Multiferroics have received enormous attention due to the coexistence of magnetically and ferroelectrically ordered states and the magnetoelectric phenomena arising from the coupling between these two. The coupling allows controlling of the magnetic properties by an application of an electric field and vice versa. As a result, it provides an additional degree of freedom in designing actuators, sensors, and data storage devices. Understanding the atomic-scale structure of multiferroics when reduced to nanosized dimensions has become increasingly important with the current advancement of nanotechnology. It is also intriguing from a fundamental point of view. An archetypal example of a multiferroic material is BiFeO$_3$. This material shows a strain induced structural transformation where the crystal retains its monoclinic symmetry (Cc) but the ratio ($c/a$) of the lattice parameters changes abruptly. Recently, an electric-field induced phase transition (Cc-Cc) has been observed in BiFeO$_3$. Such phase transitions are known as iso-structural since the underlying crystal structure symmetry of the material does not change. In general, iso-structural phase transitions are accompanied by anomalous changes in various physical properties such as specific heat, dielectric constant, etc. Pressure induced iso-structural phase transitions have also been observed. It is not obvious though how to select the order parameter of iso-structural phase transitions. Different order parameters such as defect concentration, atomic positions, compressibility, bond angles, cell volume, and lattice parameters have been suggested. The choice of the latter two has been prompted by the observation of an anomalous change of the unit cell volume and the ratio of the lattice constants ($c/a$) occurring while the underlying space group symmetry remains intact. Recently, a temperature induced isostructural phase transition was observed with another potentially important Pb and Bi free multiferroic material—YMnO$_3$. It has potential applications in electronic devices such as sensors and non-volatile random access memories. Bulk YMnO$_3$ exhibits spontaneous ferroelectric polarization below $T_{CEF} \approx 930$ K. Additionally, it shows an antiferromagnetic ordering below the Néel temperature $T_N$ of 70 K. At room temperature, bulk YMnO$_3$ is hexagonal and may be well viewed as a stack of disconnected layers of MnO$_5$ polyhedra with Y atoms positioned between those layers. The volume of the unit cell is three times that of the high temperature centrosymmetric phase (S.G. P6$_3$/mmc; $a_{PE}$, $c_{PE}$) that exhibits paraelectric properties. The lattice parameters of these two phases relate to each other as follows: $a_{FE} = \sqrt{3} a_{PE}$ and $c_{FE} = c_{PE}$. The ferroelectric phase is related to the high temperature paraelectric phase by an antiferrodistortive transition taking place at $T_{CAF}$ $\approx 1270$ K. The paraelectric to ferroelectric transition temperature $T_{CEF}$ is somewhat lower than $T_{CAF}$. The onset of the ferroelectric order in YMnO$_3$ is accompanied by buckling of the layers of MnO$_5$ polyhedra.
and displacement of the Y ions leading to a net electric polarization.\(^1\) This transition does not involve a change in the crystal symmetry and so can be characterized as an iso-structural phase transition that is of an order-disorder type.\(^1\) In the present work, we study the atomic-scale structure of YMnO\(_3\) as a function of particles size using synchrotron X-ray diffraction (SXRD) data. We found that nanosized YMnO\(_3\) exhibits an iso-structural phase transition due to the appearance of structural disorder induced by finite size confinement effects. According to the uncertainty principle such a confinement of particles to nanosized dimensions would lead to a gradual increase of the root mean square (rms) fluctuation of atoms about their average positions in the crystalline lattice.\(^1\)

The samples we investigated were prepared by an aqueous chemical synthesis route described elsewhere.\(^20,21\) The cation stoichiometry was controlled through thermogravimetric determination of the cation concentrations of the Y and Mn precursor solutions used in the synthesis to ensure a 1:1 ratio of Y and Mn. The oxygen stoichiometry of YMnO\(_3\) is determined by the thermal history, the temperature, and partial pressure of oxygen at the synthesis conditions. Thermogravimetric measurements showed that YMnO\(_3\) is oxygen stoichiometric under the synthesis conditions used to prepare the materials investigated in the present work.\(^21,22\)

Synchrotron x-ray diffraction (XRD) experiments were carried out at the 11-ID-C beamline at the Advanced Photon Source using x-rays with energy of 115.232 keV (\(\lambda = 0.1076\) Å) and a large-area (mar345) detector.

Rietveld analysis of the synchrotron powder diffraction data was carried out using the program Fullprof.\(^22\) Pseudo-Voigt function was used to define the SXRD peak profiles in the refinements. The SXRD peak profile parameters, the lattice constants, atomic coordinates, and thermal parameters were refined.

Fig. 2 shows the evolution of the SXRD patterns for YMnO\(_3\) with decreasing particle size (\(x\)), where \(x = 470, 171, 121, 49, 38,\) and 28 nm. The SXRD patterns show two types of Bragg peaks: peaks due to the underlying hexagonal (P6\(_3/mmc\)) symmetry of YMnO\(_3\) and super-lattice peaks. The latter arise from the tilting of the MnO\(_3\) polyhedra and the antiparallel displacement of Y atoms. The supercell (anti-ferrodistortive phase) of YMnO\(_3\) results from a hardening of a soft zone boundary (K\(_3\); \(q = 0 0 1/3\)) mode which causes a tripling of the cell but does not lead to an overall polarization.\(^1\) The ferroelectricity in the cell arises due to a hardening of soft zone center (K\(_1\); \(q = 0 0 0\)) phonon modes leading to identical displacements of Y atoms in each unit cell and overall polarization.\(^1\) The (102) super-lattice SXRD peak is marked with a dashed line in Fig. 2. The intensity of this peak diminishes as the size of YMnO\(_3\) particles decreases. A similar effect has been observed for bulk YMnO\(_3\) with increasing temperature.\(^1\) In the latter case, the intensity decrease is due to the increasing thermal disorder in the material.\(^1\) In order to have a clear understanding of the evolution of the super-lattice peak, we have shown it on an enlarged 2\(\theta\) scale in the inset of Fig. 2. The peak is seen to survive down to particle sizes of 28 nm. Evidently, the crystal structure of nanophase YMnO\(_3\) retains the P6\(_3/mmc\) symmetry down to \(x = 28\) nm, where the crystallinity gradually decays with decreasing particles size so the sample below 28 nm are nanocrystalline in nature. The parameters of the hexagonal lattice and the volume of the hexagonal unit cell, however, evolve not quite in line with diminishing particles size. The evolution of the lattice parameters (\(a_{\text{FE}}, c_{\text{FE}}\)) and their ratio (\(a_{\text{FE}}/c_{\text{FE}}\)) with particle size is shown in Fig. 3. As can be seen in the figure (\(a_{\text{FE}}, c_{\text{FE}}\)) and \(c_{\text{FE}}/a_{\text{FE}}\) show an anomaly around \(x = 121\) nm. The \(c_{\text{FE}}/a_{\text{FE}}\) increases when \(x\) decreases from 470 to 121 nm and then abruptly decreases with further decreasing \(x\), indicating an iso-structural phase transition. The signature of variation of the lattice constants and their ratio is marked with a dashed-dotted line in Fig. 3. Though this phase transition is of a different origin, it is similar to the temperature driven iso-structural phase transition in bulk YMnO\(_3\) observed by Gibbs \textit{et al.}\(^1\) Gibbs \textit{et al.} have shown evidence that the iso-structural phase transition in bulk YMnO\(_3\) at high temperatures is due to thermal disorder.\(^1\) Anomalies in the displacements of oxygen atoms, Y-O bond length, and the amplitude of various distortive phonon modes confirm the transition in bulk YMnO\(_3\). The ferroelectric polarization calculated from a simple ionic model also reveals an anomaly at approximately 920 K.\(^1\)

The variation of the unit cell volume \(V_{\text{H}} = a_{\text{H}}^2 c_{\text{H}}(\sqrt{3}/2)\) as obtained from the Rietveld refinements is shown in Fig. 4. The anomalous behavior of the cell volume at particle size of approximately 121 nm also suggests the presence of an iso-structural phase transition. Signatures of an iso-structural phase transition are also seen in the evolution of position of Y atoms with particles size. As shown in Fig. 5, the relative
displacements of Y atoms, \(2^*d_{Y1} + 4^*d_{Y2}\), from their average positions in the hexagonal lattice shows an anomaly at a particle size of 121 nm. Here \(d_{Y1}\) and \(d_{Y2}\) are the \(z\) displacements of the two unequivalent Y atoms in YMnO. The quantity \(2^*d_{Y1} + 4^*d_{Y2}\) can be defined as an order parameter of the iso-structural phase transition. Also, it is a measure of the ferroelectricity as the Y atoms displacements play a major role in determining the ferroelectric polarization. The abrupt change of \(2^*d_{Y1} + 4^*d_{Y2}\) at 121 nm indicates an abrupt change in the ferroelectricity. Thus similarly to the temperature driven iso-structural phase transition in bulk YMnO observed by Gibbs et al., a phase transition is observed with nanosized YMnO when the particles size is reduced to about 121 nm. Recent studies have also shown a change in the anti-ferromagnetic transition temperature with decreasing particles size of YMnO. Thus, we find a change in the physical properties associated with the iso-structural phase transition induced by quantum confinement effects.

In summary, high-energy SXRD studies reveal an isostructural phase transition with the reduction of particle size in YMnO. The phase transition has striking similarities with the high temperature phase transition of bulk YMnO at \(\sim 920\) K.

However, in nanosized YMnO it is driven not by thermal but by structural disorder due to the confinement of YMnO particles to very small dimensions.

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