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Short communication

Probing lamellar twins in spark plasma sintered $CaTiO_3$ using Electron Backscattered Diffraction

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ABSTRACT

The twinning characteristics of spark plasma sintered $CaTiO_3$ with orthorhombic perovskite structure is critically analysed using Electron Backscatter Diffraction (EBSD) technique. The twins are characterized by a sub-micron interlamellar spacing with a misorientation of $\approx 90^{\circ}$. The crystallographic relationship between the matrix and the twin has been analysed in terms of misorientation matrix using the Kikuchi patterns obtained from the EBSD scan. From the analysis of angle/axis pairs at the boundary, the twin axis was found to be of type [101]. These twins with high angle boundaries are expected to enhance fracture resistance through crack deflection and crack tip shielding mechanisms.

1. Introduction

Materials with a perovskite structure possess interesting electrical and magnetic properties, that are necessary for unique applications such as multilayered capacitors, high T_c superconducting materials, photovoltaic cells, solar cells, semiconductors and magnetoresistive elements [1–4]. Microstructural features, defects and phase transitions usually play a vital role in deciding the properties of perovskites [5–7]. Among these, twinning is one of most prominent microstructural characteristics and is known to affect both mechanical and electrical properties of perovskites [5,8,9]. Twinning is quite common in the naturally occurring perovskites (e.g. $MgSiO_3$ and $BaTiO_3$) with MgSiOwith MgSiO. Twins in such cases can be attributed to the loss of symmetry due to the phase transformation (Cubic → Tetragonal → Orthorhombic) during cooling. While twinning in $BaTiO_3$ is usually due to excess TiO_2, it is due to phase transformation in $CaTiO_3$ and $MgSiO_3$. Hence, these defects are transformation twins. In these terrestrial perovskites, twins are known to be of two fundamentally different types (i) [101] twin and (ii) [121] twin. The type (i) occurs commonly in naturally occurring perovskites. It is also known that a higher cooling rate (> 50 K/min) usually favors type (ii) twins observed in meteoritic perovskites. In contrast, a lower cooling rate favors type (i) twins [10].

The crystallographic relationships in a twinned crystal are usually determined using a TEM with complex tilting maneuvers to obtain a set of parallel poles (diffraction spots common to two different zone axes) between twinned and parent crystal at the twin boundary. The elaborate process of preparing electron transparent foils of ceramics together with the difficulty in obtaining good SAED patterns/Kikuchi lines from TEM is most often time consuming. Electron Backscattered Diffraction (EBSD), a relatively simple technique that can be used for metals and ceramics with minimal sample preparation has gained popularity for its usefulness and versatility [11–13]. EBSD can be used with polished bulk samples to obtain crystalline phase information and orientation mapping using Kikuchi patterns with the aid of a dedicated software in an automated manner. The software containing an inbuilt crystallographic database can analyze the Kikuchi patterns to determine the planes, angles and the orientation of a site on the sample with respect to reference axes. It has also been shown that an EBSD system equipped with a Field Emission Gun (FEG) SEM can attain spatial resolution of the order of 10 nm, which has extensively increased its applications in the field of quantitative materials science [14–17]. EBSD has been used to study texture, grain growth and grain boundary character, defect structures (twins and stacking faults), crystallographic relationships and deformation mechanisms with great success and reasonable effort in the way of sample preparation [18–20]. Previously reported

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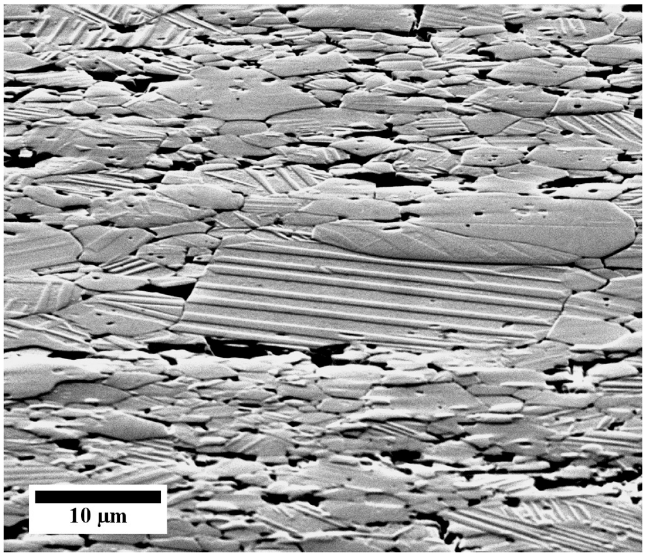

Fig. 1. SE image of etched CaTiO3 showing lamellar twins and grain boundaries.

studies on twin crystallographic relationships in perovskites using EBSD, especially in $BaTiO_3$ agree well with established results based on TEM studies [21,22]. In the current study, we report the observation of twinned microstructure through EBSD in spark plasma sintered orthorhombic $CaTiO_3$ together with the analysis of crystallographic relationships and validate it with previously reported TEM studies.

2. Materials and Methods

Calcium Titanate ($CaTiO_3$) powders (D_{50} ≈5 μm) were synthesized using the mechanochemical activation route by milling a stoichiometric mixture of CaO and TiO_2 (anatase) for 16 h in an agate jar (with ball to powder ratio 4:1), followed by calcination at 900 °C for 2 h. The powder was consolidated using multistage spark plasma sintering technique (MSSPS) (Dr. Sinter, Model 515S, SPS syntax Inc, Japan). The graphite die/punch assembly was heated by pulsed direct current to a temperature of 850 °C and held for 5 min. In the same heating cycle, the powder compact was subsequently heated to a temperature of 950 °C with a dwell time of 5 min in the same cycle, followed by a final stage of sintering at temperature of 1200 °C for 5 min. During the entire heating process, the powder compact was under uniaxial pressure of 50 MPa. A uniform heating rate of 100 °C/min was maintained throughout each heating cycle and at the end of the cycle, the sintered compact was allowed to cool to ambient temperature at a cooling rate of <50 K/min. Finally, the SPS processed samples were polished using metallographic techniques to produce flat "mirror finish" surfaces. The phase composition of the sintered compact was examined through X-ray diffraction with Cu Kα radiation (λ = 0.154 nm) followed by Rietveld refinement to ascertain the phase purity and lattice parameters (see supporting information). The microstructural investigation of the samples was performed using Scanning Electron Microscope (SEM, FEI Quanta 200), operated at 20 kV equipped with EBSD detector to obtain Backscattered electron diffraction patterns (BSED) and orientation analysis is carried out with commercial Orientation Imaging Microscopy software, TSL-OIM. The samples for EBSD analysis were prepared by polishing with SiC papers successively to #2000, and then with 9 μm, 3 μm and 1 μm size diamond paste to reduce the surface roughness, followed by polishing with colloidal silica (Struers OPS) of particle size 8 nm. The polished samples were etched at room temperature by anhydrous citric acid and distilled water in the ratio of 8:10 (by mass) and adding 2–3 drops of hydrofluoric acid (HF) for about 5 min to reveal microstructural features. EBSD was carried out by scanning a sample area of 36 μm by 140 μm with a step size of 0.14 μm at a working distance of 13 mm and tilt angle of 70° and acquisition rate of 15–20 points/second. The EBSD data was recorded with a Confidence Index (CI) of 0.3 (similar to Mean Angular Deviation in Oxford systems), indicating good match between experimental and calculated Kikuchi patterns.

3. Results

Representative SEM micrograph of the etched surface of spark plasma sintered $CaTiO_3$ is shown in Fig. 1 in which lamellar twins spanning entire grains were observed. In some of the larger grains, the twin lamellae are found to be several microns in length. The twins were observed to span entire grains are due to the transformation from higher symmetry tetragonal phase of $CaTiO_3$ to lower symmetry orthorhombic phase during cooling, and hence are transformation twins.

The image quality (IQ) map generated by the EBSD scan is presented in Fig. 2, which clearly reveals the presence of twinned

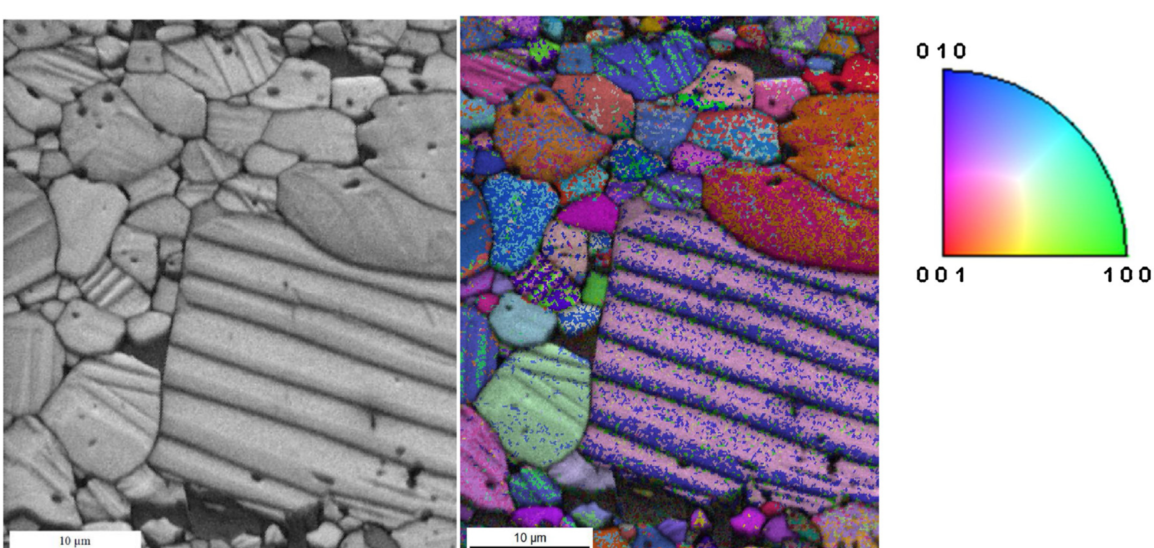

Fig. 2. Image quality (IQ) map and inverse pole figure of sintered $CaTiO_3$ showing lamellar twins. The dark spots indicate unindexed regions due to the presence of pores.