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Toroidal ferroelectricity in perovskite nanoparticles

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ABSTRACT

Now-a-days, a novel concept of toroidal ferroelectricity is at the center of interest of many researchers. However, fundamental information of toroidal ferroelectricity is limited. In the present paper some novel thoughts regarding the same were illustrated on the basis of experimental evidences of domain structures in $Pb_{0.99}TiO_3$:$La_{0.01}$ and $KNbO_3$ nanoparticles. Additional oxygen uptake in the structure seems to be a possible source of toroidal ferroelectricity. We observed a few novel toroidal geometries in $Pb_{0.99}TiO_3$:$La_{0.01}$ nanoparticles. It was concluded that, the toroidal electric dipole moment collapses to zero under some circumstances and gives rise to conditions suitable for the regular ferroelectricity.

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Undoubtedly, the interest of many researchers in perovskite ferroelectric materials like $BaTiO_3$, $PbTiO_3$, $KNbO_3$, etc. is mainly due to their widespread applications for capacitors, memory devices, logic circuits, light modulators, sonar detections, second harmonic generators (SHG), photocatalysts and photoluminescence host materials [1–6]. The interest is again due to their typical properties like non-centrosymmetric cell structure, non-zero value of spontaneous polarization which can be reversed by the application of external electric field, dielectric non-linearity and domain structures [1,7–9].

The high-temperature phase of $BaTiO_3$, $PbTiO_3$ and $KNbO_3$ is cubic perovskite and paraelectric in nature, whereas the relatively low-temperature phase is tetragonal and shows ferroelectric behavior. In the tetragonal phase, as compared to their respective cubic phases there is a slight displacement of Ti or Nb ions along the z-axis with respect to the framework of oxygen octahedron. This displacement of Ti or Nb gives rise to Ti—O or Nb—O dipoles such that (001) axis becomes the direction of polar axis and also the direction of spontaneous polarization (P_s) [7,9].

The direction of all electric dipoles in a monodomain ferroelectric crystal tends to parallel to the direction of P_s, but it is worthwhile to note that the naturally grown single crystals generally comprise multidomain structures in which the direction of dipoles in each domain is orienting differently with respect to P_s of the crystal as a whole [7–9]. In the tetragonal phase of $BaTiO_3$, $PbTiO_3$ and $KNbO_3$, the electric dipoles in a domain lay down either perpendicular or antiparallel with respect to the P_s of the crystal as a whole and hence two kinds of domain structures are formed: 90° and 180°. In first kind all the dipoles lay down perpendicular and in second kind they are antiparallel to the

P_s of the crystal, but remember that the dipoles in a domain are always parallel to the localized spontaneous polarization direction [7–9].

The world of nanoparticles seems to be diversified. Many properties which are not usually seen in bulk material are surprisingly observed in nanoparticle counterparts. Occurrences of self-activated luminescence [10,11], enhanced photocatalytic activity [12] and unexpected phases [13–15] in otherwise compounds, and change in properties as compared to their bulk counterparts [11,15–17] are the few examples. As far as ferroelectricity in nanoparticles is concerned, there are many examples which show diminishing of ferroelectric properties in nanoparticles [18–20]. On the other hand, there are also few examples which show the enhancement in ferroelectricity [21].

"Toroidal ferroelectricity" seems to be one of the highly interesting and novel outcomes of the nanoworld. Toroidal magnetic moment in fact is not a new concept in ferromagnetic material [22–24], but it is of course a new ferroelectric analogy which was not suggested before 1994. Gorbatsevich and Kopaev [25] were the first who thought about the possibility of toroidal electric dipole moment in ferroelectrics. They also put forward a model of toroidal electric dipole moment [25]. In 2004, Naumov et al. [26] carried out 'ab initio' studies on nanodisks and nanorods of $Pb(Zr,Ti)O_3$ and suggested another model of toroidal ferroelectricity. Later, it becomes the center of interest of researchers and many experimental evidences and theoretical approaches of toroidal ferroelectricity have been reported [27–34]; but evidence of Gorbatsevich and Kopaev kinds' structure is not reported yet. Furthermore, being a novel concept there might be many characteristic features which are yet to known; lacking of which evidences of toroidal ferroelectricity sometimes look elusive [34].

Toroidal ferroelectricity of Naumov et al. kinds in materials can be recognized by means of presence of 'vortex' or 'flux-closure' domain structures differed from the classical vortices as reported in

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ferromagnetic materials [22–24]. According to the reports, polarization vortices bear a tremendous potential which can be used for the development of ultra-high memory storage nanodevices and nanotransducers [3,26,35,36]. More novel applications will be explored with the enrichment of fundamental knowledge of toroidal ferroelectricity. However, at present, such knowledge is insufficient. Therefore in this present paper some logical and practical ideas regarding the toroidal ferroelectricity are discussed.

Transmission electron microscopy (TEM) and high resolution TEM images of nanoparticles of La^{3+} doped $PbTiO_3$ and undoped $KNbO_3$ were used for the study, as toroidal structure investigations by TEM are highly appreciable [27,28,30,31]. Nanoparticles of La^{3+} doped $PbTiO_3$ (i.e. $Pb_{0.99}TiO_3:La_{0.01}$) were synthesized by a simple sol-gel method [37] and that of $KNbO_3$ by a polymerized complex method. Details of preparation techniques are given in Supplementary file (S1). Obtained nanoparticle samples were structurally characterized by X-ray diffractometer (D8 ADVANCE, BRUKER, GERMANY) employing CuKα radiation (1.5406 Å). As far as for the present study points of view, the importance of X-ray diffraction characterizations is modest therefore they are also given in the Supplementary file (S1). Only significant TEM and HRTEM images of the samples taken by transmission electron microscope (TEM) (JOEL, JEM 2100) are included here.

Fig. 1a and b are the selective TEM images of $Pb_{0.99}TiO_3:La_{0.01}$ nanoparticles. Fig. 1a comprises incomplete and approximately circular black and white strips as seen in particle marked by 'A'. Recently we studied the existence of various kinds of ferroelectric nanodomain structures and the role of domain morphology for controlling the size and the shape of $PbTiO_3$ nanoparticles [37], but the structures like as seen in 'A' (Fig. 1a) and/or in 'C' (Fig. 1b) were not found. This clearly indicates that, in the present doped $PbTiO_3$ samples they are due to La^{3+} impurity. In this compound, similar to $CaTiO_3$, two types of charge-compensated structure are possible [38]: $(Pb^{2+})_{0.99} (La^{3+})_{0.01} (Ti^{4+}) (O^{2-})_{(3 + 0.005)}$ and $(Pb^{2+})_{0.99} (La^{3+})_{0.01} (Ti^{4+})_{0.99} (Ti^{3+})_{0.01} (O^{2-})_3$. The fractional change in Ti^{4+} to Ti^{3+} may give rise to a little change in Ti position in TiO_6 octahedra of perovskite structure at few sites, which in turn favors the usual ferroelectricity [7,9] rather than the unusual one. The presence of usual domain structure in crystallite 'B' (Fig. 1a) therefore indicates the occurrence of second type of charge compensation in the compound. However the domain structures in crystallites 'A' and 'C' in Fig. 1a and b respectively being different than the usual ferroelectric domains, were assigned to the first kinds of charge compensation, i.e. $(Pb^{2+})_{0.99} (La^{3+})_{0.01} (Ti^{4+}) (O^{2-})_{(3 + 0.005)}$. Thus both types of charge compensated structures are present in different particles of the compound. Nevertheless, this classification may be limited to only lower dimensional nanoparticles.

At the first site, domain structures in the crystallites 'A' and 'C' (Fig. 1) look similar to the geometry of toroidal structure as suggested by Gorbatsevich and Kopaev [25]. For better understanding their model is given schematically in Fig. 2a. Scott [35] concluded that the model of Gorbatsevich and Kopaev (Fig. 2a) is equivalent to the model of Naumov et al. [26] (Fig. 2b) at larger geometric radius or at additional atomic layers. Since, as said above, there are sufficient experimental evidences of Naumov et al. type toroidal ferroelectricity in the form of 'vortex domain' structures and 'flux-closures', the formation of Gorbatsevich and Kopaev type toroidal structures was also expected.

According to Gorbatsevich and Kopaev, the geometric image of toroidal dipoles is a solenoid folded into a torus (Fig. 2a) [25]. If such solenoids are supplemented with increasing radius, the model of Gorbatsevich and Kopaev takes the form as shown in Fig. 3. If we make the rotation of the local vortices in consecutive solenoids as opposite, the toroidal electric dipole moment (G) of the local vortices will be opposite in each solenoid, and line of contact of each solenoid becomes the toroidal 180° domain boundary. A careful observation of the cross-sectional view of such a system shows that the dotted plane in Fig. 3 is similar to the model of Naumov et al. [26]. Thus the toroidal structure in crystallite 'A' (Fig. 1a) is similar to the sketched geometry as given
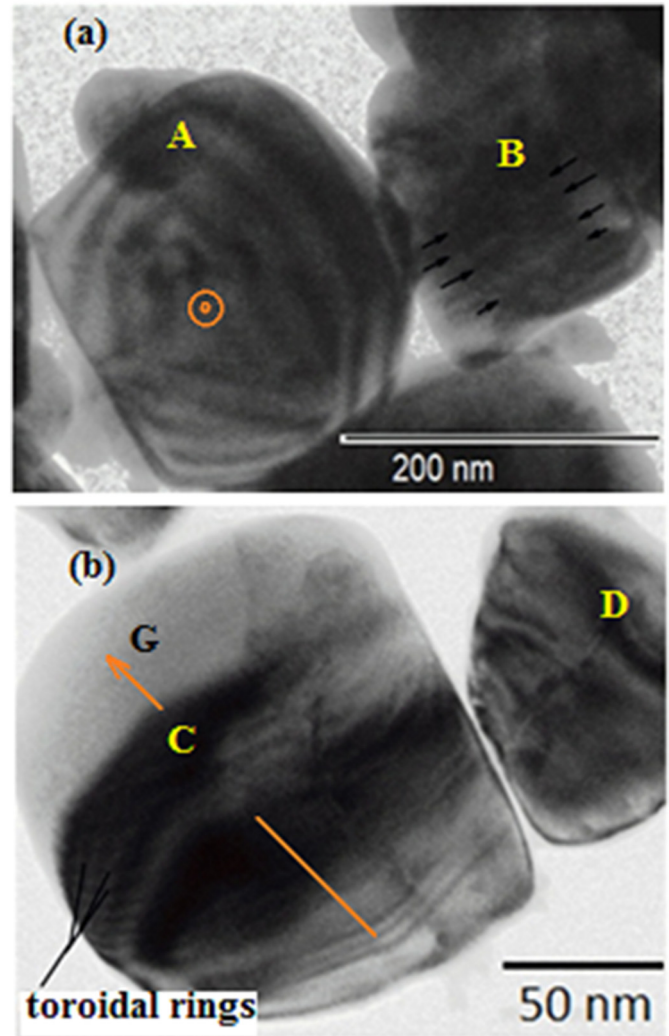

Fig. 1. TEM images of tetragonal $Pb_{0.99}TiO_3:La_{0.01}$ nanoparticles. In (a), the crystallite marked by 'A' comprises toroidal structures (black and white circular strips); circle marked at the center indicating the toroidal moment G nearly perpendicular to the plane of paper. A careful observation shows the crystallite 'B' consists of regular ferroelectric domain pattern parallel to the marked arrows. Another toroidal structure (crystallite 'C') with toroidal direction G is seen in (b); no distinguished toroidal structure is found in crystallite 'D'.

in Fig. 3. Similarly, the toroidal structure in crystallite 'C' (Fig. 1b) will be appeared similar to the one when we place solenoids of equal radius one above another with opposite local toroidal moment.

It is necessary to note that the toroidal domain structures are differing from the usual ferroelectric domains structures by means of few parameters. Ferroelectric domain structures are generally linear and P_s is one of the main parameters which define the ferroelectricity [7–9]. On the other hand toroidal domain structures are circular or flux-closure types in which the electric dipoles are continuously rotating with respect to the local polarization P. The main parameter which defines the toroidal ferroelectricity is the toroidal electric dipole moment (G) rather than the spontaneous polarization, and can be expressed by the equation [26],

$$G = 2N^{-2}\sum_i r_i \times p_i \tag{1}$$

where, p_i is the polarization of local dipole of cell i located at r_i, N is the number of cells under consideration, and $P = N^{-1}\sum_i p_i$.

Though there are many studies on toroidal ferroelectricity, the reason of toroidal moment is given by Naumov et al. [26]. According to