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Original Article

The microwave dielectric properties and crystal structure of low temperature sintering $LiNiPO_4$ ceramics

Ping Zhang*, Shanxiao Wu, Mi Xiao*

School of Electrical and Information Engineering and Key Laboratory of Advanced Ceramics and Machining Technology of Ministry of Education, Tianjin University, Tianjin 300072, China

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ABSTRACT

The $LiNiPO_4$ ceramic for the LTCC technology was prepared via the traditional solid-state reaction route and its dielectric properties were investigated for the first time. The best dielectric properties of $LiNiPO_4$ ceramics with a ε_r of 7.18, $Q \times f$ value of 27,754 GHz and τ_f of −67.7 ppm/°C were obtained in samples sintered at 825 °C for 2 h. Rietveld refinement was firstly employed to study the crystal structure and dielectric properties of $LiNiPO_4$ ceramics. Unfortunately, the relatively large negative τ_f was unfavorable to practical applications. Therefore, we introduced TiO_2, which possessed a considerable positive τ_f, to obtain a desired τ_f value. The prepared $LiNiPO_4$ ceramics with 15 wt% TiO_2 sintered at 900 °C for 2 h exhibited excellent dielectric properties of $\varepsilon_r \sim 11.49$, $Q \times f \sim 10{,}792$ GHz, $\tau_f \sim -2.8$ ppm/°C. The Ag co-fired experiments confirmed the excellent chemical compatibility with $LiNiPO_4$-TiO_2 ceramics which might be potential dielectric LTCCs for high frequency applications.

1. Introduction

With the fast development of wireless telecommunication industry, the miniaturization and integration of various components, such as oscillators, antennas and filters, have attracted considerable attentions [1]. Furthermore, the widespread use of mobile communication devices accelerates the study for new technologies to integrate miniaturized dielectric ceramic components [2]. To satisfy the demands for a wide range of practical applications, the low temperature co-fired ceramic (LTCC) technology, one of the most promising integration technologies, has shown its great potential in the production of microwave devices with excellent performances [3]. Therefore, the aspiration for exploiting high quality microwave products is in the process.

Generally, low permittivity (ε_r), high quality factor ($Q \times f$) and near-zero temperature coefficient of resonant frequency (τ_f) are the essential factors of the microwave dielectric materials for the practical applications [4]. In addition, the selected dielectric materials for LTCC technology should have a good chemical compatibility with inexpensive metal silver (Ag) which possesses low conductor loss and low electrical resistance [5].

Recently, owing to the lower melting point of phosphate, some compounds based on phosphorus, such as $LiMPO_4$ (M = Fe, Co, Mn), could be potential LTCC candidates [6]. However, the most studies for $LiMPO_4$ were merely focused on the magnetoelectric and electrochemical properties [6–9]. In 2010, Thomas et al. [2] firstly reported that $LiMgPO_4$ ceramics could be sintered very well at 950 °C for 2 h, which exhibited excellent dielectric properties of $\varepsilon_r \sim 6.6$, $Q \times f \sim 79{,}100$ GHz, $\tau_f \sim -55$ ppm/°C. Later, Hu et al. [10] investigated the dielectric properties of $LiMnPO_4$ ceramics with $\varepsilon_r \sim 8.1$, $Q \times f \sim 44{,}224$ GHz, $\tau_f \sim -90$ ppm/°C. Besides, the $LiMnPO_4$ ceramics could be co-fired with Ag without any chemical reaction. Xia et al. [11] reported the $LiZnPO_4$ ceramics ($\varepsilon_r \sim 5.3$, $Q \times f \sim 28{,}496$ GHz, $\tau_f \sim -80.4$ ppm/°C) that could be as a potential candidate for LTCC applications. To solve stability problems existed in $LiMnPO_4$ system, the TiO_2 was used as an external additive to improve the τ_f value of $LiMnPO_4$ ceramics. Xia et al. [12] reported that $LiMnPO_4$-19 wt%TiO_2 ceramics maintained satisfactory dielectric properties of $\varepsilon_r \sim 12.3$, $Q \times f \sim 38{,}671$ GHz, $\tau_f \sim 6.7$ ppm/°C at 875 °C. However, few studies have reported the dielectric properties and crystal structure of $LiNiPO_4$ ceramics.

In this work, we synthesized the $LiNiPO_4$ ceramics by the traditional solid-state reaction method. The dielectric properties of $LiNiPO_4$ ceramics were systematically studied along with the crystal structure. Moreover, TiO_2 was introduced to adjust the τ_f value to near zero. Meanwhile, the chemical compatibility of $LiNiPO_4$-TiO_2 ceramics with an Ag electrode was discussed. Rietveld refinement was employed to study the crystal structure. What's more, the chemical bond parameters were achieved to investigate the correlation between dielectric properties and crystal structure.

* Corresponding authors.
E-mail addresses: zptai@163.com (P. Zhang), xiaomi@tju.edu.cn (M. Xiao).

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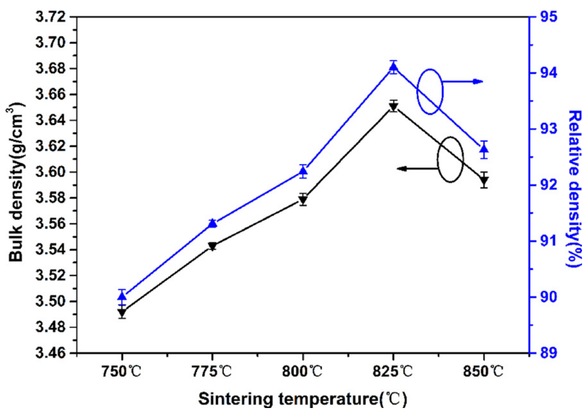

Fig. 1. The variation of bulk and relative densities for $LiNiPO_4$ ceramics.

2. Experimental procedure

The high purity powders of $NH_4H_2PO_4$, Li_2CO_3, NiO and TiO_2 were used as the raw materials. All the starting materials were weighted in accordance with the stoichiometric compositions of $LiNiPO_4$ and ball-milled for 2 h with ethanol. The slurries were dried and sieved with a 40 mesh screen. Afterwards, the obtained samples were first pre-sintered at 550 °C for 2 h followed by a secondary calcination at 700 °C for 4 h. After calcination, the $LiNiPO_4$-x wt% TiO_2 (x = 14, 15, 16, 17) mixtures were prepared by pure $LiNiPO_4$ and TiO_2, and then ball-milled again in ethanol medium for 8 h. After dried, the sieved powders were doped with 8 wt% paraffin as a binder and pressed into cylinders with 15 mm in diameter and 6–7 mm in thickness at 4 MPa. Finally, the obtained cylinders were fired at 550 °C for 2 h to exhaust the binder before sintering at 750–850 °C for 2 h with the heating rate of 3 °C/min.

The phase composition was identified by X-ray diffraction (XRD) (Rigaku D/max 2550 PC, Tokyo, Japan) with Cu Kα radiation (V = 200 kV, I = 40 mA). The diffraction pattern fitting was carried out using the FULLPROF program. The microstructures of the sintered samples polished and thermally etched were observed by a scanning electron microscopy (SEM) (ZEISS MERLIN Compact, Germany). The composition analysis was performed using an energy-dispersive X-ray spectroscopy (EDXS) (Genesis MT XV 60) attached to the SEM.

The microwave dielectric properties of the sintered samples were measured in the frequency range of 7–13 GHz with a network analyzer

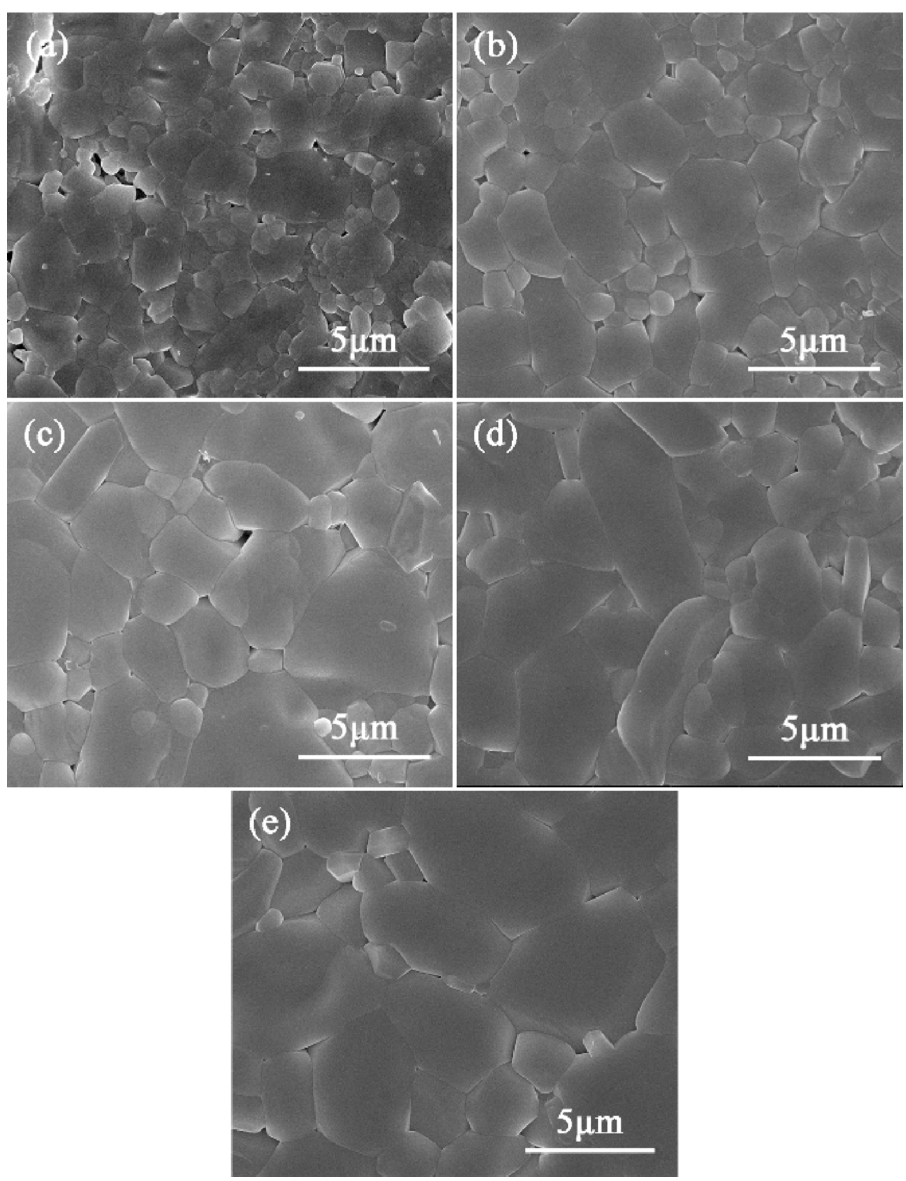

Fig. 2. The SEM micrographs of $LiNiPO_4$ ceramics sintered at various temperatures for 2 h: (a) 750 °C, (b) 775 °C, (c) 800 °C, (d) 825 °C, (e) 850 °C.