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Journal

Microwave Dielectric Characterization of a Li_3NbO_4 Ceramic and Its Chemical Compatibility with Silver

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A Li_3NbO_4 ceramic has been prepared using the solid-state reaction method and well sintered at around 930°C. The best microwave dielectric properties were obtained in the ceramic sintered at 930°C for 2 h with permittivity 15.8, *Qf* value about 55 009 GHz, and temperature coefficient about −49 ppm/°C. From X-ray diffraction, backscattered electron imaging, and energy-dispersive X-ray spectroscopy results of the ceramic cofired with 20 wt% silver additive, the Li_3NbO_4 ceramic was found not to react with Ag at 900°C. The Li_3NbO_4 ceramic is a promising dielectric material for low-temperature co-fired ceramic technology.

I. Introduction

Low-temperature co-fired ceramic (LTCC) technology has been critically important in the development of electronic devices for wireless communication. The transition from surface-mount discrete components to integrated components in a substrate requires low-temperature firing ceramics, that can be co-fired with metal electrodes. In order to use the most common electrode, silver, the ceramic must have a low sintering temperature below 960°C and chemical compatibility with Ag.[1–6]

Many ceramics with good microwave dielectric properties usually have a high sintering temperature (>1000°C). Addition of low melting point oxides and glasses is the most often used method to lower the sintering temperature. Besides this, considerable attention has been paid recently to the low-temperature firing ceramics possessing good microwave dielectric properties such as TeO_2-rich compounds,[7–9] Bi_2O_3-rich compounds,[10–12] MoO_3-rich compounds, etc.[13,14] Currently the, search for new kinds of low-temperature firing materials that have good microwave dielectric properties is still continuing.

The binary compounds in the Li_2O–Nb_2O_5 system are candidate tritium-breeding blanket materials in fusion reactors. In addition, $LiNbO_3$ finds applications as wave-guides in optoelectronic devices.[15] The phase diagram for the pseudo-binary system Li_2O–Nb_2O_5 was first compiled by Roth *et al.*[16] Several compounds with the stoichiometries Li_7NbO_6, $Li_{16}Nb_4O_{18}$, Li_3NbO_4, $LiNbO_3$, $LiNb_3O_8$, and $Li_2Nb_{28}O_{71}$[17–20] were reported to exist in the system. There are also compounds in this system with Nb being in the oxidation state $<+5$. Kumada *et al.*[21] reported the synthesis of $LiNbO_2$, and its potential application as a lithium-intercalating cathode material in secondary batteries. Gesselbracht *et al.*[22] reported the existence of superconductivity in Li_xNbO_2 ($0.45<x<0.5$) with a Tc of about 5 K. Despite the growing interest in the Li_2O–Nb_2O_5 binary system, very little work has so far been reported on their microwave dielectric properties. Yoon *et al.*[23] reported that $LiNb_3O_8$ could be sintered at around 1075°C and had a dielectric constant of 34, a quality factor ($Q\times f$ value) of 58 000 GHz, and a temperature coefficient of resonant frequency (TCF) of about −96 ppm/°C. Li_2O has a low melting point, and it is often used with other low melting point oxides to lower the sintering temperature of many ceramics.[24,25] There may exist some compounds with both good microwave dielectric properties and a low firing temperature in the Li-rich region in the Li_2O–Nb_2O_5 binary system. With this purpose, we prepared a Li_3NbO_4 ceramic using the solid-state reaction method and studied its sintering behavior. The microwave dielectric constant, *Qf* values, and TCF values of the Li_3NbO_4 ceramic were first reported and studied. In order to use the Li_3NbO_4 ceramic in LTCC technology, its chemical compatibility with Ag was also investigated.

II. Experimental Procedure

Proportionate amounts of reagent-grade starting materials of Li_2CO_3 (>98%, Guo-Yao Co. Ltd., Shanghai, China) and Nb_2O_5 (>99%, Zhu-Zhou Harden Alloys Co. Ltd. Zhuzhou, China) were prepared according to the composition Li_3NbO_4. Powders were mixed and milled for 4 h using a planetary mill (Nanjing Machine Factory, Nanjing, China) by setting the running speed at 150 rpm with zirconia balls (2 mm in diameter) as the milling media. Powders were calcined at 800°C for 4 h and then crushed and remilled for 5 h using ZrO_2 balls and deionized water. Powders were pressed into cylinders (10 mm in diameter and 5 mm in height) in a steel die under a uniaxial pressure of 20 kN/cm^2 with PVA binder addition. In order to investigate the chemical compatibility between Li_3NbO_4 and Ag, 20 wt% silver was mixed with the calcined powder, pressed into pellets, and fired at 900°C for 2 h. Green cylinder samples of Li_3NbO_4 were sintered in the temperature range from 870° to 970°C for 2 h under an air atmosphere.

The crystalline structures of samples were investigated using X-ray diffraction with Cu$K\alpha$ radiation (XRD, D/MAX-2400 X-ray diffractometry, Rigaku, Tokyo, Japan) using ground powders. The microstructures of co-fired ceramics with Ag were observed on the as-fired and fractured surfaces with scanning electron microscopy (SEM) (JSM-6460, Jeol, Tokyo, Japan). The precipitated phases in ceramics were observed using backscattered electron imaging (BEI) coupled with energy-dispersive X-ray spectroscopy (EDS). The apparent densities of sintered ceramics were measured by the Archimedes method. Dielectric behaviors in the microwave frequency were determined by the $TE_{01\delta}$ shielded cavity method using a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (DELTA 9023, Delta Design, Poway, CA). The TCF

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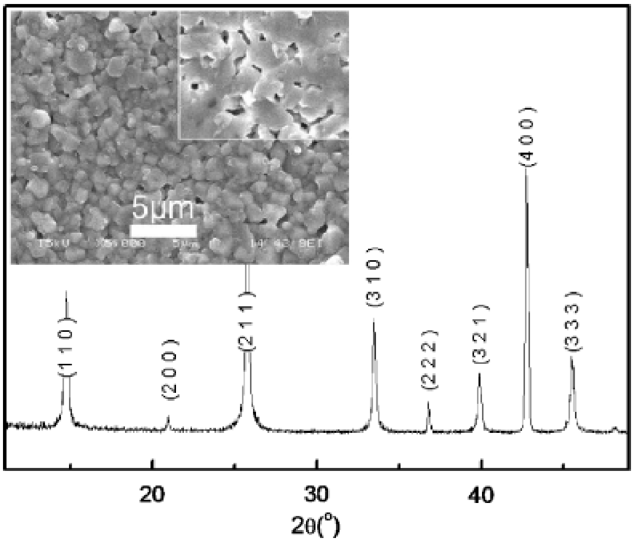

Fig. 1. Scanning electron micrographs of the as-fired surface, fractured surface (top right corner), and X-ray diffraction result of a Li_3NbO_4 ceramic sintered at 900°C for 2 h.

was calculated by the following formula:

$$\mathrm{TCF} = \frac{f_{85} - f_{25}}{f_{85} \times (85 - 25)} \quad (1)$$

where f_{85} and f_{25} are the $TE_{01\delta}$ resonant frequencies at 85° and 25°C, respectively.

III. Results and Discussions

SEM micrographs of the as-fired surface, fractured surface, and XRD result of a Li_3NbO_4 ceramic sintered at 900°C for 2 h are shown in Fig. 1. From the XRD result, all the peaks of the Li_3NbO_4 ceramic sintered at 900°C for 2 h can be indexed as a cubic structure ($I\bar{4}3m$)without a second phase, which is the same as the result reported by Ukei *et al.*[26] The lattice parameters were calculated as $a = 8.429$ Å, which agrees well with that reported by Ukei.[26] The theoretical density of the Li_3NbO_4 ceramic calculated from XRD data is about 3.941 g/cm^3. Homogeneous microstructures with little pores can be observed for the Li_3NbO_4 ceramic sintered at 900°C for 2 h. The grain sizes of the ceramic were between 1 and 2 μm. Both the as-fired surface and the fractured surface show similar microstructure.

Figure 2 presents the apparent density of Li_3NbO_4 ceramics as a function of sintering temperature. As the sintering temperature increases from 870° to 930°C, the apparent density increases from

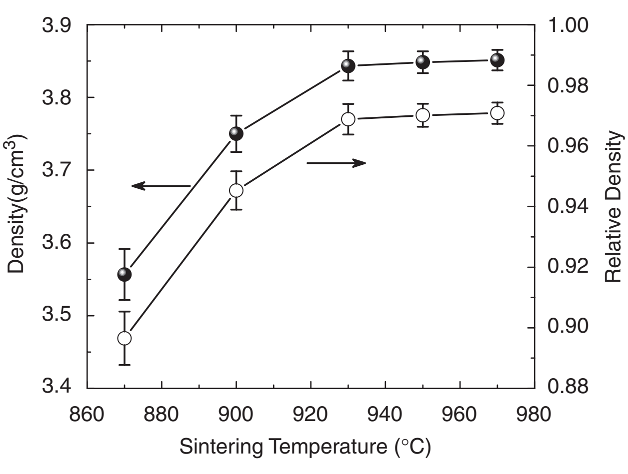

Fig. 2. Apparent density of Li_3NbO_4 ceramics as a function of sintering temperature.

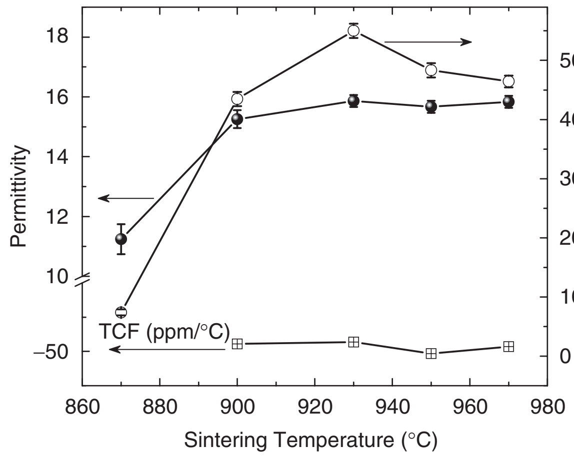

Fig. 3. Microwave dielectric constant, *Qf* values, and temperature coefficient of resonant frequency values of Li_3NbO_4 ceramics as a function of sintering temperature.

about 3.56 to 3.84 g/cm^3, which is equivalent to a relative density of about 97% of the theoretical density. When the sintering temperature increases further, the density of Li_3NbO_4 ceramics reaches saturation. This result indicates that the densified temperature of the Li_3NbO_4 ceramic is around 930°C, and this sintering temperature makes it feasible for use in LTCC technology.

The microwave dielectric properties of Li_3NbO_4 ceramics as a function of sintering temperature are shown in Fig. 3. Microwave dielectric constant versus sintering temperature of Li_3NbO_4 ceramics has a trend similar to that of the apparent density. When the sintering temperature increases to 930°C, the dielectric constant reaches to a saturated value of about 15.8. The *Qf* value of Li_3NbO_4 ceramics reaches the maximum with a value of about 55 009 GHz (at 8.99 GHz). The TCF values do not change remarkably with increasing sintering temperature and remain stable at about −49 ppm/°C. Although its microwave permittivity is large and the *Qf* value is large, the TCF of the Li_3NbO_4 ceramic is slightly large in the negative direction for LTCC application. Therefore, it can be regarded as a potential component for fabricating ceramic composites with positive TCF ceramics such as TiO_2 (TCF = +400 ppm/°C) or $SrTiO_3$ (TCF = +1200 ppm/°C) to obtain near-zero TCF ceramics.[27–29]

For LTCC application of a new microwave dielectric ceramic, its chemical compatibility with common metal electrodes must be studied. Figure 4 shows the BEI micrographs of the as-fired

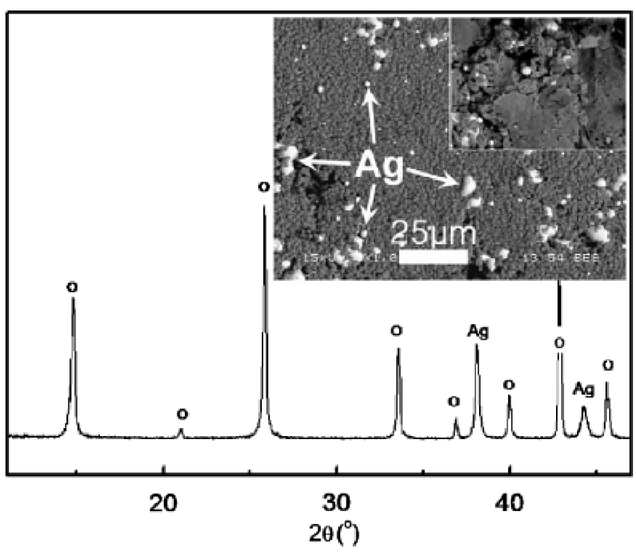

Fig. 4. Backscattered electron imaging micrographs of the as-fired surface, fractured surface (top right corner), and X-ray diffraction result of a Li_3NbO_4 ceramic co-fired with 20 wt% Ag addition at 900°C for 2 h.

surface, fractured surface, and XRD results of a Li_3NbO_4 ceramic with 20 wt% Ag addition co-fired at 900°C for 2 h. In XRD patterns, there are only peaks of the Li_3NbO_4 phase and a pure silver phase. This indicates that the Li_3NbO_4 phase did not react with silver and no other phase was formed at 900°C. In the BEI photo of the silver co-fired ceramic, it is obvious that there are two kinds of grains: most grains with a dark color and small grains with a bright color. From EDS analysis, it is identified that most grains with a dark color belong to the Li_3NbO_4 phase and the small grains with a bright color are found to be pure silver. Pure silver grains could be clearly observed both on the as-fired surface and on the fractured surface of the silver co-fired ceramic. Combined with the XRD results, it can be concluded that the Li_3NbO_4 ceramic does not react with silver at 900°C. One potential reason for the compatibility is that the niobium activity is lower in this composition than those in other high-Q compositions, which are known to react with silver, forming silver niobate.[30] This makes Li_3NbO_4 ceramic a promising dielectric material for LTCC technology.

IV. Conclusions

In conclusion, a Li_3NbO_4 ceramic was prepared by the conventional solid-state reaction method and well densified around 930°C. The structure and microstructure of the Li_3NbO_4 ceramic were studied using powder XRD and SEM analyses. Microwave dielectric behaviors were determined using the $TE_{01\delta}$-shielded cavity method. The best microwave dielectric properties were obtained in the ceramic sintered at 930°C for 2 h with a permittivity of about 15.8, a Qf value of about 55 009 GHz (at 8.99 GHz), and a TCF of about −49 ppm/°C. From the XRD, BEI, and EDS results of a Li_3NbO_4 ceramic co-fired with 20 wt% silver additive at 900°C for 2 h, it was found that the Li_3NbO_4 phase does not react with the Ag phase and these two phases existed separately in the silver co-fired ceramic. Li_3NbO_4 ceramic is a potentially promising material for LTCC technology.

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