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Abstract — **BaTiO$_3$ ceramics were doped with acceptor metallic ions (Co, Mn, Fe) and co-doped with Co and Nb. Piezoelectric ceramics were prepared using conventional solid-state reaction. Addition of Li$_2$O sintering aid allows obtaining dense ceramics at low sintering temperature. Doping with Co acceptor leads to significant improve of piezoelectric properties but induce distorted and shifted hysteresis loop due to the presence of internal bias field. Field cooling poled ceramics are in the aged state just after poling. Increasing acceptor dopant concentration increases the internal bias field while co-doping with donor (Nb) reduces it. The data are consistent with presence of defect dipoles formed by acceptor substituted in B site and oxygen vacancy of BaTiO$_3$ tetragonal structure. Alignment of defect dipoles along driven electric field was observed through low frequency switching or cycling. Aging behaviors of unpoled and poled ceramics process were investigated through the study of hysteresis loops and reveal that charge compensation is not complete**

Keywords—Baryum titanate; piezoelectric; aging effect

I. INTRODUCTION

The change of properties with time or aging is a well-observed problem in piezoelectric materials. The ferroelectric aging phenomena, observed as double hysteresis loop for aged BaTiO$_3$:Mn single crystal, is attributed to reversible domain switching process [1]. This behavior is due to the creation of electric dipoles between the defects and the oxygen vacancies when Ti^{4+} is substituted by Mn^{3+}/Mn^{2+}. The hysteresis loop is explained with the symmetry of short-range order of point defects theory [2]. Barium titanate has recently shown interesting performance, making it a promising alternative to the PZT. To ensure the replacement of lead-based piezoelectric materials, study of the aging of lead-free material is crucial to the application.

II. EXPERIMENTAL PROCEDURE

Baryum titanate based materials were fabricated using oxide powder as raw materials: BaCO$_3$, TiO$_2$, Co$_3$O$_4$, Nb$_2$O$_5$, Li$_2$CO$_3$. The cobalt doping was introduced in substitution to the titanium. The powders were mixed and ball-milled by attrition in water for 1 h and were then dried and calcined at 1100 °C for 2 h. Thereafter, calcined powders were ball-milled by attrition for 0.5 h, dried, then mixed with the Li$_2$CO$_3$ powder.

The resulting powder were then pressed into a cylinder of 16.3 mm in diameter and 10-10.5 mm in thickness using polyvinyl butyral and dibutyl phthalate as a binder and a plasticizer, which was burnt out by heating at 600 °C for 0.5 h. Sintering was performed at 1100 °C for 4 h in air. The sintered cylinder was cut into several 0.5 mm thickness pellets, which were coated with silver paint on both surfaces and fired at 500 °C for 1 h. The coated samples were then poled in a silicone oil bath by Field Cooling, consisting on the applying of a DC electric field of 600 V/mm during the cooling process of the samples from 140-150 °C to 40-50 °C. Ferroelectric hysteresis curves were measured in two ways. One is by using an oscilloscope (Lecroy Waverunner 6030) in a homemade sawyer-tower circuit through a voltage measurement and the other by using electronic cards through a current measurement by using a commercial device (Aixacct aixPES with TFAnalyzer 2000).

III. RESULTS AND DISCUSSION

A. Defect dipoles – Internal bias field

It is known that acceptor doping involves aging problems [3]. The substitution of Ti^{4+} in the perovskite structure by di and tri valent ions (M) which has lower valence require charge compensation to maintain charge neutrality. An oxygen vacancy is indeed created and a defect dipole $(M_{Ti}\text{''}-V_O^{\circ\circ})^X$ is formed. The defect dipoles can be aligned along spontaneous polarization and deformed lattice by jumps of the oxygen vacancy towards the orientation with lowest energy and internal bias field E$_{int}$ was observed [4,5]. The increase and the decrease of the internal bias proceed in BT doped with Ni or Cr were calculated and measured with different time laws [6]. The internal bias time law is thermally activated and obeys the Arrhenius law. Both laws were correctly described by relaxation model of oxygen vacancy jumps between sites of oxygen octahedron.

In the ABO$_3$ cubic perovskite structure, apex top of the oxygen octahedron are equivalent and the oxygen vacancy V$_O^{\circ\circ}$ can form on any of them. In the tetragonal structure, the oxygen octahedron is distorted and possesses two non-equivalent oxygen sites, which are located respectively within the *ab* plane and along the *c* axis. The c/a ratio is 1.0105 and 1.0505

for BT and PT, respectively. The quantum-mechanical calculation for Cu/ Fe doped $PbTiO_3$ [7, 8] show that the two sites along the c axis are non-equivalents, the most stable configuration is ($M_{Ti}-V_{c1}$), therefore the defect induced dipole is oriented in parallel to the overall spontaneous polarization P_s. Thus in equilibrium, the polarization locally increases due to the formation and alignment of local defect dipoles. In contrast, the defect dipole of the alternative *c*-axis configuration ($M_{Ti}-V_{c2}$) causes a local reduction of the polarization.

Co, Mn, Fe were added as acceptor doping and Nb^{5+} was added as donor to substitute Ti^4 in BaTiO3 ceramics. The piezoelectric properties were significantly improved for co-doped ceramics. Addition of Li_2O sintering aid allows to obtain dense ceramics ($d_{rel} > 95$ %) at low temperature, between 800 and 1100 °C instead of 1350 °C for $BaTiO_3$ (BT) conventional sintering. The piezoelectric properties were significantly improved for Co doped ceramics. Piezoelectric constant of $d_{33}=225$ pC/N and thickness mode electromechanical coupling factor of $k_t=41$ % are obtained for samples with x=0.75 mol% of Co.

Fig. 1 presents the classical hysteresis loops of BT and the distorted loops for BT doped ceramics. The effect of cobalt adding in $BaTiO_3$ on hysteresis loop is clearly observed. Pure $BaTiO_3$ exhibits a typical symmetric ferroelectric hysteresis loop (Fig. 1a) while Co doped $BaTiO_3$ shows a double hysteresis cycle for unpoled and aged ceramic. The double loop is still observed for ceramic heated above Tc (150 °C) and cooling slowly to RT whereas symmetric loop is observed for

ceramics quenched from 150 °C to RT. Thermal quenching seems to freeze cubic structure in unpoled ceramic that relax with time to reach an aged state in tetragonal phase. Ceramics poled by field cooling exhibit distorted hysteresis loop and shifted to the negative electric field (Fig. 1b). Field cooling process was used to pole BT ceramics. At 150 °C (> T_C) BT ceramic is in cubic phase, when the material is cooled down up to 40 °C the structure becomes tetragonal, the oxygen octahedron is distorted. Similar to the structure of $PbTiO_3$, the most stable site for the oxygen vacancy in the tetragonal structure of the $BaTiO_3$ would corresponds to the one allowing the defect dipole orientates along the domain polarization. Since bias field was removed, poled & doped BT ceramics are already in the aged state and hysteresis loop is asymmetric and shifted. The internal bias field is measured as 835 V/mm on the loop recorded with triangular signal of 150 mHz. The measurement frequency of the hysteresis loops at 150 mHz is probably too fast for the oxygen vacancies migration and the defect dipoles does not have time to switch with the ferroelectric domains.

The same distorted & shifted loops were obtained for Mn and Co/Fe doped $BaTiO_3$ ceramics. The internal bias field increases from 750 V/mm for Mn doped sample to 935 for Co doped sample and it is measured as 685 V/mm for Co/Fe co-doped sample. These observations would be related to ionic radius and electronegativity difference of substituting ions.

B. Compensation by co-doping

Donor co-doping has been made with Nb^{5+}. The niobium should insert in B-site of the perovskite like $Co^{2+/3+}$ and is introduced in substitution to Ti^{4+}. In addition of the $Co^{2+/3+}$ doping, the adding of Nb^{5+} could compensate the charge imbalance and decrease the formation of oxygen vacancies thus decreasing dipole defect concentration [9]. Fig. 2 presents several materials with different amount of Co/Nb co-doping. The hysteresis loop becomes less shifted when 0.75 mol% of niobium is added in BT containing 0.75 mol% of Co. The internal bias field E_{int} decreases from 935 V/mm to 660 V/mm. When the amount of niobium increases to 1.5 mol%, the loop becomes more symmetric and centered and E_{int} decreased to
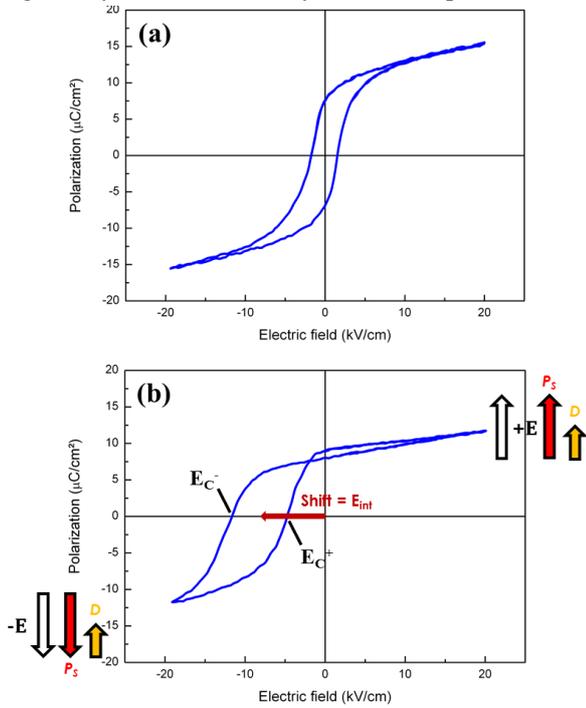
Fig. 1. P-E hysteresis loops of (a) pure $BaTiO_3$ (typical hysteresis loop) and (b) poled $Co^{2+/3+}$-doped $BaTiO_3$ with a representation of the ferroelectric domains and defect dipoles orientation depending on the applied electric field.
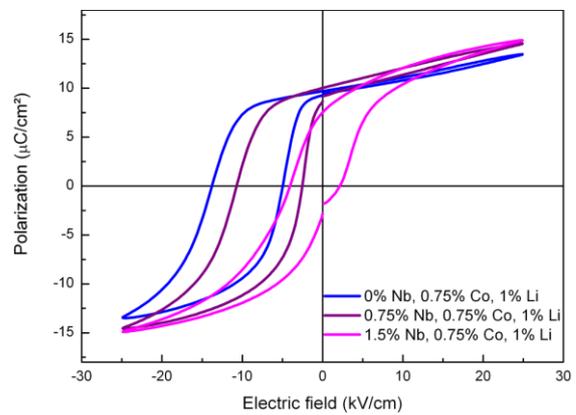
Fig. 2. P-E hysteresis loops of $BaTiO_3$ doped with $Co^{2+/3+}$ and different amount of Nb^{5+}.

150 V/mm. It can be observed that the higher the amount of niobium, the smaller the internal field. It can be suggested that defect dipoles concentration is reduced due to the reduction of oxygen vacancies concentration. However hysteresis loops remain shifted and the internal bias field is lower but not completely suppressed.

C. Cinetic of defect dipoles alignment

Measurement recorded at frequency of 150 mHz leads to the observation of the internal field on the hysteresis loop. Probably the defect dipoles do not have the time to switch. Measurements performed at a frequency of 10 mHz have been made in order to let the time for the defect dipole to switch. Results are presented on Fig. 3. It can be observed that the decreasing of the frequency make the shift of the hysteresis loop smaller. The Fig. 3a shows a hysteresis loop, which becomes symmetric at 10 mHz. Moreover E_{int} decrease from 580 V/mm to 330 V/mm and the coercive field $2E_C$ increase from 1160 V/mm to 1530 V/mm when the frequency changes from 150 to 10 mHz. It is more significant on Fig. 3b for a Co/Nb co-doped sample where the internal field is smaller: at 10 mHz, the sample recover practically a typical ferroelectric hysteresis loop with a very low value of E_{int} (50 V/mm at 10 mHz against 150 V/mm at 150 mHz). Thus, by decreasing the frequency, at least a part of the defect dipoles can reorientate and follow the switch of ferroelectric domains during hysteresis measurement.

D. Deaging by hysteresis cycling
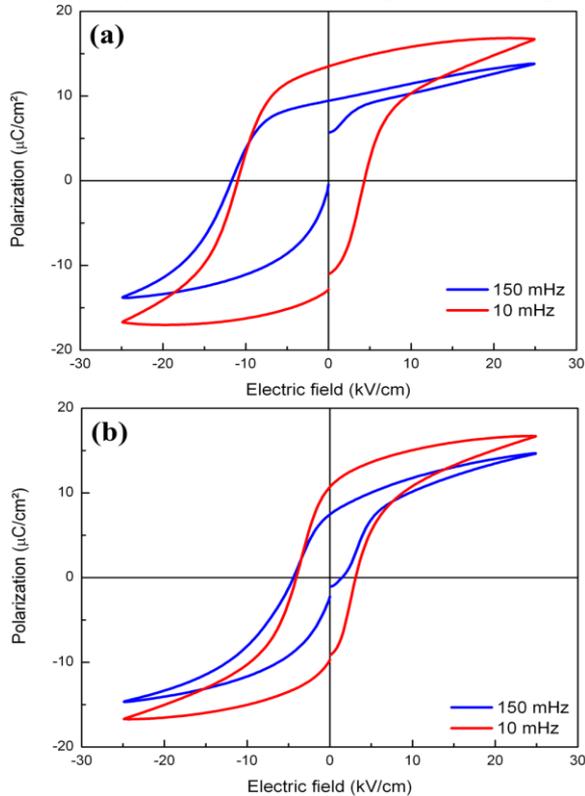
Deaged experiment has been design to test our polarized

materials and to follow the evolution of the internal field. The TFAnalyzer 2000 E has been used to apply a triangular wave of 1Hz with amplitude of 2500 V/mm on the sample for a total of 50000 cycles. Ten measurements have been performed per decade by sending a triangular pulse of 150 mHz at 2500 V/mm. Results of the experiment are presented on Fig. 4. It can be observed that throughout cycling, the shifted hysteresis loop gradually centers on the origin. The negative remnant polarization progressively decreases to become opposed to the positive remnant polarization. It corresponds to the hysteresis loop which becomes symmetric and centered. Thus when the material is subject to the electrical cycling the internal field decreased from 880 V/mm to 200 V/mm while the coercive field $2E_C$ increases from 900 to 1040 V/mm. This result can be explained by a creation of disorder among the defect dipoles. The alternative electric field applied during cycling redirects the defect dipoles and thus their orientation is not anymore parallel to the ferroelectric domain polarization. So these defect dipoles have less influence on the ferroelectric domain and therefore the internal field decreases. Moreover after the experiment, the material keeps a polarized state and thus is still a piezoelectric material.

IV. CONCLUSION

An addition of just 0.5 mol% of $Co^{2+/3+}$ is enough to create a strong internal field inside the $BaTiO_3$. This internal field is interpreted as the creation of defect dipoles formed by acceptor substituted in B site and oxygen vacancy of $BaTiO_3$ tetragonal structure leading to the distorted and shifted hysteresis loops. This behavior would be explained by the fact that the polarization is locally modified due to the formation and alignment of local defect dipoles along two non-equivalents *c*-axis configurations. Field cooling poled ceramics are in the aged state just after poling. For a poled cobalt doped sample, the internal field leads to an important shift of the hysteresis loop. An effective way to hinder the formation of the internal field is the co-doping with donor as the Nb^{5+} which significantly decreases it. But even with the niobium adding of twice the cobalt concentration, a small internal field remains in the material. Moreover depending on

Fig. 4. Hysteresis loops measured at 150 mHz and 10 mHz of (a) cobalt doped $BaTiO_3$ and (b) niubium and cobalt co-doped $BaTiO_3$.
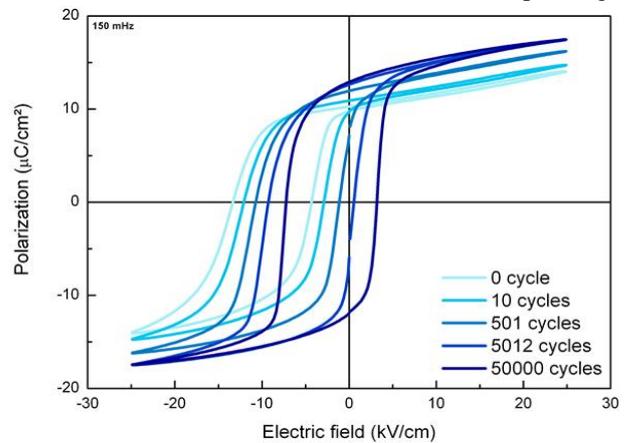

Fig. 3. Hysteresis loops after cycling during deaged experiment on cobalt doped sample.

the frequency during hysteresis measurement, the defect dipoles will not respond in the same way. A lower frequency indeed allows the switching of a part of the defect dipoles during hysteresis measurement. Furthermore it has been shown that after aging, a way to rejuvenate the ceramic was the electrical cycling. We have seen that through the de-aged experiment, the internal field of the ceramic decrease from 900 V/mm to 200 V/mm. After cycling, an internal field also remains in the material. Thus it could be interesting to go further and try to completely suppress the internal field.

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