Giant texturing effect in multiferroic MnWO₄ polycrystals

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Abstract
Different methods of texturing polycrystalline materials have been developed over the years to use/probe anisotropic material properties with relative ease, where complicated and expensive single crystal growth processes could be avoided. In this paper, particle morphology assisted texturing in multiferroic MnWO₄ has been discussed. Detailed powder x-ray diffraction vis-a-vis scanning electron microscopic studies on differently annealed and processed samples have been employed to probe the giant texturing effect in polycrystalline MnWO₄. A quantitative measure of the texturing has been carried out by means of the Rietveld analysis technique. Qualitative presentation of magnetic and dielectric data on textured pellet demonstrated the development of clear anisotropic physical properties in polycrystalline pellets. Finally, we established that the highly anisotropic plate-like particles are formed due to easy cleavage of the significantly large crystalline grains.

(Some figures may appear in colour only in the online journal)

1. Introduction

Single crystals by definition are the purest form of solid materials and naturally the most exclusive form for carrying out direction-dependent bulk experimental studies or for technological uses. However, entropy-related effects often facilitate the presence of imperfections in the microstructure of solids, such as impurities, inhomogeneous strain or crystallographic defects, and as a result, perfect single crystals of reasonable volume are extremely difficult to produce in the laboratory and even then, it might be possible only under precisely controlled conditions. On the other hand, material ‘texturing’, i.e. the ability to impose preferential orientation to small, crystalline grains of a polycrystalline material, could provide a rather useful and viable solution to this problem. As most of the crystallographic properties are coupled with the crystallographic directions, the attempt of texturing could help in realizing many desired, direction specific properties and also in probing anisotropic properties in an otherwise polycrystalline sample. Obviously, if the polycrystalline ceramics with properties close to single crystal can be fabricated by ‘texturing’, they would be advantageous due to their ease of fabrication, shaping and cost-effectiveness. Following this idea, various experimental techniques have been developed in the last few decades to reinforce preferential orientation in materials having versatile anisotropic properties. For example, textured α-Al₂O₃-based ceramics have been made by a number of techniques, e.g. tape casting [1], templated grain growth (TGG) etc. [2], while Matsuzawa et al. reported the TGG-type directed growth of ferrites in 1982 [3]. Reactive templated grain growth (RTGG) is another industrial development, which has been utilized to prepare various textured ferroelectric ceramics such as Bi₁₅Ti₃O₁₂ [4], CaBi₄Ti₄O₁₅ [5], or pyroelectrics (e.g. (ZnO)₅In₂O₃ [6], NaCo₂O₄ [7]), as well as piezoelectric ceramics (e.g. K₃.₅Na₀.₅NbO₃) [8]. Texturing of magnetic materials is also demonstrated at high temperature by solidification under an applied magnetic field [9].

Interestingly, certain materials may naturally promote ‘texturing’ in polycrystalline forms, which can on the
other hand create difficulties because absence of prior information about the degree of such natural ‘texturing’ may mislead researchers while describing physical properties of polycrystals of such materials. But, a more general and questionable issue is the extraction of crystallographic information of such materials through powder diffraction experiments, a method employed to all samples grown either as single crystal or polycrystal, because the diffraction data are normally analysed with an inherent assumption that the experimental results are average, isotropic responses of the material, which obviously turns invalid if the polycrystalline powder becomes strongly textured. In this paper, we report that substantial natural ‘texturing’ occurs in the well-known multiferroic MnWO₄ [10, 11, 12] in its polycrystalline form. Therefore, all the powder diffraction data providing crystallographic information, inherently connected to its multiferroic property, should be analysed very carefully with detailed, prior knowledge about the ‘texturing’ that may remain in the sample under study. Moreover, a fair body of research on polycrystalline MnWO₄ also exists [13] which naturally involves serious uncertainties. On the other hand, this natural texturing tendency of the grains in polycrystalline MnWO₄ could be consciously exploited to create nearly single crystal-like properties and single crystal-like anisotropies in MnWO₄ polycrystals. Also, the high sensitivity of the electrical conductivity of MnWO₄ to the level of surrounding humidity makes it a potential system for designing humidity sensors [14, 15], and the tendency of texturing could be exploited for making single crystal-like films easily, which could be useful for applications [16].

2. Experimental methods

Polycrystalline MnWO₄ was synthesized using the solid-state reaction method. Stoichiometric amounts of MnO (99.9%) and WO₃ (99.9%) were mixed in an agate mortar and prolonged grinding was carried out in C₂H₅OH medium to ensure maximum possible homogeneity in the starting mixture. The resultant powder was then thermally treated under different conditions to study the grain growth and texturing; the details are shown in figure 1. In all cases, the samples were annealed for 12 hours in inert atmosphere to avoid Mn oxidation at temperatures mentioned in figure 1 and ramping rates during heating/cooling were maintained at 5 K min⁻¹. MnWO₄ single crystals were grown by the floating zone technique. The feed and seed rods were made by annealing an isotropically pressed polycrystalline rod in inert atmosphere at 1200 °C for 24 h. The growth rate was maintained at 4–5 mm h⁻¹. The phase purity was checked by the powder x-ray diffraction (PXRD) method in a Bruker AXS: D8 Advance x-ray diffractometer using Cu Kα (λ = 1.54059 Å) x-ray source and the sample morphologies were probed by scanning electron microscopy (SEM) in a JEOL JSM-6700F FESEM instrument. The magnetic measurements were carried out in a Quantum Design SQUID magnetometer, while an indigenously built laboratory setup with TEGAM 3550 LCR meter was used for dielectric measurements.

3. Results and discussions

To have a quantitative idea of the anisotropy in grain shapes, we simply applied manual pressure on the polycrystalline powder during the sample arrangement for PXRD measurements, thus enforcing preferential orientation of anisotropically shaped grains [17], if present. All the peaks of PXRD patterns from all the samples could be indexed perfectly with the P₂/c space group with the crystallographic parameters a = 4.829 Å, b = 5.758 Å, c = 4.996 Å and β = 91.146°, which confirm phase purity of all the samples. In figure 2(a), the PXRD pattern from sample A (open circles) is shown along with the standard powder data (red columns) from the literature [18]. Before collecting these data, a chunk of the fine powder was pressed and flattened on the sample holder by a glass slide. Although the PXRD pattern matches with the literature data at a first glance, a closer look reveals that the relative intensities of a few crystalline peaks differ rather strongly from the standard data with the strongest discrepancies corresponding to the planes parallel to (0 1 0) Miller index (see the insets to figure 2(a)), indicating a preferential orientation of grains along this direction. The SEM image of the same pressed sample is also shown in the inset. The particles are nearly spherical with few open facets, which are expected to be along the (0 1 0) planes. Usually almost all polycrystalline powder samples, due to the presence of certain level of anisotropy in their grain shapes, are more or less affected by preferred orientation [19], but the gigantic effect observed in high-temperature annealed MnWO₄ samples (figure 2(b)) is unprecedented. In this case, the sample was annealed at 1200 °C in the form of a pellet (sample B), thoroughly ground to fine powder (equivalent to sample B3, figure 1) and then placed onto a diffraction sample holder under manual pressure. Evidently, giant enhancements in the peak intensities could be observed at reflections (0 1 0), (0 2 0), (0 3 0), (0 3 1) etc., which has to be extrinsic and should be an outcome of heavy texturing.

![Sample B](image1)

![Sample C](image2)

Figure 1. Hierarchy chart showing annealing conditions for MnWO₄ samples A, B and C and pre-PXRD grinding times for samples B1, B2 and B3.
Consistent with this assumption, the SEM experiments (see the inset, panel (b)) exhibit plate-like grains for sample B3.

In order to check the true PXRD patterns of these samples, we employed the simplest known method to avoid preferred orientation in sample preparation for PXRD, namely the ‘razor tamped surface’ (RTS) method and obtained random particles at the surface of the measurement holder [20]. Here, the sample surface was tamped by the sharp edge of a razor blade during sample preparation, and the PXRD results for samples A and B3 under this new preparation have been plotted in figure 3. It is evident from figure 3 that PXRD patterns for both the samples showing correct relative intensities could be reverted using this method. Therefore, it is established that the grains of sample B3 are highly anisotropic and can be textured very easily and the lack of prior knowledge about the morphology of polycrystalline MnWO$_4$ being studied may lead to misleading diffraction or other experimental results [21].

As mentioned earlier, this high texturing tendency of polycrystalline MnWO$_4$ could on the other hand be exploited to an important advantage as well. Careful processing of these polycrystals could generate nearly single crystalline anisotropy and related properties, which should be of significant help to material physicists or technologists. But to make use of the texturing one first needs to quantify the extent of grain alignments in MnWO$_4$ which we did next by applying small manual pressures to the samples and carefully analysing the experimental PXRD patterns. Now, in order to have such quantitative idea about the particle shape and the fraction of textured particles, the PXRD pattern of the compressed sample B3 was fitted with the help of modified March’s function as implemented in the Fullprof program [22, 23]. The experimentally observed, calculated and difference profiles are presented in figure 4 with (panel (b)) and without (panel (a)) taking into account the preferential orientation along (0 1 0) while fitting. It is to be noted that the value of $R_{wp}$ is reduced to 17.9% from 72.6% after adding the preferred orientation along (0 1 0) along with a large improvement in fitting, indicating the presence of high preferential orientation of the grains along the (0 1 0) planes. The result of the fitting indicates highly plate-like morphology of the grains and as high as $\sim 50\%$ grain texturing along the (0 1 0) planes.

This amount of texturing would then surely be manifested through the anisotropic physical properties of a sample. Using magnetic and dielectric measurements, here we illustrate

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**Figure 2.** X-ray powder diffraction from pressed MnWO$_4$ samples: A (a) and B3 (b) at 300 K displaying the observed data (open circles) and standard data from the literature (red columns) normalized at maximum intensities, along with insets showing corresponding SEM images and enlarged (0 1 0) and (0 2 0) reflections.

**Figure 3.** X-ray powder diffraction from ‘razor tamped’ MnWO$_4$ samples: A (a) and B3 (b) at 300 K showing the observed data (open circles) and the standard data from literature (red columns) normalized at maximum intensities, along with enlarged (0 1 0) and (0 2 0) reflections as insets.
the apparent anisotropy in the properties of polycrystalline MnWO₄ pellets. MnWO₄ undergoes successive magnetic transitions at 13.5 K (Tₐ), 12.7 K (T₂) and 7.6 K (T₁) corresponding to three antiferromagnetic (AFM) phases [10]. Neutron diffraction studies have established that AFM1 (T < T₁) and AFM3 (T₂ < T < Tₐ) possess collinear phases, while AFM2 (T₁ < T < T₂) is a spiral magnetic phase [24], where all the important functionalities (e.g. magnetic field-induced polarization reversal) are observed. Also, the dielectric constant shows a sharp peak at the onset of ferroelectric transition (T₂), when measured along the b direction of a single crystal in the absence of magnetic field [10]. Single crystals of MnWO₄ show anisotropic magnetic behaviour across these AFM phases only [10, 12] and thus we chose this temperature range to investigate anisotropic features in our textured pellet. These pellets were made employing unidirectional pressure in a pressure die, which enforce substantial texturing in the pellets where at least 50% of the particles (equivalent to sample B3) are expected to be textured having the crystallographic b direction perpendicular to the flat pellet surface. The magnetic moments with varying temperatures (M(T)) were measured on such a sintered polycrystalline pellet by applying a field of 1000 Oe. The pellet was mounted in two different configurations with respect to the magnetic field direction. The main features of the M(T) data clearly resemble the reported data [24], while a clear anisotropy can be observed between the two measured directions. To compare the measured anisotropy, the M(T) data were simulated by a linear superposition of the same from a reported single crystal [10] and the measured M(T) data from bare powders, so that an overall 50% texturing is ensured. In figure 5 the measured (main panel) and simulated (inset) M(T) data are plotted for the two aforementioned directions. The clear similarity between the two offers the evidence for the presence of large anisotropy in the polycrystalline pellet due to large texturing effects.

Figure 5. Magnetization M(T) data observed (main panel) and simulated (inset) for MnWO₄ pellet (equivalent to sample B3) with the magnetic field parallel (red triangle) and perpendicular (black circle) to the flat pellet surface.

The variation in dielectric constants with temperature was measured on a similarly made pellet, once across the flat surface and once perpendicular to it. Dielectric constant of a single crystal of MnWO₄ was also measured in order to make a comparison with the values obtained from the pellet. The electrodes for the dielectric measurements were made up of cured silver paste. An ac electric field of frequency 1.0 MHz is used for all the measurements. Figure 6 shows the normalized values of relative dielectric constants for the two directions of the polycrystalline pellet and the data obtained for the single crystal in the inset. The normalized values (εⁿ) have been calculated using

$$\epsilon^n = \frac{\epsilon_m - \epsilon_b}{\Delta \epsilon_s}$$

where ε_m, ε_b, and Δε_s are the measured dielectric constants of the polycrystalline pellet, the corresponding background values and the peak height of the single crystal, respectively.
One must mention at this point that a proper comparison of the degree of texturing in these samples is an exceedingly hard task because nearly all the PXRD peaks get affected under the influence of significant texturing, making the pattern normalization at any certain invariant 2θ peak nontrivial. However, a careful look at figure 4(a) gives the intensities of the observed and calculated profiles match better at (1 1 0) compared with (1 0 0), (0 1 1), (1 1 1) (see the inset to figure 4(a)), among the reflections those are not parallel to [0 1 0]. From the consideration of the preferred orientation function [25], it is understood that the (1 1 0) group of planes will indeed be the least affected ones, while there would be significant intensity variations for all other groups of planes. Thus, in order to compare different levels of preferred orientation, the patterns were normalized at (1 1 0), where the effect is minimal. From figures 7(c), (d) and (e), one can clearly see that the intensities at (0 1 0), (0 2 0) and other related reflections are increasing with increasing grinding times. The PXRD patterns in figure 7 thus indicate that the as-formed sample B does not exhibit texturing and all the anisotropic crystallites originate only as a result of mechanical grinding.

SEM images collected from samples A, B, C and B3 and are shown in figure 8. The SEM image from sample B stands out from A and C, as huge single crystal-like faceted grains are seen. We have already discussed earlier that it is only sample B which exhibits significant texturing effects after thorough grinding indicating that the formation of large crystallite grains is a pre-requisite for texturing. The SEM image from sample B3, i.e. the portion of sample B which underwent maximum grinding, shows large flat plates. Therefore, one could conclude that large crystalline grains of MnWO4 (sample B) are cleaved along preferential faces during mechanical grinding (samples B1, B2 and B3), which in the end gives rise to strong texturing effects. However, this preferential cleaving along the crystallographic b [0 1 0] direction has to be a manifestation of the intrinsic crystal structure of MnWO4. The crystal structure of MnWO4 has been shown in figure 8(e), where a clear anisotropy in atomic arrangements can be observed in terms of bond lengths. In this structure, repeated sheets of MnO6 and WO6 octahedra are well packed along the a [1 0 0] direction, and the edge shared Mn/WO6 octahedra run along the c [0 0 1] direction in a zigzag fashion [10, 11]. However, atomic planes remain well separated from each other along the b [0 1 0] direction due to the inherent monoclinic distortion. The movements of Mn and W ions (see arrows in figure 8(e)) inside the highly distorted MnO6 and WO6 octahedra create three types of Mn–O and W–O bond lengths, marked by solid (short), dashed (medium) and dotted (long) lines. A careful view of the structure reveals that the set of planes parallel to (0 1 0) (see figure 8(e)) pass across the weaker (longer) M–O bonds, which explains the easy generation of (0 1 0) group of facets upon mechanical grinding. Thus, the rise in number of facets with increasing grinding time enhances the (0 1 0), (0 2 0), etc. peak intensities as shown in figure 7. However, after an upper limit of the grinding time (∼40 min), the effect of texturing saturates. We have invariably observed in different batches of large grain samples that after 30–40 min of grinding the (0 1 0), (0 2 0) peaks do not enhance

Figure 6. Normalized relative dielectric constants measured with changing temperature for MnWO4 pellet (equivalent to sample B3) along (red triangle) and perpendicular (black circle) to the flat pellet surface. The inset shows the value obtained for a single crystal of MnWO4.

Expectedly, the peak heights from the polycrystalline pellet are substantially lower compared with the single crystal (maximum $\epsilon_n$ being 0.25) but more importantly, the clear contrast in the $\epsilon_n$ peak heights for the two different directions brings out yet another proof of single crystal like anisotropy generated in a polycrystalline sample by texturing.

Next, it is important to understand the formation mechanism of the preferentially oriented plate-like grains in polycrystalline MnWO4 for further uses. We have carried out a few controlled measurements to figure out the aligned grain formation mechanism. In figure 7, x-ray diffraction patterns from samples A (annealed at 1050 °C), B (annealed at 1200 °C in pellet form), C (annealed at 1200 °C in powder form), B1, B2 and B3 are shown in different panels. The pre-PXRD sample preparations, however, were different for different samples. Samples A and C, annealed as powders, were thoroughly ground before collecting the PXRD, while in the case of sample B, the hard annealed pellet was just broken into powder and any severe grinding was avoided. On the other hand, samples B1, B2 and B3 were prepared from sample B with increasing grinding times (see figure 1). All the samples were then placed on the sample holder and pressed with glass slides before measurement, so that, should aligned grains be already present in any of them, the texturing effect would show up in PXRD. Interestingly, the XRD patterns reveal that preferential alignment is absent in samples A, B and C, refuting the idea of any preferential grain growth in these samples.

One must mention at this point that a proper comparison of the degree of texturing in these samples is an exceedingly hard task because nearly all the PXRD peaks get affected under the influence of significant texturing, making the pattern normalization at any certain invariant 2θ peak nontrivial. However, a careful look at figure 4(a) gives the intensities of the observed and calculated profiles match better at (1 1 0) compared with (1 0 0), (0 1 1), (1 1 1) (see the inset to figure 4(a)), among the reflections those are not parallel to [0 1 0]. From the consideration of the preferred orientation function [25], it is understood that the (1 1 0) group of planes will indeed be the least affected ones, while there would be significant intensity variations for all other groups of planes. Thus, in order to compare different levels of preferred orientation, the patterns were normalized at (1 1 0), where the effect is minimal. From figures 7(c),(d) and (e), one can clearly see that the intensities at (0 1 0), (0 2 0) and other related reflections are increasing with increasing grinding times. The PXRD patterns in figure 7 thus indicate that the as-formed sample B does not exhibit texturing and all the anisotropic crystallites originate only as a result of mechanical grinding.

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any more. Rather, in a few cases we found it to be decreasing, but only to a little extent. This result is in contradiction to the usual expectation that after a certain level of grinding, the plate-like particles should break into smaller isotropic ones, thereby destroying the texturing. In our case, the particle size can not be decreased below a certain limit by means of manual grinding and the maximally ground sample has a particle size of $\sim 1 \mu m$ along the flat faces (see figure 8(d)), which is the typical size one generally achieves this way.

4. Conclusions

MnWO$_4$ exhibits a natural cleaving tendency and hence texturing. Careful treatment of polycrystalline MnWO$_4$ can produce aligned ingots where the crystalline anisotropy could be as high as 50%. Our results show that large crystallites, ground heavily to form powders, create plate-like highly anisotropic grains, which can give rise to huge texturing under application of small manual pressures. Hence, powder diffraction experiments carried out on crushed single crystals or highly dense polycrystalline ingots of MnWO$_4$ could be highly prone to such effects and as a result can provide largely misleading crystallographic information. The magnetic and dielectric properties measured along two perpendicular directions on a pressed pellet show clear development of the anisotropic materials properties, which further ensure the morphology-induced texturing in MnWO$_4$. 

Figure 7. X-ray powder diffraction ($I_{(110)} = 1.0$ for all the panels) from pressed MnWO$_4$ samples A, B, C, B1, B2 and B3 in (a)–(f), respectively. (e) and (f) have been scaled up to accommodate the large preferred orientation effect.
Figure 8. SEM images from pressed MnWO$_4$ samples A, B, C and B3 in (a)–(d), respectively, showing sample morphology. (e) Crystal structure of MnWO$_4$. Movement of Mn and W ions inside the distorted octahedra is shown by arrows. Three types of MnO and WO bond lengths are marked by solid (short), dashed (medium) and dotted (long) lines.

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