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Non-180° domains formation mechanism in $LiTaO_3$ grains of an $Al_2O_3/LiTaO_3$ composite

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Abstract

High density (>99.5%) $Al_2O_3/LiTaO_3$ (ALT) composite was obtained by hot pressing at 1300 °C/25 MPa in nitrogen atmosphere. The microstructure, which included a domain structure in $LiTaO_3$ grains, was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Most of the domains observed in $LiTaO_3$ grains of the $Al_2O_3/LiTaO_3$ (ALT) composites belong to a non-180° type domain, which cannot exist in $LiTaO_3$ single crystals. This non-symmetry domain microstructure belongs to ferroelectric twinning with $\{\bar{1}\,0\,1\,2\}$ twin composition plane. The non-180° domains formation mechanism was proposed.

Keywords: A. Hot pressing; B. Composites; B. Electron microscopy; D. Al_2O_3; $LiTaO_3$

1. Introduction

Lithium metatantalate ($LiTaO_3$) has various applications due to its excellent pyroelectric, piezoelectric and electrooptic properties [1,2], which are based on its actual ferroelectric structure. The ferroelectric structure variety of $LiTaO_3$ at room temperature has been determined by Zruiyuk et al. [3]. The Li and Ta atoms occupy two-thirds of the face-sharing octahedral sites in the hexagonal close-packed oxygen sublattice and cationic shifts along *c*-axis at the paraelectric–ferroelectric transition in $LiTaO_3$. The symmetry decides that spontaneous polarization of $LiTaO_3$ occurs only along *c*-axis, so the domain structure, which is the direct result of crystallography development corresponding to the paraelectric to ferroelectric phase transition [4], exists only as a 180° domain type.

In recent years, there have been many studies on the growth and properties of $LiTaO_3$ single crystal, however microstructures of $LiTaO_3$ ceramic matrix composites were rarely reported [5]. One reason for this is that it is difficult for $LiTaO_3$ to consolidate because of its decomposition and volatilization of one decomposed product, Li_2O, at a high sintering temperature range (>1300 °C). In our previous work, Al_2O_3 ceramic matrix composite incorporated with $LiTaO_3$ particles was successfully densified with a relative density value of >98.5% [6], and a piezoelectric $LiTaO_3$ phase with different kinds of domain structures was found to be quite compatible with Al_2O_3 during sintering process. Moreover, a non-180° domain structure, which cannot form in a $LiTaO_3$ single crystal, was observed in $LiTaO_3$ grains [7]. It is well known that various properties of this composite depend largely on the domain configuration and domain motion, and the transformation of the domain structure is beneficial to mechanical properties due to stress release at the crack tip zones induced into the ceramics [7,8]. However, the non-180° domains formation mechanism in ALT composite is still unclear. In this paper, therefore, the non-180° domains formation mechanism and its atomic structure were investigated.

2. Experimental

Commercially available Al_2O_3 powder (High Tech Ceramic Institute, Beijing, China) and $LiTaO_3$ powder (Dongfang Tantalum Joint Stock Limited Company, Ningxia, China) were

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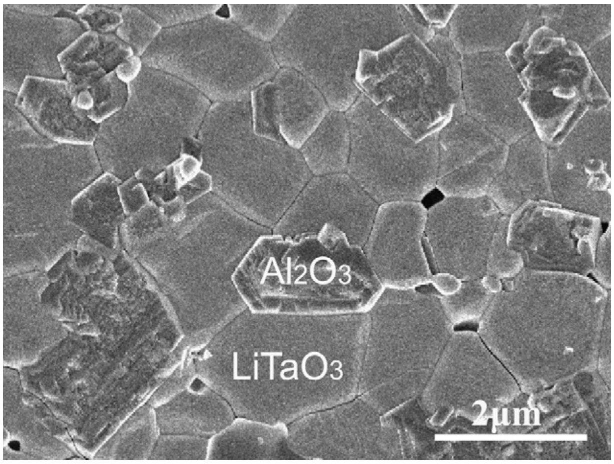

Fig. 1. A typical SEM image of the thermally etched 15 vol.% $Al_2O_3/LiTaO_3$ composite ceramic.

used as starting materials. They were weighed respectively according to a given ratio ($V_{Al_2O_3} : V_{LiTaO_3} = 15 : 85$) and then ball-milled for 24 h with Al_2O_3 balls using ethanol as a medium. The slurry was stirred and dried to get 15 vol.% $Al_2O_3/LiTaO_3$ composite powders. Then they were consolidated by hot-pressing conducted at 1300 °C for 0.5 h under a pressure of 25 MPa in a nitrogen atmosphere. Samples for scanning electron microscopy (SEM) observations were polished then thermally etched at 1200 °C for 1 h with a heating/cooling rate of 5 °C/min. Morphologies of domains in $LiTaO_3$ grains were examined using a Hitachi S-570 type SEM. Samples for TEM observations were cut and then polished to a thickness of less 50 μm using SiC abrasive papers. Ion thinning of the disc samples was performed by argon ion milling with an incident angle of 10° until perforation occurred. Microstructure observations were carried out using a Philips CM12 type TEM operated at 120 kV.

3. Results and discussion

In our previous work, highly densified $Al_2O_3/LiTaO_3$ (ALT) composites with a relative density value higher than 99.5% were obtained by hot-press sintering at 1300 °C/25 MPa in a nitrogen atmosphere [9]. Fig. 1 shows a typical SEM micrograph of the thermally etched 15ALT composite. The fresh grey grains shown in Fig. 1 are $LiTaO_3$ matrix, and the dark-grey particles with sharp angles are Al_2O_3. As indicated, the Al_2O_3 particles are homogenously distributed among the $LiTaO_3$ matrix grains. Furthermore, a few pores located at the tri-junctions of the $LiTaO_3$ grains can also be observed because the densification of pure $LiTaO_3$ is very difficult even at high temperature. In contrast, pores are rarely found around the Al_2O_3 grains showing that Al_2O_3 grains are well bonded with the $LiTaO_3$ grains. This further proves that the Al_2O_3 has a good wettability with the $LiTaO_3$ grains, which is very beneficial for the densification of the ALT composite.

A magnified image of typical $LiTaO_3$ grains in the 15ALT composite is shown in Fig. 2(a). Multi-steps formed in the $LiTaO_3$ grains on the surface of a thermally etched sample, showing the typical morphology of domain structures in $LiTaO_3$ grains. It's well known that the energy of 180° boundary walls is less sensitive to crystallographic orientation, thus 180° boundaries usually have morphology of ''water-mark'' [10], and the non-180°/90° domain boundaries usually exist as ''herringbone'' or ''banded'' shape. So, formation of the multi-steps is due to the existing of non-180° domain structures in addition to the 180° boundaries in $LiTaO_3$ grains. The domain boundaries are straight in the central area of the $LiTaO_3$ grain. In contrast, domain deformation occurred, which lead to morphology of a mixture of non-180° and 180° domain walls, near the $LiTaO_3$ grain boundary as a black arrow indicated in Fig. 2(a) due to the restriction of the adjacent grains. If polarization vectors are assigned to each domain shown in Fig. 2(a), a non-180° domain configuration formed is schematically shown in Fig. 2(b).

Microstructure of the ferroelectric domains in the ALT composites has been investigated in detail using TEM. Similar to that of the $LiTaO_3$ single crystal, 180° domain structures were observed in $LiTaO_3$ grains of the ALT composites which exhibiting the characteristics of ''water-mark'', as shown in Fig. 3. Another type of domain, which has a banded structure, was observed in the $LiTaO_3$ grains in the ALT composites, as

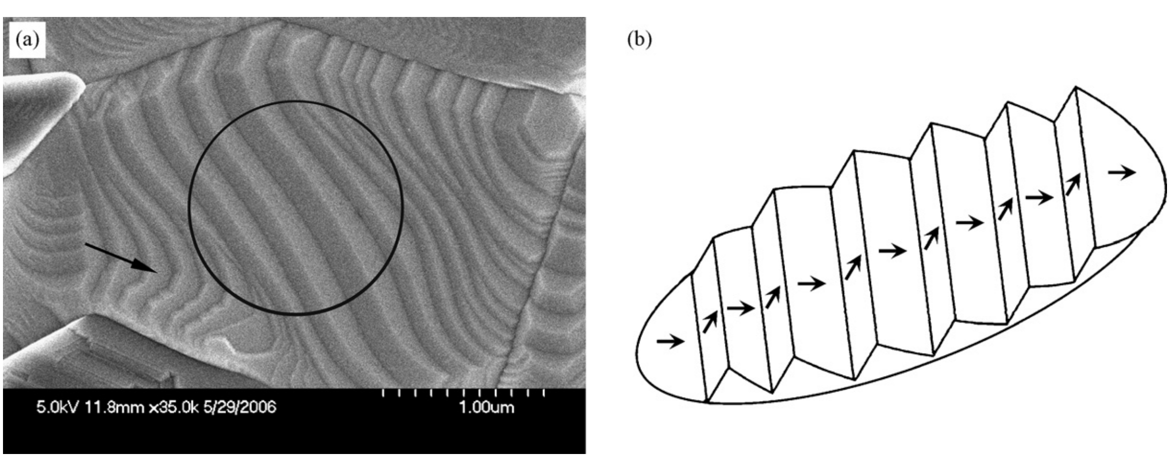

Fig. 2. SEM typical domain structures in a $LiTaO_3$ grain (a) and a schematic of the formation of non-180° domain (b).

Fig. 3. TEM image of a 180° domain in a $LiTaO_3$ grain of the 15 vol.% Al_2O_3/$LiTaO_3$ composite ceramic.

shown in Fig. 4(a). Fig. 4(a) shows a well-developed twinning domain structure, and the sharp straight boundaries appeared within the ferroelectric domains identified as rhombohedral twin lamellae readily. The selected-area electron diffraction (SAED) pattern and the indexed result of the corresponding region are shown in Fig. 4(b) and (c), respectively. The SAED pattern indicates that the ferroelectric domain has a twin structure and the twin plane is the domain boundary (or domain wall). TEM observation result shows that the composition plane of domain walls (twin boundaries) lies on $\{\bar{1}\,0\,1\,2\}$, and the twin plane is always the $(\bar{1}\,0\,1\,2)$ plane. Fig. 5 shows a schematic of atomic twin structure along [0 1 0] direction of $LiTaO_3$ grain and the twin plane is $(\bar{1}\,0\,1\,2)$. The angle between $(1\,0\,4)_M$ and $(1\,0\,4)_T$ is about 172°. According to the spontaneous polarization direction of schematic (c-axis), it can be confirmed that the angle of this non-180° domain is 67°, which is different from other square or cubic crystal.

Moreover, some ‘‘dark dots’’ are presented along the domain walls shown in Fig. 4(a). These irregular dots are considered to be a result of the strain contrast, because they are easily discerned when the domain boundaries tilted edge-on. The type of contrast usually represents defects or lattice distortion, such as dislocations in α-quartz, whose existence has induced significant strain fields in the material [11,12]. The 180° domain formed in the $LiTaO_3$ single crystal free of strains. While, in the ALT composites, the $LiTaO_3$ grains were clamped and the stress generated during the sintering and cooling process. If the inverted 180° domain in $LiTaO_3$ grains formed only along one direction elongated or shortened, bigger strain energy would be needed, which is contradictory to the lowest energy law. Therefore, it is impossible for only the 180° domain to appear in $LiTaO_3$ grains of ALT composites, so, other non-180° domains might be formed as a way of decreasing strain energy if symmetry allows.

Based on the above analysis, the non-180° domains formed in $LiTaO_3$ grains due to the mechanical restriction, which cannot exist in $LiTaO_3$ single crystal, i.e. the domain structure was changed by mechanical restriction in hexagonal $LiTaO_3$

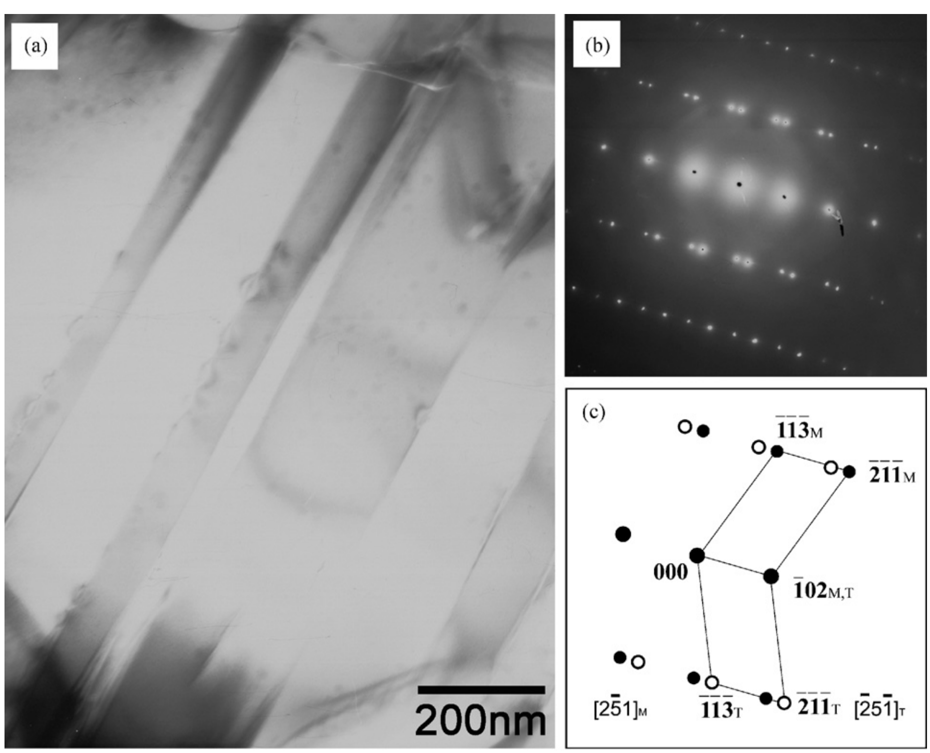

Fig. 4. TEM image of non-180° domain structure (a), its corresponding SAED pattern (b) and indexed result (c).

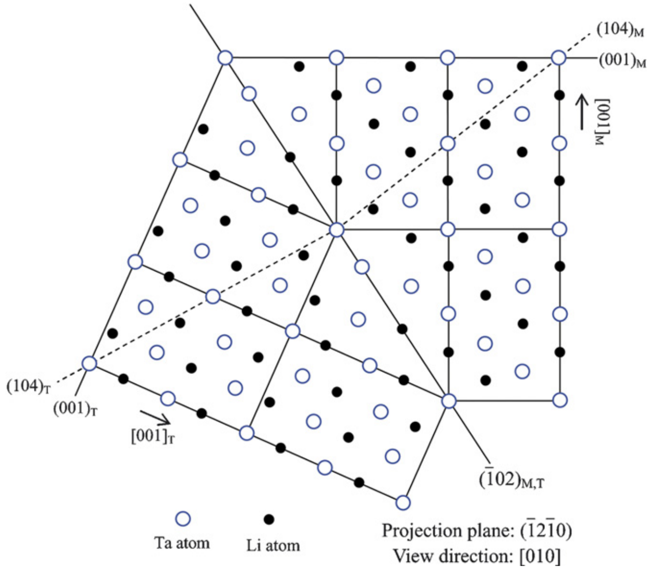

Fig. 5. Atomic model of the ferroelectric domain structure of $LiTaO_3$ in ($\bar{1}$ 2 $\bar{1}$ 0) plane.

grains. The clamped condition make plastic deformation, if any, occurs by twinning rather than by slipping, especially when few available slip systems are unfavorably oriented with respect to the deformation axis. This is particularly true in hexagonal and rhombohedral materials, in which slip is usually restricted to the (0 0 0 1) basal plane. Such materials usually deform by twinning on a ($\bar{1}$ 0 1 2) plane, i.e. a pyramidal plane. Since lithium tantalum is a rhombohedral material, which may also be indexed as a pseudo-hexagonal structure, it is not surprising that deformation occurs by twinning on the ($\bar{1}$ 0 1 2) plane.

Since the polarity of a domain is determined by the direction of the displacement of lithium and tantalum atoms with respect to the (0 0 0 1) sheets of oxygen atoms, the lithium and tantalum atoms in the twinned region are moved through the sheet of oxygen atoms and the polarity of the twinned region is reversed with respect to that of the matrix. This leads to the formation of non-180° domain in the $LiTaO_3$ grains. This mechanism works in spite of the polarity of the matrix. So, the internal stress generated due to mechanical restriction during cooling and the deformation restricted to the (0 0 0 1) basal plane in hexagonal and rhombohedral materials leads to the formation of the non-180° domain in $LiTaO_3$ grains of the ALT composites.

4. Conclusions

Since Al_2O_3 has a good wettability with the $LiTaO_3$ grains, high-density $LiTaO_3$ matrix ceramic composite incorporated with 15 vol.% of Al_2O_3 particles was successfully densified by hot pressing technique. Both non-180° domains and 180° domains were observed in $LiTaO_3$ grains of the ALT composites. The formation of the non-180° domains, which are absent in $LiTaO_3$ single crystal, is due to the mechanical restriction. The mechanical restriction make plastic deformation, if any, occurs by twinning rather than by slipping, especially when the few available slip systems are unfavorable oriented with respect to the deformation axis. The non-symmetry domain microstructure belongs to ferroelectric twinning with {$\bar{1}$ 0 1 2} twin composition plane. The internal stress generated during cooling and the deformation restricted to the (0 0 0 1) basal plane in hexagonal and rhombohedral materials play a key role in the non-180° domain formation in $LiTaO_3$ grains.

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