Correlation between structure and properties in multiferroic
La$_{0.7}$Ca$_{0.3}$MnO$_3$/BaTiO$_3$ superlattices.

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Abstract

Superlattices composed of ferromagnetics, namely La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO),
and ferroelectrics, namely, BaTiO$_3$(BTO) were grown on SrTiO$_3$ at 720$^\circ$C by
pulsed laser deposition process. While the out-of-plane lattice parameters of
the superlattices, as extracted from the X-ray diffraction studies, were found
to be dependent on the BTO layer thickness, the in-plane lattice parameter
is almost constant. The evolution of the strains, their nature, and their dis-
btribution in the samples, were examined by the conventional $\sin^2\psi$ method.
The effects of structural variation on the physical properties, as well as the
possible role of the strain on inducing the multiferroism in the superlattices,
have also been discussed.

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I. INTRODUCTION

Superlattices, which are composed of thin layers of two or more different structural counterparts that are stacked in a well-defined sequence, may exhibit some remarkable properties that do not exist in either of their parent compounds. For example, a \((\text{LaFeO}_3)/(\text{LaCrO}_3)\) superlattice stacked on \((111)-\text{SrTiO}_3\) exhibits a ferromagnetic behavior, whereas each parent material is antiferromagnetic\(^1\). Similarly, perovskite based superlattices have shown new or enhanced properties such as high temperature superconductivity, ferroelectricity, \textit{etc.}\(^2\)–\(^9\) In recent years, various efforts have been made to synthesize and study the structure and properties of various superlattices based on perovskite oxides. Hence, the superlattices offer a novel approach to create a new type of materials or tailor the existing one for their suitability in real applications. Generally, the properties of the superlattices depend on the various factors, such as type of layer materials, their thickness, morphology, interfacial structure between them, substrate, etc. Moreover, the lattice mismatch among the individual type of layer materials employed for creating the superlattices, and between the substrate and the individual type of layers, play an important role in determining the interfacial structure which in turn governs their electronic and magnetic properties\(^5\).

Materials in which ferromagnetism and ferroelectricity coexist\(^10\) and eventually, possess multiferroic coupling, \textit{i.e.}, magnetic domains can be tuned by the application of an external electric field (and likewise electric domains are switched by magnetic field) are known as multiferroics. Thus, these materials offer an additional degree of freedom in designing the various novel devices, \textit{e.g.}, transducers, actuators, and storage devices, which are unachievable separately in either ferroelectric or magnetic materials\(^11\). Hitherto, very few materials exist in nature or synthesized in laboratory which exhibit multiferroism\(^12\)–\(^18\). Why and under what circumstances a large multiferroic coupling should come about is an open question. However, this problem has been proven difficult to tackle owing to the lack of materials which possess large multiferroic coupling. The scarcity of multiferroics with large multiferroic coupling at moderate conditions is also one of the big hurdle in the realization of
multiferroic devices. Thus, it is very important to design novel multiferroics with essential properties.

To synthesize the artificial structures which exhibit multiferroism, various approaches have been made. One of the most common approach, which can be used for synthesizing the artificial multiferroics is doping of the magnetic impurities in ferroelectric host. Other alternative direction which have been adopted is to synthesize the composites by mixing the ferroelectrics and ferromagnetic in the form of either bulk or thin films. Superlattices approach that have been adopted for synthesizing the new materials, can also be employed for designing multiferroics. In our previous works, we have demonstrated that superlattices composed of ferromagnetic and ferroelectric layers posses extraordinary magneto-electrical properties and such results have been understood based on the possible multiferroic coupling in these structures. Furthermore, we have also shown that their magneto-electric properties are depending on the nature layers, i.e. ferroelectric or paraelectric. For example, a drastic enhancement in the magneto-electric properties of Pr$_{0.85}$Ca$_{0.15}$MnO$_3$/Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ superlattices is observed, whereas it was absent in Pr$_{0.85}$Ca$_{0.15}$MnO$_3$/SrTiO$_3$ superlattices confirming the importance of the nature of the layers for the multiferroic properties. Very recently, we have also shown the presence of magnetocapacitance effects in La$_{0.7}$Ca$_{0.3}$MnO$_3$/BaTiO$_3$ superlattices, which demonstrate that these superlattices are behaving as multiferroics. Furthermore, La$_{0.7}$Ca$_{0.3}$MnO$_3$/BaTiO$_3$ superlattices also have exhibited an enhancement in their magnetization with the progressive increase in the ferroelectric layer thickness, indicating that such superlattices can exhibit multiferroism under suitable conditions.

As discussed above, various recent studies on the superlattices shown that their properties depend strongly on their structures, e.g., morphology, thickness, compositions, strains etc. Thus, it is expected that the multiferroism in the superlattices will be dependent on their structure, which in turn will govern their properties and consequently, the performance of the devices based upon them. Therefore, we have investigated the structure of superlattices composed of La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) and BaTiO$_3$ (BTO) in order to study their structure. The evolution of the strains as a function of the BTO layer thickness, and the structural

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coherency have been analyzed by utilizing asymmetrical X-ray reflections and the $\sin^2\psi$ method. A correlation between structure and properties has been established and our results are reported in this article.

II. EXPERIMENTAL DETAILS

The deposition of the La$_{0.7}$Ca$_{0.3}$MnO$_3$/BaTiO$_3$ (LCMO/BTO) superlattices on (001)-oriented SrTiO$_3$ (STO) were carried out at 720°C in a flowing 100 mTorr O$_2$ ambient by a multitarget pulsed laser deposition technique. Superlattices composed of individual BTO layer thickness varying from 1 to 25 unit cells (u.c.) and the 5 u.c. LCMO with a total periodicity of 25 were realized. 5 u.c. of LCMO were chosen because thin layers of LCMO behave as a ferromagnetic insulator, which is an important factor in designing the artificial multiferroics.$^{24}$

The epitaxial nature and the structural characterization of the films were performed using the Seifert 3000P and Phillips X’Pert X-ray diffractometers (Cu K$\alpha$, $\lambda=0.15406$ nm). The $\theta−2\theta$, $\phi$, and rocking curve ($\omega$) -scans were recorded on the samples. Morphological study of the films was carried out by atomic force microscopy. Magnetization (M) of the films was measured as a function of temperature (T) and magnetic field (H) using a superconducting quantum interference device magnetometer (SQUID). DC electrical properties of films were measured in four-point probe configuration.

III. RESULTS AND DISCUSSION

A. Structural studies

Both LCMO and BTO possess the perovskite structure and their structures are well studied and documented.$^{25}$ LCMO exhibits a cubic symmetry and its bulk lattice parameter is 0.386 nm. Thus, the lattice mismatch between the SrTiO$_3$ (STO) (a = 0.3905 nm) and LCMO is about $-1.17\%$. In contrast, BTO exhibits several crystallographic polymorphs.
The most stable polymorphs are tetragonal \((a = 0.39926 \text{ nm} \text{ and } c = 0.40309 \text{ nm})\) and cubic \((a = 0.4006 \text{ nm})\). The lattice mismatch between BTO and STO is close to \(+2.2\%\).

To investigate the crystallinity and epitaxial nature of the films, X-ray diffraction (XRD) studies were carried out on various samples. Fig 1 shows \(\theta - 2\theta\) XRD patterns of the films around the \((002)\) reflection with varying BTO layer thickness. The presence of higher order satellite peaks (denoted by the number \(i\) which corresponds to the \(i^{th}\) satellite peak) adjacent to the main peak (denoted by \(i = 0\)) indicates the formation of a new structure having a periodic chemical modulation \((\Lambda)\) of the constituents and a coherently grown film, \(i.e.,\) with the single value of in-plane lattice parameter throughout the entire thickness. The out-of-plane lattice parameter of the superlattice \((\Lambda)\), calculated from \(\theta - 2\theta\) XRD patterns (Fig. 1b) is in good agreement with theoretical values. To extract the information about the coherency at interfaces, we have carried out a quantitative refinement of the superlattice structure using the DIFFAX program.\(^{26}\) The experimental and simulated diffraction profiles of the \((5/10)\) superlattice structure are shown in Fig 2a. The simulated profile is in close agreement with the observed XRD pattern revealing a coherently grown structure.

Furthermore, to examine the in-plane coherence, \(\Phi\)-scan was recorded around the 103-reflection of the superlattices. A typical pole figures (\(i.e.,\) a series of \(\Phi\)-scans plotted in three dimensions) for \((5/10)\) superlattice is shown in Fig 2b. Four peaks are clearly observed at 90° from each other, indicating a four-fold symmetry as expected for the perovskite structures-LCMO and BTO. Similar scan recorded on the substrate confirms that the superlattice grown epitaxially "cube-on-cube". Thus, from the observed XRD pattern it is evident that films have well-defined interfaces. To get more in-depth information about the strain and as well as coherence in the films, rocking curves around the 002-reflection of the film were recorded. A typical rocking curve for a 5/10 superlattice is shown in the inset of Fig 3a. The observed full-width-at-half-maximum (FWHM) of the rocking curve recorded around the fundamental \((002)\) diffraction peak is close to the instrumental broadening \((< 0.3°)\), indicating a good crystallinity and a good coherency. The FWHM as a function of BTO u.c. is plotted in Fig 3a. It shows that the FWHM of the film is varying with the BTO
thickness and attains maximum value (~0.2°) for the (5/15) superlattice. The FWHM of the XRD peak in thin films usually comes from various factors, *e.g.* crystallite size, strain, defects, substrates and film/substrate interface etc. Moreover, in the case of epitaxial film, it basically arises from the strain, the composition, and the microstructure of the thin film. In the present case, since all the samples were grown under identical conditions, the increase in FWHM is mostly arising from the strains in the film. Thus, it reveals that first, the strain induced in these heterostructures are dependent on the BTO thickness layer and second, that it is maximum in the case of the (5/15) superlattice (5 u.c. LCMO / 15 u.c. BTO). Moreover, the decrease of the FWHM values at higher thickness of BTO suggests that there is a relaxation of the strains in the films.

To investigate further the structure of the films, we have calculated the in-plane (a) and out-of-plane (c) lattice parameters of the films from XRD data by measuring the asymmetric reflections, namely 10{l} (where l=1, 2, 3). The lattice parameters of the films plotted as a function of the BTO layer thickness are shown in Fig 3b. The experimental error is about ±0.01Å. Fig. 3b reveals that the out-of-plane lattice parameter is approaching to the bulk value of the BTO lattice parameter (close to 4.1Å) as the number of BTO u.c. increases. However, the in-plane lattice parameter is almost independent of the number of BTO u.c and does not show any clear trend. Therefore, we have also plotted in Fig 3c, the \( (c/a) \) ratio of the in-plane (a) and the out-of-plane (c) lattice parameters as a function of number of BTO u.c. since it provides information about the distortion of the perovskite structure. As shown in Fig 3c, the \( (c/a) \) ratio is varying in the range of 0.96 to 1.04 depending on the number of BTO u.c. The error (based on the errors of the lattice parameters) is close to ±0.02Å and the \( (c/a) \) ratio is increasing from 0.97 to 1.04 when increasing the number of BTO u.c. from 5 to 15, leading to a distortion larger than 1 above 5 u.c. This suggests that the thickness of the individual BTO layer is playing a very important role in governing the superlattice structures.

We are now trying to correlated these results with the properties. The ferroelectricity in BTO depends on the details of TiO\(_6\) polyhedra. In other words, tetragonal-BTO is fer-
roelectric whereas it is paraelectric in the cubic form. From the lattice parameter point of view, the lattice parameters difference between cubic and tetragonal forms of BTO is not very large. However, further investigation of the distortion of the TiO$_6$ octahedra-as inferred by the $(c/a)$ ratio-yields the reason for the two observed electrical forms. In the tetragonal BTO $(c/a = 1.01)$ Ti is undersized for the TiO$_6$ octahedra and will align ferroelectrically in the $c$-direction. On the other hand, in the cubic form of BTO, Ti is not constrained to align only in a particular direction and a paraelectric state is observed. Thus, the ferroelectricity in BTO depends on the degree of distortion in TiO$_6$ octahedra. To create the multiferroic superlattices, one expects that the BTO should be ferroelectric in nature and it is possible only if the total superlattice structure is showing a distorted perovskite structure i.e. '$c/a$' ratio should not be equal to 1. In addition, the electrical polarization in thin films of BTO depends on their thickness. However, the superlattices composed of BTO and oxide dielectrics have shown that even one unit cell of BTO possess the electrical polarization. Thus, the presence of the ferroelectricity in superlattices will be dependent on the details of the layered materials, their thickness, and the strain in the films. On the contrary, the magnetic properties of the manganites are governed by the Mn$^{3+}$-O-Mn$^{4+}$ structure. In other words, by varying the Mn-O bond lengths and Mn$^{3+}$-O-Mn$^{4+}$ bond angle, its possible to control (or suppress) the ferromagnetism in manganites confirming that the strain in the film plays a major role in determining the Mn$^{3+}$-O-Mn$^{4+}$ structure. Consequently, for designing a superlattice for multiferroics, it will be important to find an optimum stress/strain in the film, so that both the ferroelectricity and ferromagnetism are present. Furthermore, the ferromagnetic layer should be insulating in nature, otherwise due to the high leakage current the ferroelectricity will be suppressed in the structure. Thus, one has to find a delicate balance between the strain/stress in the superlattices together with the properties of the individual components. In the present case, the distortion of the superlattices depends on the layer thickness of the BTO. As mentioned above the distortion in $(5/5)$ is in-plane whereas it is out of plane in the $(5/15)$ superlattice case. Keeping in mind the easy axis direction of BTO polarization, the $(5/15)$ superlattice should exhibit the maximum coupling. Here, it is also worth noting...
that the easy axis of electrical polarization of bulk BTO is parallel to the \( c \)-axis (i.e. the out-of-plane direction). Thus, to have a large ferroelectricity, and consequently a maximum multiferroic coupling in the case of LCMO/BTO, the sequence should be \((5/15)\). Finally, such results show that the lattice parameters and the \((c/a)\) ratio (Fig 3b and 3c) extracted from the XRD data corroborate our FWHM-rocking curve findings.

The investigation of the nature of strains and their distribution in the samples were carried out by the conventional \( \sin^2 \psi \) method, where \( \psi \) is the angle between the lattice plane normal and the sample surface. The \( \sin^2 \psi \) method is non-destructive and commonly used technique to investigate the elastic properties of the polycrystalline materials.\(^{27,28}\) This techniques have been extended sucessfully to study the average elastic properties of the multilayer films under certain approximation.\(^{8,29,30}\) It provides a good information about the average strain distribution and their nature in the films. In the bi-axial model for a cubic structure, the strain (\( \varepsilon \)) in the film along the \([hkl]\) can be defined as\(^{27}\)

\[
a = \left( \frac{d_{hkl}(\phi \psi) - d_o}{d_o} \right) = \varepsilon_{11} - \varepsilon_{33} \sin^2 \psi + \varepsilon_{33} \ldots \ldots \ldots (1)
\]

where \( \phi \) is the angle between the projected lattice plane normal and in-plane axis. The parameters \( d_{hkl} \) and \( d_o \) are the strained and unstrained plane spacing of the samples, respectively. \( \varepsilon_{11} \) and \( \varepsilon_{33} \) are the in-plane and out-of-plane strain component of the film. To estimate the strain in-plane and, out-of-plane the \( d_o \) value was calculated by assuming that all the samples have same Poisson’s ratio (\( \nu \)) and using the theoretical value (0.37) of manganites since, the Poisson’s ratio is in the range of 0.3-0.5 for perovskites.\(^{31,32}\) However, we are well aware of the shortcomings of the present assumptions that will be discussed hereafter. For investigating the strain in the film, we have chosen a unique direction with constant \( h \) and \( k \) to measure the diffracted X-ray intensity as well as \( \psi \) from the reflection. Value of the \( \psi \) is sensitive to the alignment of the sample and to minimize it, we have averaged over all \( \phi \)-directions. A typical \( d_{10l} \) vs. \( \sin^2 \psi \) is shown in the inset of Fig 4a. It shows that \( d_{10l} \) varies linearly with respect to \( \sin^2 \psi \), which shows that the strains are uniformly distributed in the film. The estimated \( d_{103} \) of the superlattices is plotted as a function of BTO u.c. and shown in Fig 4a. Fig 4a clearly shows that the \( d_{10l} \) varies a little with the increase in BTO
u.c. The estimated value of the in-plane and out-of-plane strains as a function of BTO u.c. are shown in Fig 4b. From Fig 4b, it is evident that the film has large in-plane tensile strain and compressive strain in out-of-plane direction. To understand Fig. 4b, we need to define the terms superlattices, strained multilayers, and relaxed multilayer structures. In theory, an ideal superlattice can be defined as a single extended crystal having perfect registry with the orientation of the underneath layer and its \(a\) and \(b\) lattice parameters are basically governed by the substrate whereas the 'c' parameter is closed to the sum of the bulk 'c' lattice parameters of each stacked material employed for fabricating the superlattice. However, in reality due to the lattice mismatch and the cationic size of the various constituents generating various kinds of defects, strain at the interfaces occured, and in practice a superlattice is considered as strained multilayer structures. Thus, in case of multilayer the nature of strain will be varying between the two types of strains: the interface film/substrate and the interfaces of the distinct layers used for creating them. Therefore, one may expect that variation of strains in a multilayer system, whereas in the case of a fully relaxed multilayer system, the lattice parameters of the film should be close to the bulk materials (composed of identical compositions of the superlattices). In other words, ideally a fully relaxed multilayer system will exhibit a lattice parameter equivalent to their bulk counterpart. In the present case, it is evident that the film has a large in-plane tensile stress and an out-of-plane compressive strain and its origin can be understood as follows. The lattice mismatch between LCMO/STO is -1.17%, BTO-STO is + 2.2 % and LCMO-BTO is 3.8 %, respectively. Thus, the nature of the strain will be varying from interface to interface, because the substrate will induce a compressive strain whereas the LCMO/BTO will induce either compressive or tensile strain depending on the underneath layer. In addition, strains at the interfaces of LCMO/BTO will be increasing due to the variation in cationic sizes. Similar results have been obtained in the case of SrRuO\(_3\)/SrMnO\(_3\) superlattices.\(^8\) In these films, Padhan et. al. have demonstrated that the variation in cationic sizes of Ru\(^{4+}\) and Mn\(^{4+}\) are imposing strains in the perovskite lattice. Similarly to our superlattices, they have shown that the values of \(\varepsilon_{11}\) (in-plane stress) and \(\varepsilon_{33}\) (out-of-plane stress) depend on the thickness details
of the individual layers with the same order of magnitude as LCMO/BTO superlattices. Thus, our results are comparable to the other oxides-based superlattices. Furthermore, with increasing the BTO thickness more than 15 u.c. the out-of-plane strain decreases, which will result in the stiffening of the lattices that generates defects at the interfaces. Hence our system will behave as a relaxed multilayer and a similar trend has been shown by the FWHM plot (Fig.3a) and the out-of-plane lattice variation (Fig.3b). Thus, the strain analysis corroborates our lattice parameters/FWHM findings. In addition, the creation of defects can result in rough interfaces, which might suppress the multiferroic coupling in the films as illustrated later.

However, we are aware that there are some shortcomings in the present technique for extracting the strains/stress of multilayer films. In this methodology, one assumes a single layer structure and evaluates the average strain/stress in the film, because the XRD can not distinguish between individual interfaces. As a result, the XRD patterns provide only average information about all interfaces and layers. Consequently, it does not give any information about strain/stress distribution at the individual interfaces. However, in multilayer structures, it is evident that the strain at the different interfaces will be different due to the lattice mismatch between the substrate, and various type of oxides employed for growing the superlattices. Despite of the above shortcoming, the present structural data provide a good qualitative information about the strain distribution in the film.

**B. Morphological studies**

As seen through the structural analysis, the strain and the lattice parameters of the superlattices strongly depend on the BTO layer thickness. The morphology were also examined using atomic force microscopy. Morphological parameters, such as the root mean square (RMS) roughness of the superlattices, were extracted from the $2 \times 2 \mu m^2$ AFM micrographs and were found to be in the range of 0.3-0.6 nm. Note that the RMS values are very close to one unit cell of superlattices indicating that the films have smooth surfaces. Fig. 5 shows
the 2D-AFM micrographs of two samples, namely (5/5) and (5/15) superlattices. Fig 5 clearly reveals that the samples are mostly free-from particulates. The particulate density was found to be around 0.3/µm². Furthermore, the AFM micrographs of the superlattices show that the mounds are spherical in nature and they are very uniform in size. Moreover, the average size of the mounds are found to be dependent on the details of the superlattices. For example, in a (5/15) superlattice, the average mound size is of the order of 65 nm whereas in a (5/5) superlattice it is close 40 nm. The mound size in the films usually depends on various factors, such as the deposition temperature, substrate, etc. However, in the present case all samples were grown under identical conditions. Thus, the morphological variation in the superlattices is arising basically from their structural variations.

C. Physical properties

The variations in the structure and morphology of the superlattices were clearly evident in their physical properties. Detail physical properties of these films and the experimental details have been reported elsewhere²³. For the sake of discussion, we are plotting the magnetic and magneto-electric properties of these superlattices as a function of number of BTO unit cells employed for designing them and the result is shown in Fig.6. It shows that the magnetization and magnetoresistance of the superlattices increased with the progressive increase in the number of BTO unit cells and attains a maximum in the case of (5/15) superlattices. Moreover, it is worth to keep in mind that the magnetic layer in the sample is LCMO. Therefore, the present enhancement in magnetization and magnetoresistance of the superlattices may be explained, based on the possible multiferroic coupling in these structures. This also consistent with the structural point of view, i.e., the (5/15) superlattice possesses the lattice distortion in the c-direction (Fig.3). With further increase in BTO layer thickness above 15 u.c., magnetization suppressed, which can be understood based on lattice stiffening that results in the relaxation of the film structure and in turn create defects at the interfaces. Hence, the presence of interfacial defects will suppress the multiferroic coupling
in the superlattices and results in the decrease of magnetizations and magnetoresistance. Hence, the structure of the superlattices is playing an important role in the determination of their multiferroic properties.

**IV. CONCLUSION**

To summarize, we have successfully grown (BaTiO$_3$/La$_{0.7}$Ca$_{0.3}$MnO$_3$) superlattices on (001)-oriented SrTiO$_3$ by pulsed laser deposition process. Despite the lattice mismatch between substrate and La$_{0.7}$Ca$_{0.3}$MnO$_3$ ($-1.17\%$), and BaTiO$_3$ ($+2.2\%$), the films were grown heteroepitaxial. The structural analysis showed that the strains are uniformly distributed in the samples and vary with the BaTiO$_3$ layer thickness. In addition, it appears that first the strain induced in these heterostructures are dependent on the BaTiO$_3$ thickness layer and second, that it is maximum in the case of the (5/15) superlattice (5 u.c. LCMO / 15 u.c. BTO). The physical properties measurements indicated that there is a multiferroic coupling in these structures and that the strains play a particular role in optimizing such behavior. This study may provide a way to design new multiferroics.

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Figure captions:

Figure 1: (a) Θ-2Θ XRD pattern of the superlattices with varying BTO u.c. and (b) chemical modulation (Λ) of the superlattices as a function of BTO u.c. Solid line in Fig 1b is just a visual guide.

Figure 2: (a) Θ-2Θ XRD pattern and simulated XRD pattern of the (5/10) superlattice (b) pole-figure of 5/10 superlattice recorded around the 103-reflection.

Figure 3: (a) FWHM of 002-rocking curve as function of BTO u.c., (b) ’a’ and ’c’ lattice parameters of the films plotted as a function of BTO u.c., and (c) the variation of ’c/a’ ratio as a function of BTO u.c. Inset of Fig 3a shows the rocking curve (ω-scan) for (5/10) superlattice. Solid lines are just visual guides.

Figure 4: (a) Variation of d_{103} as a function of BTO u.c. and (b) in-plane and out-of-plane stress as a function of the BTO u.c. Inset of Fig. 4a shows the sin²ψ vs. d_{10l} plot for (5/10) superlattices and the solid line is the linear fit to experimental data.

Figure 5: 2D-AFM micrographs of (a): (5/5) and (b): (5/15) superlattices.

Figure 6: Magnetic moment (solid circle) measured at 10 K and magnetoresistance (open circle) measured at 100 K of films plotted as a function of number of BTO u.c. The solid straight and dash line are just visual guide.