{0.05}O_{15}$ are orthorombic with space group $A2_1am$. Preliminary examination of the raw X-ray powder diffraction data for the doped composition suggested that these powders are single phase compounds and also can be indexed with the orthorombic symmetry. The Rietveld refinement with orthorombic and $A2_1am$ space group were then carried out and proceeded without incident. Typical Rietveld plot are shown in Figure 1.

The powder X-ray diffraction patterns of all composition $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (A = Pb, Al, Ga, In) and $BaBi_4Ti_{3.95}Ta_{0.05}O_{15}$ suggest that all doped samples are isostructure with the parent $BaBi_4Ti_4O_{15}$ [13-15]. The cell parameters of the different as prepared materials are listed in Table 1. From the development of the cell parameters, several distinct effects can be deduced depending on the fraction of iso- and aliovalent substitutions. For all groups of materials, the *a, b, c* axis remains basically constant and the volume of the unit cell still within 1 estimated standard deviation (esd)

Table 1. Cell parameters for $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (A = Pb, Al, Ga, In), $BaBi_4Ti_{3.95}Ta_{0.05}O_{15}$ were determined using Rietveld refinement applying orthorhombic system, in space group $A2_1am$.

Parameters	$BaBi_4Ti_4O_{15}$ [12]	Dopant				
		Pb^{2+}	Al^{3+}	Ga^{3+}	In^{3+}	Ta^{5+}
a (Å)	5.4707(2)	5.47116(4)	5.47104(4)	5.47112(4)	5.47111(4)	5.47134(4)
b (Å)	5.4565(2)	5.45636(5)	5.45634(4)	5.45648(4)	5.45645(5)	5.45588(4)
c (Å)	41.865(11)	41.8649(3)	41.8640(3)	41.8643(3)	41.8649(3)	41.8639(5)
V (Å^3)		1249.7816	1249.7223	1249.7779	1249.7929	1249.6743
R_p	4.35	7.821	5.980	5.368	6.385	8.180
R_{wp}	5.32	3.861	2.013	2.580	2.587	4.905
R_{Bragg}		10.39	11.61	5.02	5.74	6.71

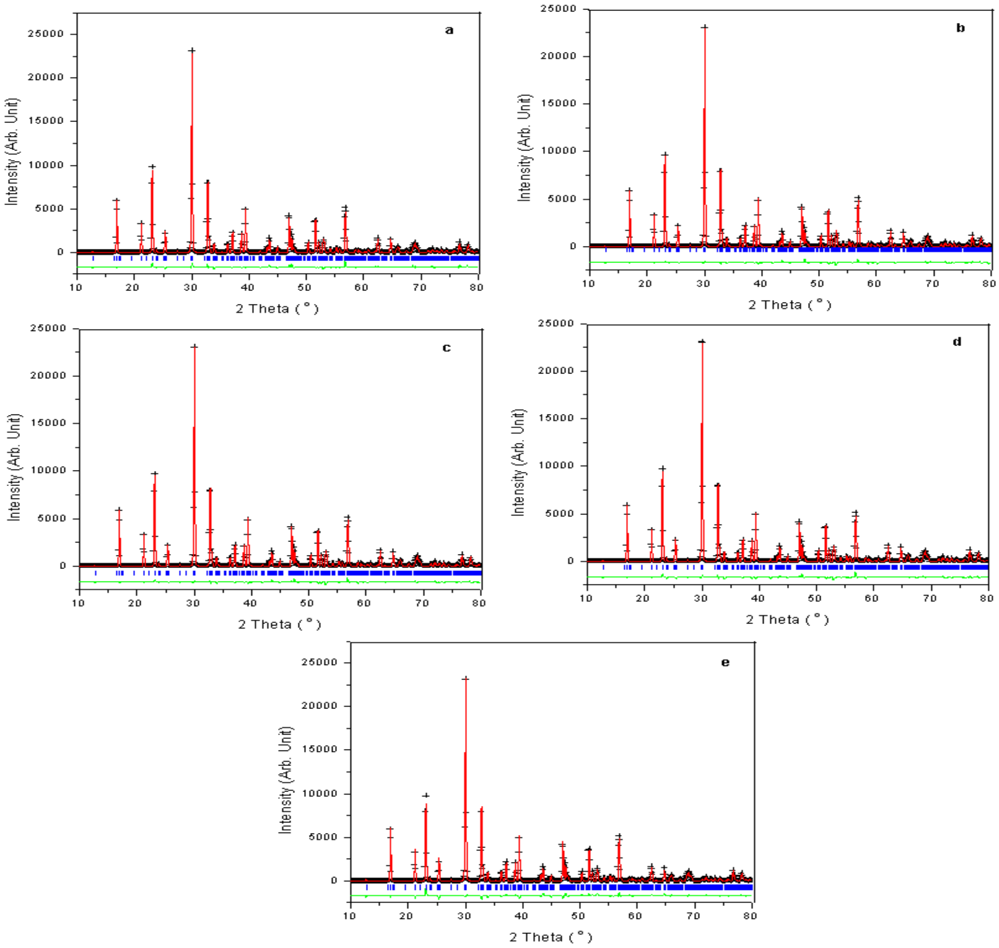

Figure 1. Rietveld refinement plot showing the observed (+), calculated (solid line) and difference for $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (A = Pb, Al, Ga, In) **a-d** respectively and $BaBi_4Ti_{3.95}Ta_{0.05}O_{15}$ **e**. The tick marks show the positions of the allowed Bragg reflections in space group $A2_1am$

As pointed out by Armstrong and Newnham the $[Bi_2O_2]^{2+}$ layers constrain the size of the perovskite block. Site mixing, therefore, occurs to equilibrate the lattice dimensions between the $[Bi_2O_2]^{2+}$ layers and the perovskite block. The refinement results directly support the theory [16]. As can be seen in Figure 1, the pattern calculated under the assumption that $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (A = Pb, Al, Ga, In) and $BaBi_4Ti_{3.95}Ta_{0.05}O_{15}$ have the structure of m = 4 fits fairly well to the observed data. The R-weighted pattern, R_{wp}, which is the standard of the degree of difference of calculated and observed values, is small. Furthermore, the goodness of fit shows that the excellent fitting was attained in this Rietveld analysis. However, the values of R factors, R_{Bragg} for $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (A = Pb, Al) became so large that their structure were no longer that of the starting structure of $BaBi_4Ti_4O_{15}$. The Rietveld plots suggested that the value for oxygen atoms parameters is believed as a result of insensitivity of X-ray diffractometer data to light atoms, despite that all

Table 2. The remanent polarization (*P_r*) of the $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (*A* = Pb, Al, Ga, In) and $BaBi_4Ti_{2.95}Ta_{0.05}O_{15}$.

Parameters	$BaBi_4Ti_4O_{15}$ [19]	Dopant				
		Pb^{2+}	Al^{3+}	Ga^{3+}	In^{3+}	Ta^{5+}
P_r ($\mu C/cm^2$)	15.0	15.225	15.925	16.625	15.57	17.2827
E_c (kV/cm)	2	33.96	35.724	36.504	32.925	37.44

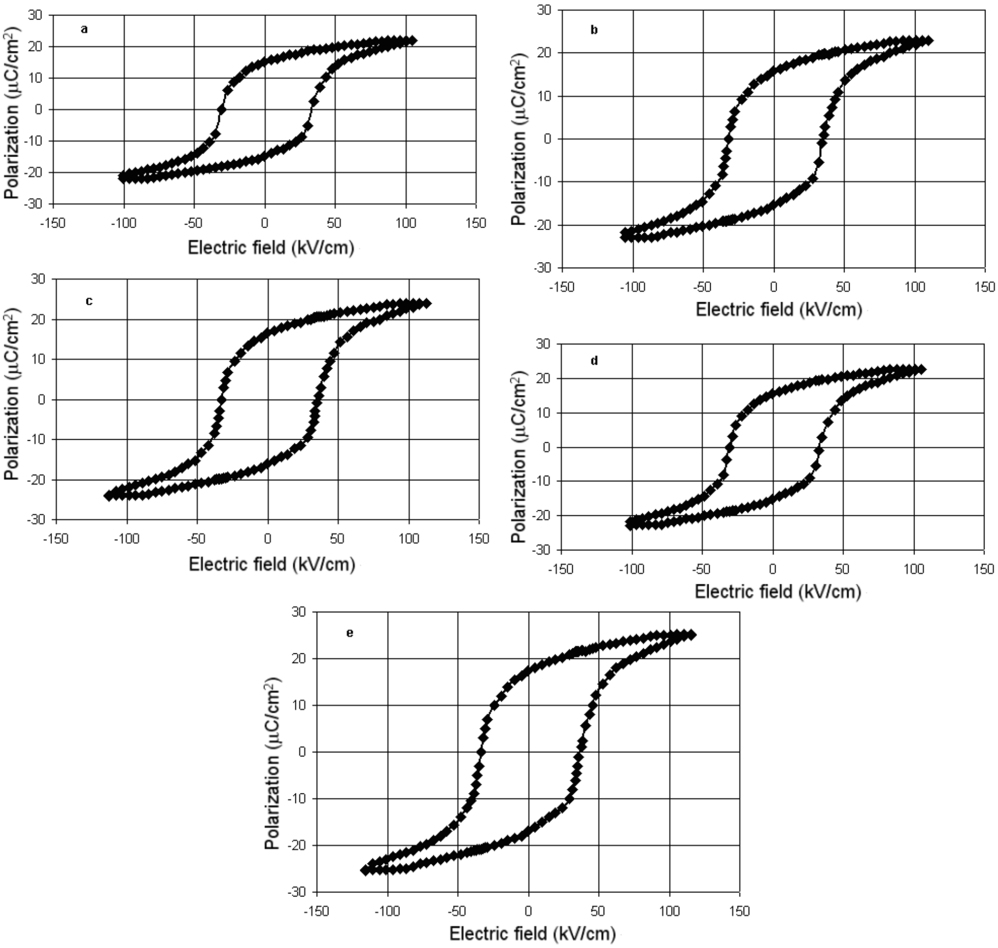

Figure 2. The P-E hysteresis loops of the $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (*A* = Pb, Al, Ga, In) **a-b** respectively and $BaBi_4Ti_{3.95}Ta_{0.05}O_{15}$ **e** ceramics.

oxygen atoms were assumed to have the same parameter. The same reason can be used to explain the relatively large estimated standard deviation for *R* factors, R_{Bragg} on $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (*A* = Pb, Al). For all groups of materials, $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (*A* = Pb, Al, Ga, In) and $BaBi_4Ti_{3.95}Ta_{0.05}O_{15}$, the Rietveld refinement rapidly converged and still within 1 estimated standard deviation (esd).

Atomistic simulation techniques have been employed to investigate the Aurivillius oxides phases: Bi_3TiNbO_9, $Bi_4Ti_3O_{12}$, $BaBi_4Ti_4O_{15}$ and $Ba_2Bi_4Ti_5O_{18}$ [11] The simulation suggested that M^{3+} dopants (Al, Ga, In) and Pb^{2+} are favourable in Bi(2) sites in $(Bi_2O_2)^{2+}$ block and unlikely to occur at any of the perovskite sites (Bi sites and Ti sites). This seems in contrary to the expected, since in term of coordination preference and ionic size these three cations are suitable to substitute Ti^{4+}. However, this reconfirms that vacancy creation in perovskite block needs very high energy. On the other hand, the calculation on Ta^{5+} dopant shows that substitution is likely to occur at any of the perovskite sites on energetic grounds. The formation single phase compounds and the similarity of the diffraction patterns of $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (*A* = Pb, Al, Ga, In) and $BaBi_4Ti_{3.95}Ta_{0.05}O_{15}$ gave further evidence of these site preferences.

The bismuth barium-titanates, $BaBi_4Ti_4O_{15}$ have the orthorhombic structure. The structure of $BaBi_4Ti_4O_{15}$ is thus built up of $[Bi_2O_2]^{2+}$ layer between wich $[BaBi_2Ti_4O_{13}]^{2-}$ layers are inserted. In the $BaBi_4Ti_4O_{15}$ units, Ba^{2+} and Bi^{3+} ions are at the *A* sites and Ti^{4+} ions are at the *B* sites of the perovskite blocks.

Thus $BaBi_2Ti_4O_{13}$ units pose a remarkable similarity to the perovskite-type structure. The height of the perovskite-type layer sandwiched between Bi_2O_2 layers in $BaBi_4Ti_4O_{15}$ is equal to 8 for O-Ba/Ti-O distances or approximately to m = 4 ABO_3 perovskites.

Aurivillius ceramics are interesting ferroelectrics. The layered structure makes this kind of ferroelectrics have good fatigue endurance [17]. We would like to investigate, what are the effects of doping on the ferroelectric properties. Figure 2 shows the P-E hysteresis loops of the $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (*A* = Pb, Al, Ga, In) and $BaBi_4Ti_{3.95}Ta_{0.05}O_{15}$ ceramics, which indicates the ferroelectricity in this compound. The remanent polarizations (P_r) of the different as-prepared materials are listed in Table 2. The disadvantage of the layer-structured perovskite materials for high-temperature piezoelectric applications is their relatively high ferroelectricity. This ferroelectricity is electronic-type and, therefore, can be suppressed by doping [18-19]. The layer-structured perovskite materials are related to the creation of ion resulting from the compensation of intrinsic structural defects (cations) or acceptor impurities. The dominant structural defects producing cation interstitial in $BaBi_4Ti_4O_{15}$ are not known. The concentration of ions and, consequently, the material's ferroelectricity are increased by acceptor doping and decreased by donor doping [20-22]. However, the effect of aliovalent dopants is relatively small.

These results show that the polarization can be reoriented only in the plane parallel to the Bi_2O_2 layers (the *ab*-plane of the orthorombic structure). No hysteresis loops were observed in the ***c***-axis oriented regions. This observation suggests that the macroscopic polarization depends on the degree of *ab*-axis orientation in the Aurivillius doped. The P_r and E_c values in the samples are caused by the random orientation of the grains. Newnham *et al.* [23] have reported that the perovskite layers in BSLFs compounds 'zigzag' along the *c*-axis depent on dopant.

The layer-structured ferroelectric oxides exhibit a high degree of anisotropy in their electrical properties owing to their crystal structure. A high dielectric constant in the *ab*-plane and a comparatively low dielectric constant along the *c*-axis have been observed in $BaBi_4Ti_4O_{15}$ single crystal [21]. There is a belief that Bi-layer-structured ferroelectric oxides with even *m* exhibit no spontaneous polarization along the *c*-axis, whereas those with odd *m* exhibit spontaneous polarization along the ***c***-axis [24].

Based upon the above consideration, it seems that the ferroelectric hysteresis loops obtained in $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (*A* = Pb, Al, Ga, In) and $BaBi_4Ti_{3.95}Ta_{0.05}O_{15}$ ceramics are solely due to *a*-axis oriented crystallites as do not observe any ferroelectric hysteresis loop in the *c*-axis oriented region of the ceramics.

CONCLUSION

The combined X-ray diffraction and Rietveld refinement confirm that series of $BaBi_{3.95}A_{0.05}Ti_4O_{15}$ (*A* = Pb, Al, Ga, In) and $BaBi_4Ti_{3.95}Ta_{0.05}O_{15}$ adopt orthorhombic system, in space group $A2_1am$. The the P-E hysteresis loops of the ceramics indicates the ferroelectricity in these compounds.

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