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Synthesis of Epitaxial Metal Oxide Nanocrystals via a Phase Separation Approach

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ABSTRACT

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3 Perovskite phase instability of BiMnO_3 has been exploited to synthesize epitaxial metal oxide magnetic
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5 nanocrystals. Thin film processing conditions are tuned to promote the breakdown of the perovskite
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7 precursor into Bi_2O_3 matrix and magnetic manganese oxide islands. Subsequent cooling in vacuum
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9 ensures complete volatilization of the Bi_2O_3 , thus leaving behind an array of self-assembled magnetic
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11 Mn_3O_4 nanostructures. Both shape and size can be systematically controlled by the ambient oxygen
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13 environments and deposition time. As such this approach can be extended to any other Bi-based
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15 complex ternary oxide system as it primarily hinges on the breakdown of parent Bi-based precursor and
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17 subsequent Bi_2O_3 volatilization.
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KEYWORDS

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29 Epitaxial nanocrystals, pulse laser deposition, metal oxide, phase separation, volatilization.
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Magnetic spinel nanocrystals are an important class of functional oxides that possess interesting magnetic, magnetoresistive, and magneto-optical properties.¹⁻⁶ These properties are a strong function of the shape, size, and crystallinity of the nanocrystals and consequently, the ability to synthesize high-density nanocrystals with controlled spacing, shape and size has emerged as one of the most dominant themes.⁷⁻¹⁶ While a number of soft-chemistry routes to high-density magnetic nanocrystals have been reported,^{5,11,17-20} the generation of discrete magnetic nanocrystals on an underlying oxide substrate without the use of templates still remains a substantial challenge. The use of oxide substrates provides a pathway to explore the fundamental properties of these oxide nanostructures with strict control of different orientations, shape and morphology, which may not be easily achieved by other methods.

In this report we present a new and facile physical deposition method to fabricate free-standing high-density Mn_3O_4 magnetic spinel nanocrystals. Interest in this material is driven by not only magnetic but also novel electrochemical,²¹ biomedical²²⁻²⁴ and catalytical properties.²⁴⁻²⁶ Additionally, the possibility to oxidize the high-density Mn_3O_4 spinel nanocrystal array under ex-situ conditions to manganese dioxide (MnO_2) offers significant potential in battery applications. Here we demonstrate that under certain (high-) temperature and relatively oxygen-rich conditions, pulsed laser deposition (PLD) of the BiMnO_3 perovskite precursor can yield completely phase-separated constituent Bi_2O_3 and Mn_3O_4 phases. Subsequent cooling of the sample in high-vacuum conditions (10^{-7} Torr) results in complete volatilization of the Bi_2O_3 component and thus leaves behind an array of ordered Mn_3O_4 ferromagnetic spinels. Critically, we show that the shape, size and spacing of the Mn_3O_4 nanostructures can be easily tuned by altering the oxygen environments and deposition time.

As we exploit the formation of Bi_2O_3 in oxygen rich conditions as our primary method to create the nanocrystals, this approach is fundamentally unlike previous efforts that have used oxygen-deficient vacuum conditions to generate metal oxide nanostructures.²⁷ Secondly our end product has uniformly separated nanostructures without any matrix. This is a significant distinction from “pillar and matrix” phase-separated nanocomposite forms that have been reported previously for complex metal oxides.^{6,28-}

RESULTS AND DISCUSSION

Figures 1A and 1B illustrate this concept of phase separation and evaporation approach. The first and most important step {Step 1-Figure 1A} of this synthesis approach is to create an environment that promotes perovskite instability *via* the formation of phase-separated Bi_2O_3 and manganese oxide islands. Previously reported phase diagrams³¹⁻³² show that such conditions are typically found for oxygen rich environments and higher temperatures. In our case, this is achieved by depositing at 860 °C (substrate temperature) and 35 mTorr (chamber oxygen pressure). Once the deposited film forms a phase-separated material (comprising of Bi_2O_3 and manganese oxide), it is crucial to completely remove the Bi_2O_3 . Now we exploit the high volatility of Bi_2O_3 (particularly under high vacuum) by cooling down in high-vacuum (10^{-7} Torr), as shown in step-2 in Figure 1B. This eventually leaves behind the manganese oxide nanocrystals as confirmed by the 52° tilted scanning electron microscopy (SEM) image shown in Figure 1C. The corresponding X-ray diffraction data (XRD) shown in Figure 1D reveals only (00k) peaks of the Mn_3O_4 (JCPDS, 24-734) spinel phase, indicating an oriented growth of the single-crystalline nanostructures. Detailed size-analysis of the tilted SEM image reveals highly populated synthesis of hut-shaped nanostructures with a rectangular base of size $\sim 125 \text{ nm} \pm 10 \text{ nm}$ and height $\sim 75 \text{ nm} \pm 5 \text{ nm}$ with an average inter-nanostructure distance of $75 \text{ nm} \pm 10 \text{ nm}$. Low magnification conventional transmission electron microscope (TEM) imaging {Supplementary Figure S1A} confirms a high density of discrete Mn_3O_4 nanostructures with the corresponding energy dispersive X-ray (EDX) spectra confirming the absence of any residual Bi in these samples {Figure S1B}.

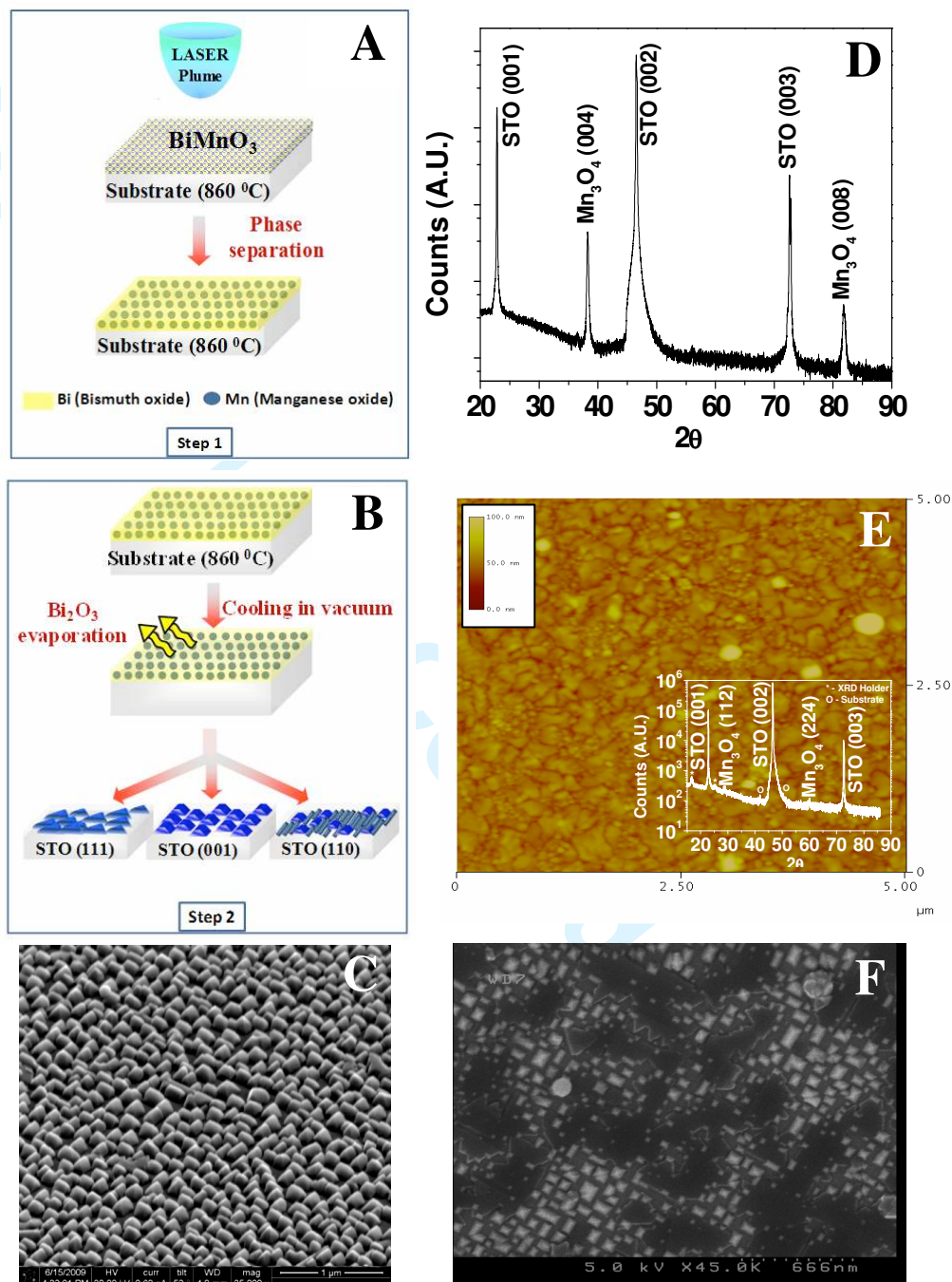


Figure 1. Synthesis technique of Mn_3O_4 nanocrystals. (A) schematic representation of (A) step-1: synthesis approach is to create an environment that promotes perovskite instability via the formation of phase-separated, (B) step-2: bismuth oxide evaporation during sample cooling and formation of Mn_3O_4 nanocrystals on (110), (001), (111) oriented SrTiO_3 substrate, (C) a corresponding tilted SEM view (sample tilt = 52°) of Mn_3O_4 nanostructures grown on (001) SrTiO_3 substrate. (D) θ - 2θ XRD pattern of

1 the sample in (C), (E) AFM topology image of a sample processed under high-vacuum conditions. The
2 inset XRD confirms polycrystalline Mn_3O_4 , (F) SEM image of the sample synthesized in phase-
3 separation conditions but quenched in full oxygen where, a number of irregularly distributed hut-shaped
4 islands are observed. Chemical and XRD analysis of this sample confirms existence of bismuth
5 distribution between the islands (see S1).
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14 The importance of carrying the synthesis process under the two-stage “phase separation followed
15 by volatilization” conditions is further demonstrated in Figure 1E and 1F. Figure 1E is a tapping mode
16 atomic force microscopy (AFM) topology image of a sample that was processed fully under high-
17 vacuum conditions. Here we find that the resultant sample is essentially a rough but continuous thin
18 film. Although the corresponding XRD (inset) and EDX microanalysis confirms the presence of only
19 polycrystalline Mn_3O_4 phases (*i.e.* Bi-containing phases were distinctly absent), Figure 1E shows that
20 high-vacuum alone is not sufficient to realize individual nanocrystals. This significant Bi-loss under
21 oxygen deficient processing conditions agrees with studies focused on BiMnO_3 perovskite thin film
22 synthesis.³³ Next we synthesized a sample where PLD was carried out in phase separation oxygen
23 environments (35 mTorr) but then quenched under full oxygen conditions. Figure 1F is a SEM image of
24 this sample. It shows a large number of nucleated islands with pyramid or hut morphology in an
25 irregular manner separated by flat patches. Wave-dispersive spectroscopy (WDS) analysis
26 {Supplementary Figure S1C} of the sample confirmed a patchy distribution of bismuth in the regions
27 between the islands and XRD pattern of the same sample shows several weak peaks of Mn_3O_4 as well as
28 Bi-containing phases {Supplementary Figure S1D}. Thus Figure 1E and 1F collectively outline the
29 importance of using a two-step process in our approach.
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51 To understand the role of oxygen environments in the synthesis of the Mn_3O_4 nanostructures,
52 PLD synthesis was carried out for a range of chamber oxygen partial pressures (from 10 to 400 mTorr)
53 at the same temperature and pulse conditions. Each sample was then cooled in identical vacuum
54 conditions. Figure 2 is panel of SEM images for some of the more significant partial pressures. The film
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deposited at 10 mTorr, Figure 2A, shows connected small pyramidal shaped nanostructures. On the other hand, the film deposited at 35 mTorr consisted of distinct nanostructures with nearly square based truncated pyramids and rectangular shaped huts, as shown in Figure 2B. Further increase in chamber oxygen partial pressure, up to 400 mTorr, leads to the formation of individual nanostructures with larger lateral size and inter-nanostructure distance, as shown in Figure 2C.

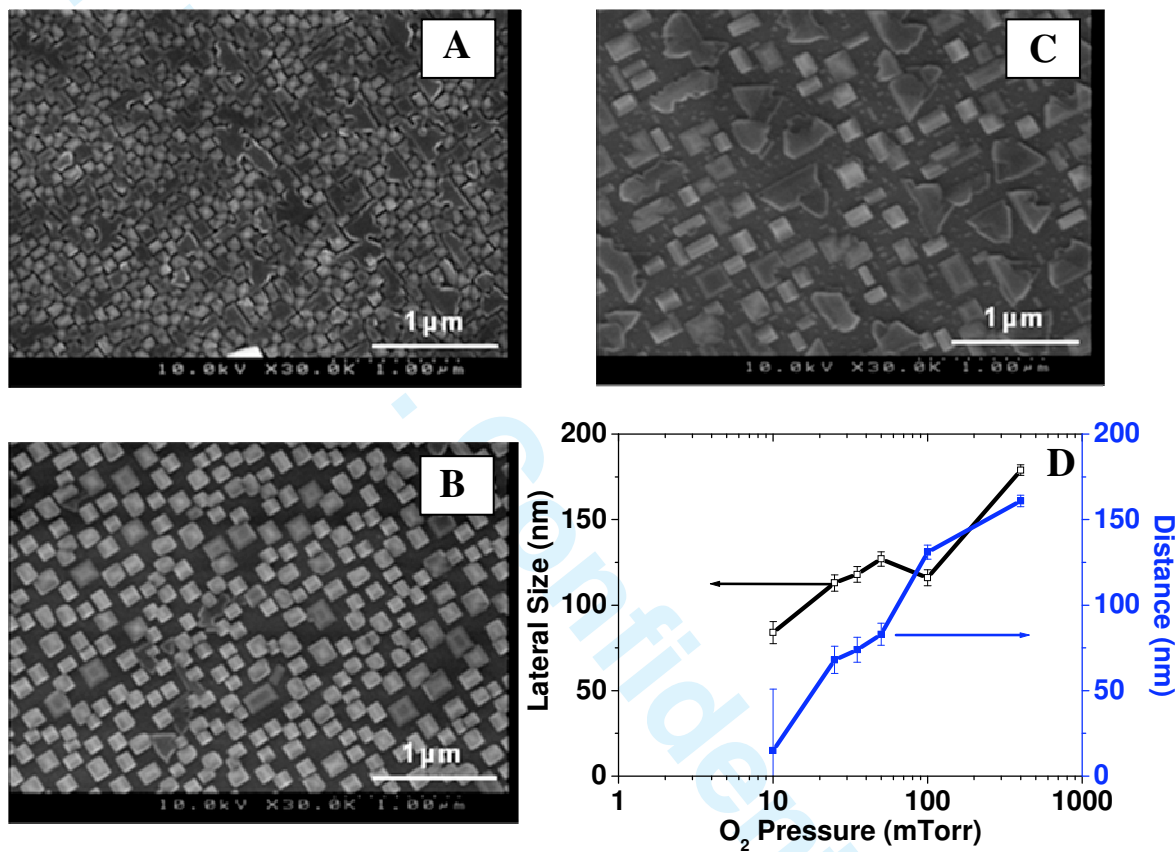


Figure 2: SEM images of the Mn₃O₄ nanostructure samples deposited on (001) oriented SrTiO₃ substrate at (A) 10, (B) 35 and (C) 400 mTorr oxygen partial pressures; (D) variation in the mean lateral size and inter-nanostructure distance with chamber oxygen partial pressure.

This systematic variation in the shape evolution of the nanostructures can be understood on the basis of interaction of plume contents with the chamber oxygen along with its effects on nucleation and growth. Lower deposition pressure results in a fast-moving plume due to low probability of collision between plume contents and chamber oxygen. A high nucleation density occurs upon deposition with very little growth in nanostructure size. As the chamber oxygen pressure increases the collision

1 probability increases, and as a consequence creates a slower plume, which allows more time for larger
2 sized nanostructures to grow.³⁴ Size and inter-nanostructure distance analysis of these SEM images
3 reveals that the mean lateral size and inter-nanostructure distance increases (80 to 180 nm and 15 to 160
4 nm) with increasing oxygen partial pressure, from 10 to 400 mTorr {shown in Figure 2D}. An
5 analogous dependence on laser pulse frequency was also found, where increasing the pulse rate from 5
6 Hz to 20 Hz for a fixed oxygen partial pressure and temperature reduced the inter-nanocrystal distance
7 as well as the mean lateral size.

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Figure 3 is a panel that illustrates TEM investigations of the Mn_3O_4 nanostructure sample deposited for 20000 laser pulses at 860 °C in 35 mTorr chamber oxygen pressure {Figure 1C}. Figure 3A is a cross-section TEM image, showing several Mn_3O_4 nanoislands. In combination with selected area diffraction pattern (inset) obtained from the middle nanostructure, several key points can be inferred.

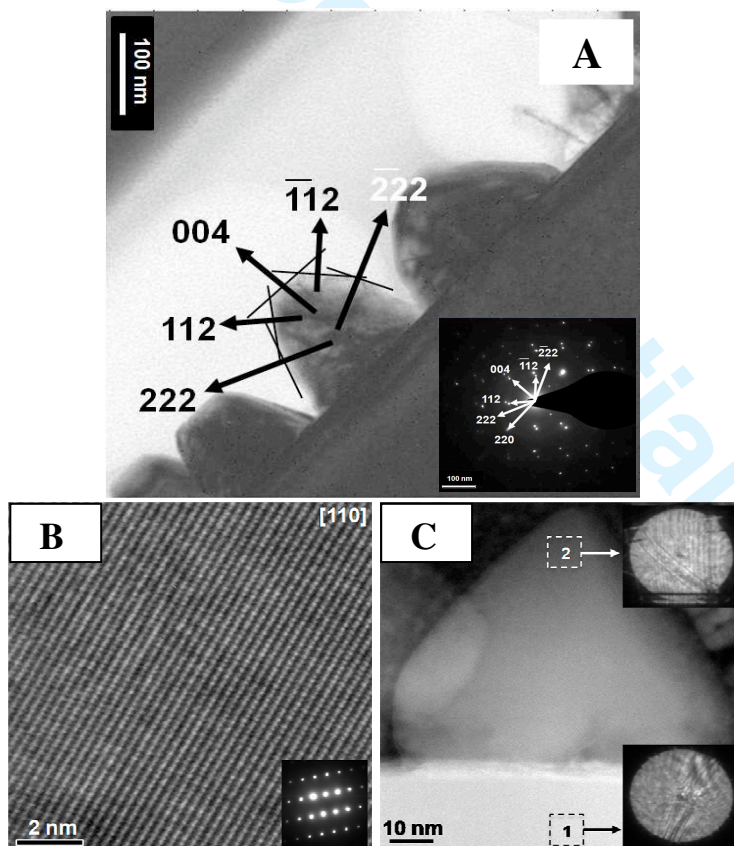


Figure 3: Structural analysis of the Mn_3O_4 nanostructures: (A) TEM imaging and selected area diffraction pattern (inset) demonstrate firstly that the bounding surface crystallography of the Mn_3O_4

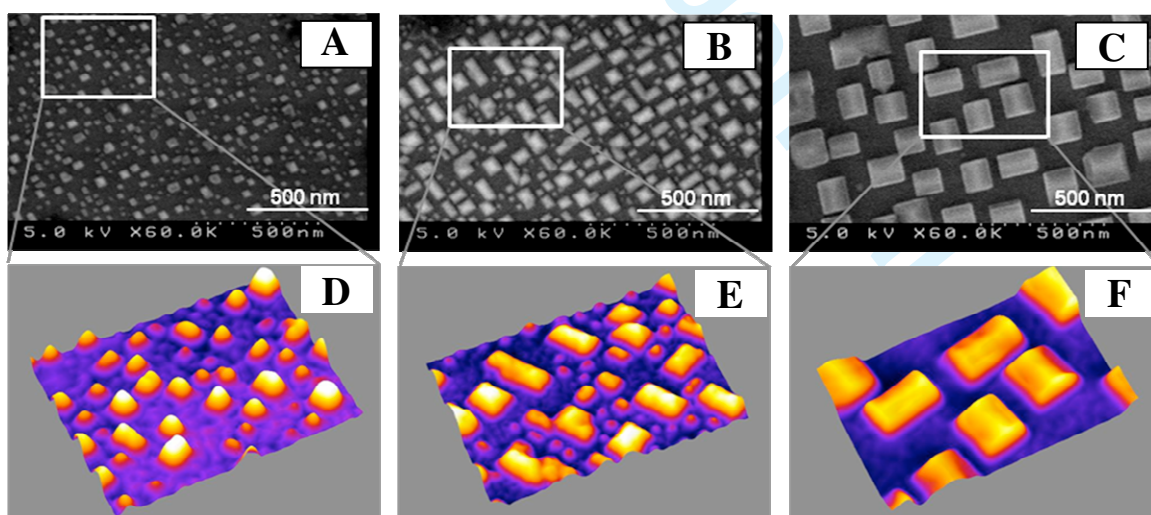
islands is often relatively complex and secondly that the [100] zone axis for the SrTiO₃ substrate corresponds to the [1 $\bar{1}$ 0] zone axis for the Mn₃O₄, (B) high-resolution TEM (HRTEM) and (C) high angle annular dark field (HAADF) image, where the insets show the Kikuchi patterns for the substrate (1) and the Mn₃O₄ nanostructure (2).

Firstly, both the image and diffraction pattern were taken with the electron beam aligned parallel to the [100] of the SrTiO₃ substrate. Indexing of the diffraction spots from the Mn₃O₄ indicates that this beam direction is simultaneously parallel to the [1 $\bar{1}$ 0] zone axis for Mn₃O₄. The in-plane orientation relation must therefore be such that [100]_{STO} // [110]_{Mn3O4}, and by implication [110]_{STO} // [100]_{Mn3O4}. A 45° misorientation of the primary lattice vectors at the interface plane should be expected as $\sqrt{2}a_{\text{STO}} \approx a_{\text{Mn3O4}}$, and suggests some level of interface coherency.

Secondly, the nanostructures in general have relatively complex bounding surface crystallography. As can be seen, the middle nanostructure in Figure 3A has seven different facets parallel to the [1 $\bar{1}$ 0]_{Mn3O4} beam direction, five of which are explicitly labeled to allow the link between the observed facets and the electron diffraction pattern to be understood (indexed to the I4₁/amd space group). Figure 3B is a high resolution TEM (HRTEM) image acquired along the [110] zone axis, showing clear lattice fringes and hence confirming the single-crystalline nature of each nanocrystal. Scanning TEM (STEM) imaging allows a fine electron probe (~1Å), which can be freely positioned, to be focused onto the given specimen and, when the probe is well over-focused Kikuchi lines are visible.³⁵⁻³⁷ Figure 3C is the high angle annular dark field (HAADF) image of a single nanostructure and substrate, acquired under STEM mode. The inset marked as 1 displays the Kikuchi pattern from the substrate, it shows three lines intersecting with each other which is characteristic of the [110] zone axis for STO. While the inset marked as 2 displays the Kikuchi pattern from the nanostructure, it shows several lines forming a 'triangular' shape, where there is more than one intersecting point. This confirms that the nanostructure has an in-plane rotation with respect to the [100] direction of the underlying substrate. Plan view

1 examination (not shown) of several samples confirmed that the islands grow parallel to the $\langle 110 \rangle$
2 direction of the STO substrate. Again, this can be expected on the basis of lattice mismatch arguments
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5 where $\sqrt{2}a_{\text{STO}} \approx a_{\text{Mn}_3\text{O}_4}$.
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8 We have also investigated the dependence of the shape of the Mn_3O_4 nanocrystals on their
9 volume by tuning the number of laser pulses during the PLD deposition. Figure 4 shows high
10 magnification SEM images of the nanostructure samples deposited at 2000 {Figure 4A}, 5000 {Figure
11 4B} and 20000 {Figure 4C} laser pulses, where the other PLD parameters (860 °C substrate
12 temperature, 35 mTorr O_2 pressure and cooling in vacuum) were kept identical. The SEM image shown
13 in Figure 4A, along with its interactive 3D image generated from a smaller area of the SEM image
14 {Figure 4D}, clearly illustrates square based pyramidal shape nanostructures growth on the substrate
15 {also see Figure S2A}. As the deposition proceeds to 5000 laser pulses {Figure 4B}, one observes the
16 islands beginning to coalesce into larger sized nanostructures. Secondly a clear shape transition from
17 pyramids to hut-shaped nanocrystals begins to occur. This shape transition process via nanostructure
18 aggregation can easily be resolved in Figure 4E (and S2). Furthermore, at 20000 laser pulses almost
19 99% of the nanostructures have shape of the roof of hut, as shown in Figures 4C, 4F and Figure S2C.
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53 **Figure 4:** Morphology of the Mn_3O_4 nanostructures grown on (001) oriented SrTiO_3 substrate for (A)
54 2000, (B) 5000 and (C) 20000 laser pulses along with their respective interactive 3D images ((D), (E)
55 and (F)).
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Further shape control of the Mn_3O_4 nanocrystals can be achieved by exploiting their epitaxial relationship with the STO substrate. STO has a lattice parameter $a=b=c=3.905 \text{ \AA}$. Mn_3O_4 has lattice parameters of $a=b=5.77 \text{ \AA}$ and $c=9.44 \text{ \AA}$. For a STO (001) substrate this results in Mn_3O_4 nanocrystals having an (001) interface with an in plane rotation of 45° , and results in a 4% compressive lattice mismatch. Therefore if Mn_3O_4 nanocrystals are nucleated on STO (111) or STO (110) substrates, in order to minimize the interfacial energy, one would expect them to be oriented along [111] and [110] directions. This results in dramatically different shapes for the nanocrystals, as demonstrated in Figure 5 which shows SEM images along with their XRD data of Mn_3O_4 nanostructures fabricated using (001), (111) and (110) oriented SrTiO_3 substrates.

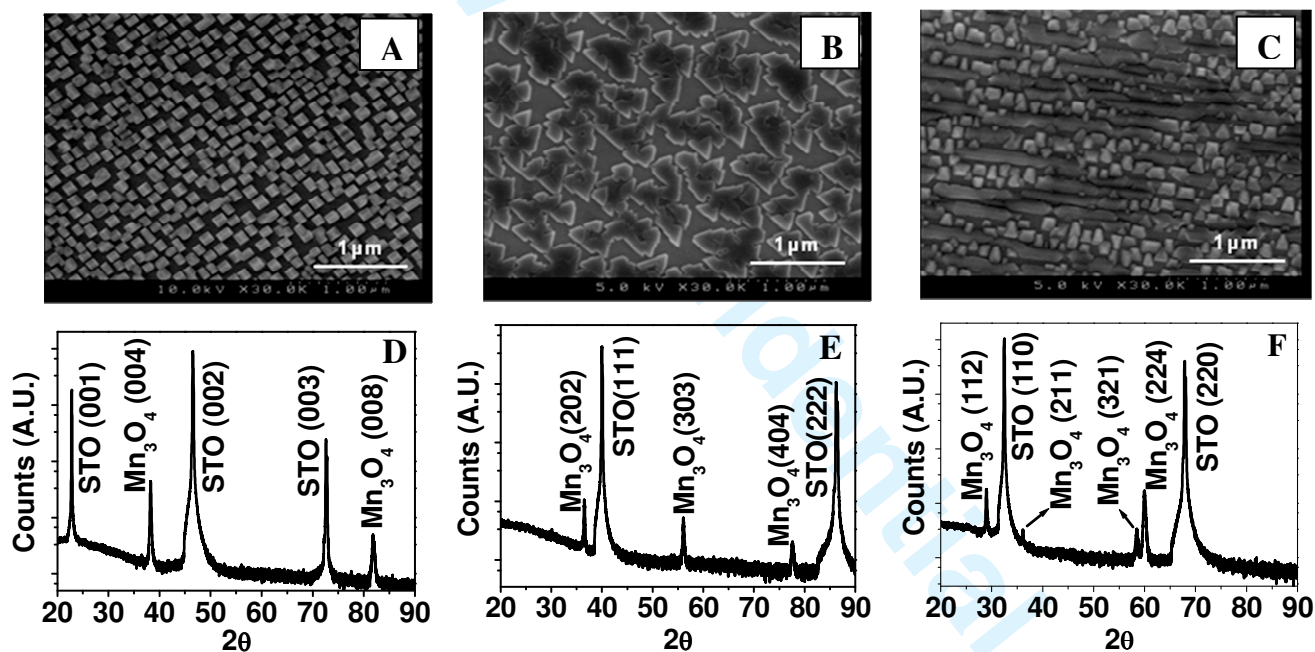


Figure 5: SEM images and respective XRD patterns for Mn_3O_4 nano-structures grown on (A & D) (001), (B & E) (111) and (C & F) (110) oriented SrTiO_3 substrates. These samples were deposited at substrate temperature of $860 \text{ }^\circ\text{C}$, oxygen partial pressure of 35 mTorr, pulse repetition rate of 5 Hz and 20000 laser pulses.

1 As it has been discussed previously for the (001) oriented SrTiO₃ substrate, isolated Mn₃O₄
2 nanostructures having a hut shape are formed. The corresponding XRD data shown in Figure 5D for
3 nanostructure grown on (001) oriented SrTiO₃ substrate, reveals only (00k) peaks, indicating an
4 epitaxial growth of the single-crystalline nanostructures. Conversely the shape of the nanostructure
5 grown on (111) oriented SrTiO₃ substrate is entirely different. More or less flat and inter-connected
6 triangular platelet-shaped nanostructures are observed {see Figure 5B} and its XRD data {see Figure
7 5E} indicates that these nanostructures are (101) oriented, which is the natural direction of growth of
8 Hausmannite.³⁸ On the other hand the Mn₃O₄ nanostructures grown on (110) SrTiO₃ substrate have a
9 mixture of different shapes {see Figure 5C and its XRD data}. Figure 5F indicates that these are of
10 multiple orientations in nature.
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23 The observations above, namely that Mn₃O₄ nanocrystal shape is influenced both by volume and
24 substrate orientation, raises the tantalizing prospect of tuning the nanocrystal shapes to optimize their
25 properties for particular applications. In general, the equilibrium shape of a supported crystallite can be
26 determined using Winterbottom's construction,³⁹ also known as the Wulff-Kaichew theorem. The
27 equilibrium crystal shape is determined by considering the surface energies of the crystallite facets, the
28 interface energy between the crystallite and the substrate, and the surface energy of the substrate. What
29 this theorem does not include are factors relating to interface strain or the effect of metastable shapes
30 and orientations. For example, if lattice mismatch strain is not relieved via misfit dislocations, then the
31 strain energy in the nanocrystals will grow disproportionately to their volume. This will result in shape
32 changes as the nanocrystals grow, as observed in this study for the [001] oriented Mn₃O₄ nanocrystals,
33 and commonly seen in semiconductor epitaxy.⁴⁰ Furthermore, if there is a particularly favorable
34 epitaxial relationship between the supported crystal and the substrate, then the crystal orientation can be
35 determined in the early nucleation stages giving rise to a metastable shape. This may be occurring for the
36 STO (110) oriented substrates shown here.
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56 Of note also is the strong temperature dependence of the ultimate nanostructure shape in this
57 process. The exponential dependence of vapor pressure on temperature would imply that even a slight
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change in temperature should have strong change in the evaporation of the bismuth oxide phases. Whilst all data discussed in this paper is for fixed synthesis temperature, we indeed have found that slightly decreasing or increasing the growth temperature ($\sim 10^\circ\text{C}$) results in dramatically altered nanostructure shape (unpublished). Further in-situ investigations are currently being performed to understand this.

Finally, we explore the functional behavior of these nanostructures. Temperature dependent magnetization for (001) oriented and (101) oriented Mn_3O_4 nanostructures grown on (001) oriented SrTiO_3 at 860°C were acquired using a Quantum Design MPMS-XL. The measurements were done in 500 and 100 Oe applied magnetic fields, respectively. As shown in the Figure 6, Mn_3O_4 nanostructure shows ferrimagnetic behavior at low temperatures, where the T_c for the (001) and (101) oriented Mn_3O_4 samples was found at 40 K and 42 K. In comparison, it has been reported that bulk Mn_3O_4 hausmannite has a Curie temperature $\sim 42\text{ K}$.³⁸

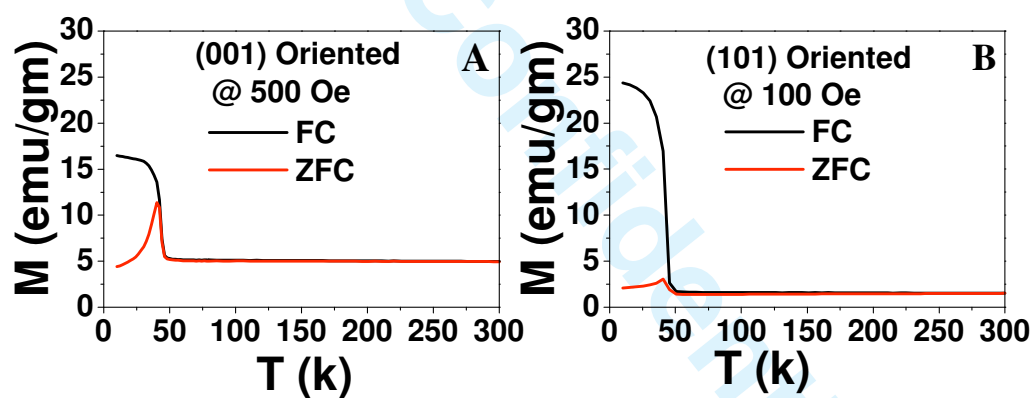


Figure 6: Temperature dependent magnetization at (A) 500 Oe for (001) oriented and (B) 100 Oe for (101) oriented Mn_3O_4 nanostructures grown on (001) oriented SrTiO_3 at 860°C in 35 mTorr oxygen for 20000 laser pulses. They were measured at 500 and 100 Oe applied magnetic field. Mn_3O_4 nanostructure shows ferrimagnetic behavior at low temperature. For bulk Mn_3O_4 hausmannite curie temperature is about 42 K, where as in our case for (001) and (101) oriented Mn_3O_4 sample T_c was found at 40 K and 42 K.

CONCLUSION

To conclude, we present template-free facile approach for the synthesis of Mn_3O_4 metal oxide nanocrystals using BiMnO_3 perovskite precursors, employing the concept of perovskite instability and phase separation followed by bismuth oxide evaporation. Distinct variations in the morphologies, size and spacing were observed. These could also be easily tuned by the processing conditions. Nanocrystal shape control is a particularly active field in materials research because of the shape/property relationships that can be exploited. The Mn_3O_4 nanocrystal on STO substrate system appears to be an excellent candidate for this type of study. As our process primarily hinges on the phase separation and subsequent volatilization of Bi_2O_3 , it can be extended to any other Bi-containing complex metal oxide system. We have carried out similar pilot experiments on the creation of technologically important magnetite (Fe_3O_4) and titania (TiO_2) nanostructures (see supplementary file). These studies demonstrate the applicability of the phase separation synthesis method over a broad range of oxides.

METHODS

Nanostructures used in this study were grown on vicinal single crystalline (001) SrTiO_3 substrates procured from SHINKOSHA-Japan. A bulk BiMnO_3 ceramic target was used as precursor. Nanostructures were grown using pulsed laser deposition (PLD) with a KrF ($\lambda = 248$ nm) excimer laser at a laser density of ~ 2 J cm^{-2} . The effects of substrate temperature (in the range from 800 to 900 °C), chamber oxygen partial pressure (in the range from 2 to 400 mTorr) and deposition rate (0.1 to 2 nm min^{-1}) were also investigated. To ensure repeatability each growth run was repeated thrice using identical conditions. Nanostructures were characterized using a Hitachi S4500 field emission scanning electron microscope (FESEM) with resolution of ~ 2 nm. Elemental analysis was carried out on the Hitachi with an Oxford Isis energy dispersive X-ray analyzer. A Philips X'pert MRD thin film X-ray diffractometer was used for XRD spectra. Cross-sectional TEM samples were prepared by both, standard tripod polishing and ion milling techniques,³⁵ as well as focused ion beam milling on an

1 FEI200TEM FIUB microscope. HRTEM studies were performed using a JEOL FEGTEM operated at
2 300 kV and a FEI Tecnai F20 FEGTEM operated at 200kV, while HAADF studies were performed
3 using a double-corrected Titan S-Twin microscope operated at 300 kV. Temperature dependent
4 magnetization was measured by MPMS-XL of Quantum Design. The magnetic fields for both
5 measurements were applied along the in-plane direction with respect to the substrates.
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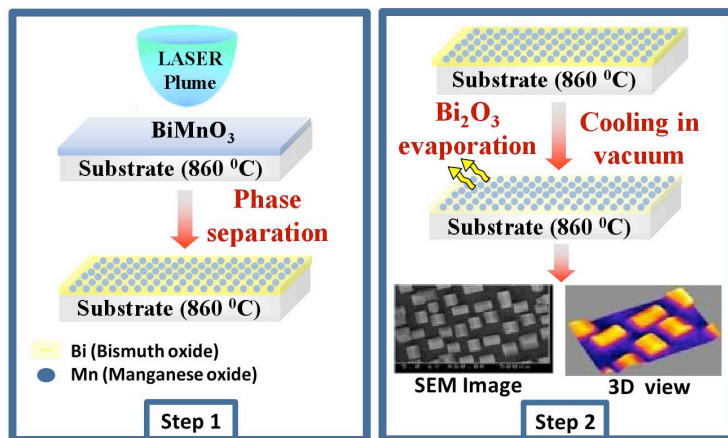
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