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Short communication

Sintering mechanism and dielectric properties of $LiTaO_3$ matrix composites with the addition of Al_2O_3 particles

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Abstract

Highly densified $Al_2O_3/LiTaO_3$ (ALT) ceramic composites were fabricated by hot-pressing in a nitrogen atmosphere. The addition of Al_2O_3 particles could significantly improve the densification of $LiTaO_3$. Sintering mechanism of the $LiTaO_3$ ceramic incorporated with Al_2O_3 particles is proposed. Dielectric constant of 5 vol.% $Al_2O_3/LiTaO_3$ (5ALT) composite ceramic was slightly increased in the range from 30 kHz to 10^6 Hz, but the dielectric loss was lowered in the whole range from 10^3 Hz to 10^6 Hz. Piezoelectric constant (d_{33}) of the 5ALT ceramic composite is about 50% of that of $LiTaO_3$ single crystal.

Keywords: A. Sintering; A. Hot pressing; B. Interfaces; 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]. Many studies were concentrated on the growth and properties of $LiTaO_3$ single crystal, but the sintering behavior, microstructure, and properties of $LiTaO_3$ ceramic matrix composites were rarely reported [3]. $LiTaO_3$ is difficult to be sintered because of volatilization of Li_2O at high temperature (>1300 °C). In previous studies, multifarious solid solution systems were proposed, such as $(1-x)LiTaO_3$–$xCaTiO_3$ [3], Mg-doped $LiTaO_3$ [4] and $Li_{(1-x)}Ag_xTaO_3$ [5]. Densification of $LiTaO_3$ can be improved by addition of oxide or fluoride, but the relative densities of the sintered composites were still very low [6–9]. Our research group proposed a new Al_2O_3 ceramic matrix composite with the addition of $LiTaO_3$ particles. High densities of the Al_2O_3 ceramic matrix composites (CMCs) were obtained and $LiTaO_3$ phase was found to be compatible with Al_2O_3 during the sintering process [10]. In our previous study, Al_2O_3 particles were added to $LiTaO_3$ ceramic matrix in order to improve the densification and mechanical properties of $LiTaO_3$ ceramic composites and the mechanical properties of the ALT ceramic composites were investigated [11], but further investigations on sintering mechanism and dielectric properties of the $LiTaO_3$ ceramic composites with addition Al_2O_3 are needed. In this paper, therefore, the sintering mechanism of $LiTaO_3$ ceramics in the presence of Al_2O_3 and the dielectric properties of the ALT ceramic composite will be reported.

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 used as starting powders. The volume fraction of Al_2O_3 in $LiTaO_3$ matrix is 5%. Al_2O_3 and $LiTaO_3$ powders were weighed, then mixed by wet ball milling for 24 h with Al_2O_3 balls. Ethanol was used as a medium for the ball milling. The slurry was stirred and dried slowly to remove the ethanol. The pure $LiTaO_3$ ceramic and $Al_2O_3/LiTaO_3$ (ALT) composite ceramics were hot-pressed at 1300 °C for 0.5 h under a pressure of 25 MPa in a nitrogen atmosphere. Samples for scanning transmission electron microscopy (STEM) and HREM observations were cut and then polished to a thickness of less 50 μm

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using SiC abrasive papers. Ion thinning of the disc samples was performed by argon ion thinning with an incident angle of 10° until perforation occurred. Microstructural observations were carried out using a JEM-2010F type HREM at 200 kV. The ALT composite ceramic samples were ground into specimens of 12 mm in diameter and <1 mm in thickness. The two opposing surfaces of samples were sprayed with Au electrodes. Dielectric property measurements were carried out on an automated system with LCR meter (Agilent4294A for frequency dependence). Frequency dependences of dielectric constant and dielectric loss were measured pseudo-continuously at room temperature from 40 Hz to 10^6 Hz. Piezoelectric constant (d_{33}) was measured by a d_{33} meter (ZJ-3A) made by the heat treated at 1000 °C for 3 h to ensure the electrodes well contact with the surfaces of the specimens.

3. Results and discussion

Highly densified ALT ceramic matrix composites were fabricated by hot-press sintering in a nitrogen atmosphere. Relative density the ALT composite can be as high as 99.5% when it was hot-pressed at 1300 °C under a pressure of 25 MPa [11], but the relative density of the pure $LiTaO_3$ ceramic was only 91.5%. The mechanical properties of pure $LiTaO_3$ ceramic and $LiTaO_3$ matrix composite added Al_2O_3 particles were investigated in our previously study. In comparison of the pure $LiTaO_3$ ceramic, the flexural strength and the fracture toughness of 5 vol.% Al_2O_3/$LiTaO_3$ (5ALT) ceramic composite increased up to 118.5 MPa and 2.36 MPa $m^{1/2}$, respectively, which were 4 and 5 times larger than that of pure $LiTaO_3$ ceramic [11].

Fig. 1 shows dielectric constants and dielectric loss (tan δ) of the sintered pure $LiTaO_3$ ceramic and 5ALT ceramics composite as a function of frequency. The dielectric constant and dielectric loss of the samples were measured at frequencies from 40 Hz to 10^6 Hz. The values of dielectric constant for pure $LiTaO_3$ ceramic and 5ALT ceramic composite are 33 and 35, respectively. The dielectric loss values are in the range of 0.021–0.073 for pure $LiTaO_3$ ceramic and 0.018–0.076 for 5ALT ceramic composite. The dielectric constant of $LiTaO_3$ ceramics was slightly increased with the addition of Al_2O_3 but the dielectric loss was lowered. The electroded ceramics samples were polarized before measurements. The applied electrical field was perpendicular to the circular faces of the pellet. The value of piezoelectric constant (d_{33}) of 5ALT ceramic composite is 5×10^{-12} C/N. This value represents about 50% of the d_{33} value previously measured for a $LiTaO_3$ single crystal and enhances approximately 20–30% compared with results from other researchers [7].

To investigate the sintering mechanism of the ALT ceramic composite, the interface microstructure between $LiTaO_3$ and Al_2O_3 in the composite ceramic was investigated. Fig. 2 showed a typical HREM micrograph of interface between $LiTaO_3$ and Al_2O_3. The $LiTaO_3$ grains were well bonded with the Al_2O_3 grains and the interface between $LiTaO_3$ grains and Al_2O_3 grains was clear and clean. It can be seen from Fig. 2 that $(\bar{1}\,1\,2)_{LiTaO_3}$ plane is parallel to that of $(0\,1\,3)_{Al_2O_3}$, and the

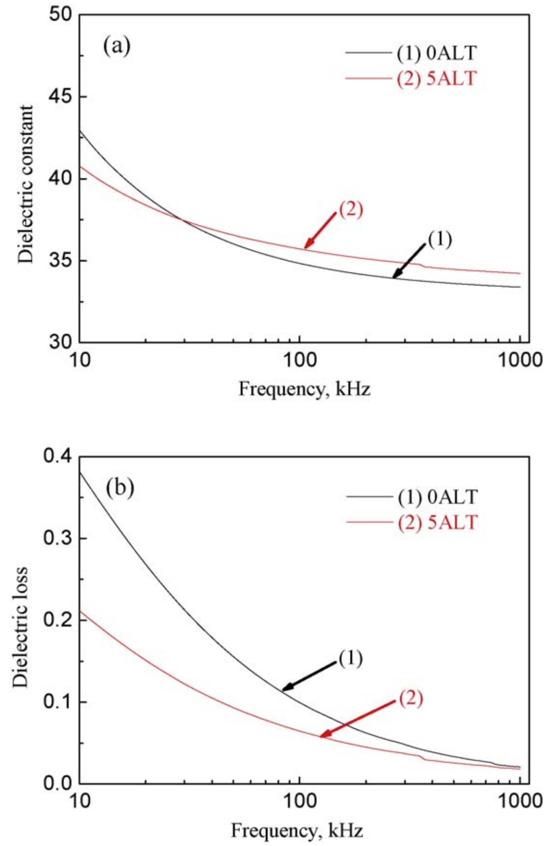

Fig. 1. Dielectric constant and dielectric loss (tan δ) of the ALT composites at room temperature as a function of frequency: (a) dielectric constant; (b) dielectric loss.

schematic of crystal lattice constant of $(0\,1\,3)_{Al_2O_3}$ and $(\bar{1}\,1\,2)_{LiTaO_3}$ proposed is shown in Fig. 3. The matching of the two planes is very good, calculated in the $(\bar{1}\,1\,2)_{LiTaO_3}$ plane come forward with $(0\,1\,3)_{Al_2O_3}$ lattice mismatch rate of only about 1%. Moreover, many interfaces with lower lattice mismatching rate have been observed in this composite system.

Fig. 4 shows that STEM micrograph at interface and X-ray line scanning map of Al, Ta, O. As it indicated, interdiffusion of Al and Ta elements took place at the Al_2O_3/$LiTaO_3$ boundary and Ta element content is close to zero across the diffuse area, but some Al element still exist in $LiTaO_3$ grain across interface area. This indicates that small content of Al atoms may diffused into $LiTaO_3$ grains. Since the ionic radius of O^{2-} (r = 0.140 nm) is much larger than that of Ta^{5+} (r = 0.064 nm) or Li^{+} (r = 0.074 nm), it seems that the rate-controlling step during sintering process of $LiTaO_3$ is the diffusion of oxygen. The ionic radius of Al^{3+} (r = 0.057 nm) is a little smaller than that of Ta^{5+}, suggesting that Al^{3+} ions could substitute for Ta^{5+} or diffused into octahedron interstice in the $LiTaO_3$ lattice, thereby producing oxygen vacancies which facilitate the diffusion of oxygen in $LiTaO_3$ and its rapid densification. In addition, according to results of Shimada et al. [9], $LiTaO_3$ is difficult to be sintered because of volatilization of Li_2O at the required high sintering temperature (>1300 °C), and the densification of pure $LiTaO_3$ occurs concurrently with grain growth, and prolonged

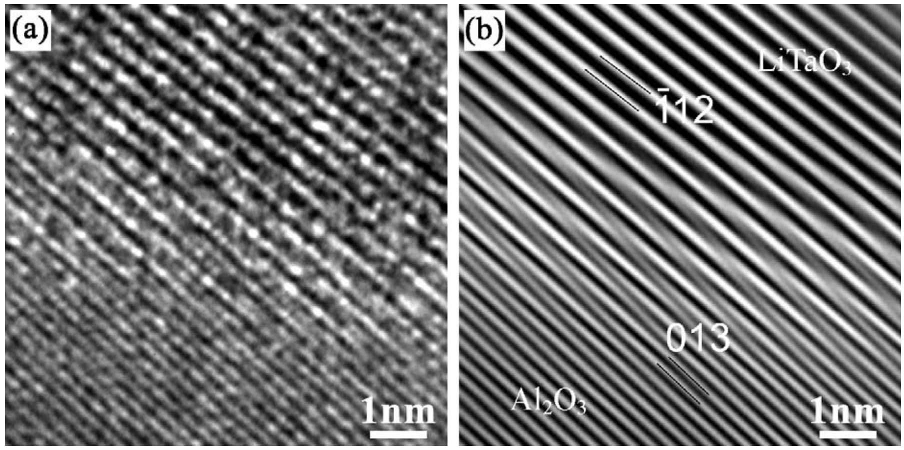

Fig. 2. HREM image (a) and reproduced image by inverse Fourier transformation according to the Fourier transformation pattern (b) of $Al_2O_3/LiTaO_3$ interface in ALT ceramic composite.

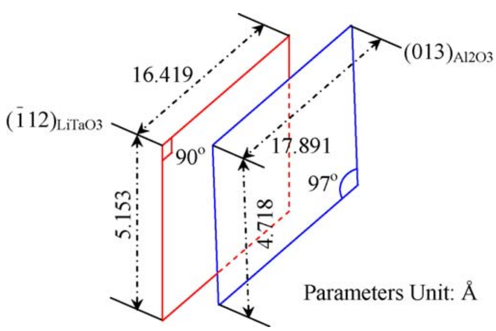

Fig. 3. Schematic of crystal lattice constant of $(0\,1\,3)_{Al_2O_3}$ and $(\bar{1}\,1\,2)_{LiTaO_3}$.

heat treatment for $\geq$120 min at 1300 °C results in the development of large grains, resulting from the onset of exaggerated grain growth. According to our previously study, dramatic grain growth is not observed [11]. It seemed that the addition of Al_2O_3 particles could lower the volatilization of Li_2O as a result of the low interface energy between Al_2O_3 and $LiTaO_3$ due to their good lattice matching, therefore the sinterability of the ceramics is improved. Moreover, the applied pressure further enhance the densification process thus could shorten the sintering time, eventually, the grain growth of $LiTaO_3$ could be prohibited effectively.

To summarize, the addition of Al_2O_3 particles enhanced the sinterability of $LiTaO_3$, which could be attributed to the lower lattice mismatching rate between Al_2O_3 and $LiTaO_3$ grains, the substitute or diffusion of Al^{3+} ions.

4. Conclusions

The addition of small amount of Al_2O_3 particles significantly improved the sinterability of $LiTaO_3$ ceramic thus highly densified ALT ceramic composites were fabricated by hot-pressing in a nitrogen atmosphere. Several factors, such as abundant $Al_2O_3/LiTaO_3$ interfaces of lower lattice mismatching rate, substitute or diffusion of Al^{3+} ions at the interfaces, etc. contributed to improving the sinterability of $LiTaO_3$ composite ceramics. Dielectric loss could be further lowered with the dielectric constant increased slightly during the wide range of frequency from 40 Hz to 10^6 Hz. The piezoelectric constant (d_{33}) of 5ALT ceramic composite is about 50% of that of the $LiTaO_3$ single crystal and enhances approximately 20–30% compared with results from others.

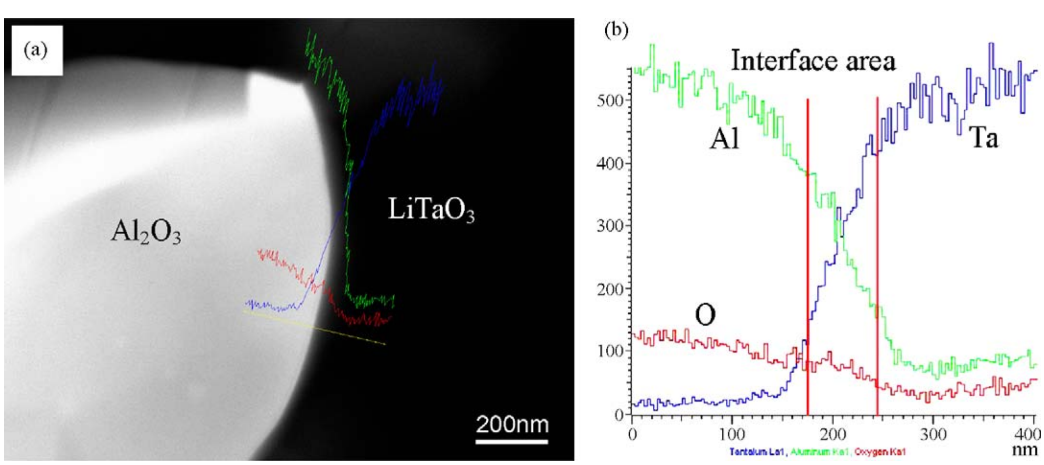

Fig. 4. STEM micrograph (a) and X-ray line scanning map of Ta, Al, O elements (b) of near the $Al_2O_3/LiTaO_3$ boundary in 5ALT ceramic composite.

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