Journal Pre-proofs

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PII: S0167-577X(20)30725-4
DOI: https://doi.org/10.1016/j.matlet.2020.128020
Reference: MLBLUE 128020

To appear in: *Materials Letters*

Received Date: 5 March 2020
Revised Date: 16 May 2020
Accepted Date: 18 May 2020

Please cite this article as: K. Wang, H. Zhou, X. Luan, S. Hu, X. Zhou, J. Deng, S. Li, Microwave dielectric properties of $LiSmTa_4O_{12}$ ceramics with A-site deficient perovskite structure, *Materials Letters* (2020), doi: https://doi.org/10.1016/j.matlet.2020.128020

Microwave dielectric properties of $LiSmTa_4O_{12}$ ceramics with A-site deficient perovskite structure

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Abstract

$LiSmTa_4O_{12}$ ceramics were prepared via the conventional solid-state method, and their microwave dielectric properties were studied. The ceramics could be densified at 1425 °C~1525 °C. X-ray diffraction (XRD) analysis suggested that $LiSmTa_4O_{12}$ is single phase with A-site deficient perovskite structure a, whereas the impact from sintering temperature is weak. The excellent microwave dielectric performances of ε_r = 59.60, $Q \times f$ = 7 760 GHz (at 5.065 GHz), and τ_f = +41.8 ppm/°C were achieved when the ceramics were sintered at 1500°C for 4 hours, which means that the ceramics are suitable for miniaturized electronic devices.

Keywords: Ceramics; Dielectrics; X-ray techniques

1. Introduction

With the device structure tends to integration and miniaturization, modern wireless communication equipment tends to be smaller and more efficient. It is generally known

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that high relative permittivity (ε_r) is good for miniaturization of equipment, besides, high quality factor and temperature stability are required for the efficient operation of equipment [1,2].

Recently, rutile-structured of $ZnTa_2O_6$ ceramics with high Q values and excellent microwave dielectric properties ($Q \times f$ = 87,580 GHz, ε_r = 30.30, and τ_f = +9 ppm/°C) have been investigated [3]. $Ba_3LaTa_3O_{12}$ have cation deficient perovskites structure and excellent microwave dielectric properties with $Q \times f$ = 16,800 GHz, ε_r = 39.4, and τ_f = -46 ppm/°C [4]. Lithium ion conductors of perovskite-type compounds $LiSmTa_4O_{12}$ were synthesized, and its crystal structure and lithium ion conductivity were characterized by Mizumoto [5]. The perovskite-type solid solutions $LiLaTa_4O_{12}$ derived from $La_{1/3}TaO_3$ and the crystal structure characterized by Belous [6]. In this work, $LiSmTa_4O_{12}$ ceramics were prepared by the solid state reaction (SSR) method. Furthermore, the sintering behaviour, phase composition, microstructure and microwave dielectric performances of ceramics were also investigated.

2. Experimental procedure

$LiSmTa_4O_{12}$ ceramics were prepared using SSR method. Raw powders with high-purity of Li_2CO_3 (99.95%), Sm_2O_3 (99.99%), and Ta_2O_5 (99.99%) were stoichiometrically weighted. To remove water and CO_2, Sm_2O_3 raw powders were pre-fired at 900 °C before used. Subsequently, the milled powders were pre-calcined in air at 1300 °C for 6 h. Finally, the cylindrical samples which granulated by using 5 wt% polyvinyl alcohol (PVA water solution) were sintered at 1425 °C~1525 °C for 4 h.

The phase structure of the samples was identified by an X-ray diffractometer (PANalytical, Almelo, Netherlands). Scanning electron microscopy (Model JSM6380-LV) was used to observe the microstructures of the natural surfaces of the ceramics. The bulk density was measured using Archimedes' method.

The microwave dielectric properties of $LiSmTa_4O_{12}$ ceramics were tested using the TE01δ method via a network analyser (E5071C, Agilent Co., CA, USA, 10 MHz to 20 GHz). The τ_f values were calculated using Equation (1):

$$\tau_f = \frac{f_T - f_{T_0}}{f_{T_0}(T - T_0)} \quad (1)$$

where f_T and f_{T_0} are the resonant frequencies at 85 and 25 °C, respectively.

3. Results and discussion

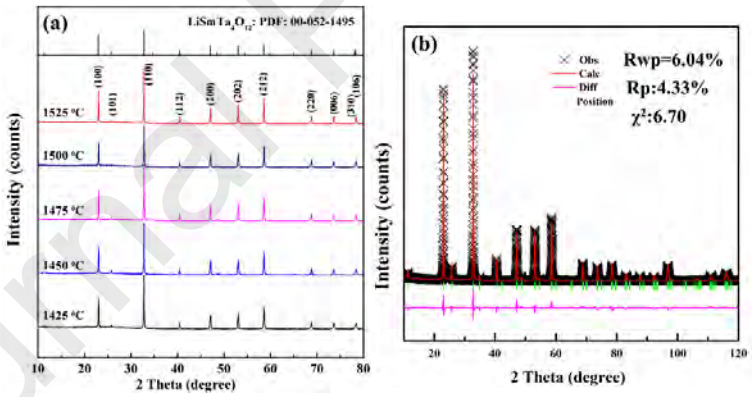

FIG. 1 (a) XRD patterns of $LiSmTa_4O_{12}$ ceramics sintered at different temperatures; (b) Rietveld refinement of XRD data for $LiSmTa_4O_{12}$.

Room-temperature XRD patterns of $LiSmTa_4O_{12}$ ceramics sintered at different temperatures are illustrated in FIG. 1(a). The XRD results of $LiSmTa_4O_{12}$ ceramics have no significant change with rising temperature from 1425 ℃ to 1525 ℃, indicating that the ceramics exhibited the stable phase structure. All peaks found in the XRD

patterns can be indexed as standard diffraction lines of $LiSmTa_4O_{12}$ (PDF code: 052-1495) with tetragonal perovskite structure. The phase structural refinement was performed by using the GSAS program and the results are illustrated in Figure 1(b). Using $La_{0.33}TaO_3$ phase (ICSD Code: 020281) as the reference structure of refinement, an available result is obtained (Rwp=6.04). The low value of Rwp indicating that $LiSmTa_4O_{12}$ and $La_{0.33}TaO_3$ have similar crystal structure, also the fitting results are satisfactory. The lattice parameters of the $LiSmTa_4O_{12}$ are a= 3.852255(15)Å, b=3.852255(15)Å, c= 7.72766(8), and V= 114.6775(14).

FIG. 2 shows the natural SEM pictures of the $LiSmTa_4O_{12}$ ceramics sintered at different temperatures. It can be observed that $LiSmTa_4O_{12}$ ceramic sintered at 1425 ℃ existed many pores because of incomplete growth of grains. Increasing the sintering temperature, the porosity of ceramic was reduced and average grain size was increased from 2.44 μm to 5.79 μm, as exhibited in the inset of FIG. 2. The ceramic exhibited dense microstructure with distinct grain boundaries at 1500 °C. However, with further increasing the sintering temperature to 1525 °C, the stomata reappear due to high temperature which makes the ceramic difficult to discharge the gas, as FIG. 2 (d) shown.

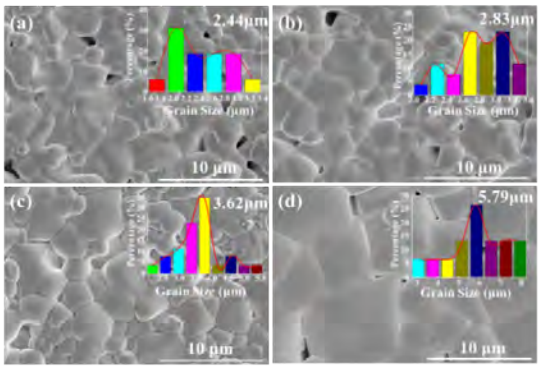

FIG. 2 Scanning electron microscope images of the $LiSmTa_4O_{12}$ ceramics sintered at different temperatures: (a) at 1450, (b) at 1475, (c) at 1500, (d) at 1525.

The permittivity, relative density and bulk density of $LiSmTa_4O_{12}$ ceramics have similar changes with increasing temperature, as shown in FIG. 3. As the sintering temperature of $LiSmTa_4O_{12}$ ceramic was 1500 °C, the bulk density and relative density reach to the maximum values of 7.56 g/cm^3 and 97.4 %, respectively. At the same time, the relative permittivity reached the maximum value of 59.6. Combined with the results of SEM analysis, the densest crystal structure of $LiSmTa_4O_{12}$ ceramic at 1500 °C results in the highest bulk density. It is generally known that relative permittivity mainly depends on the ionic polarizability grain size, density, and phase composition etc [7-9].

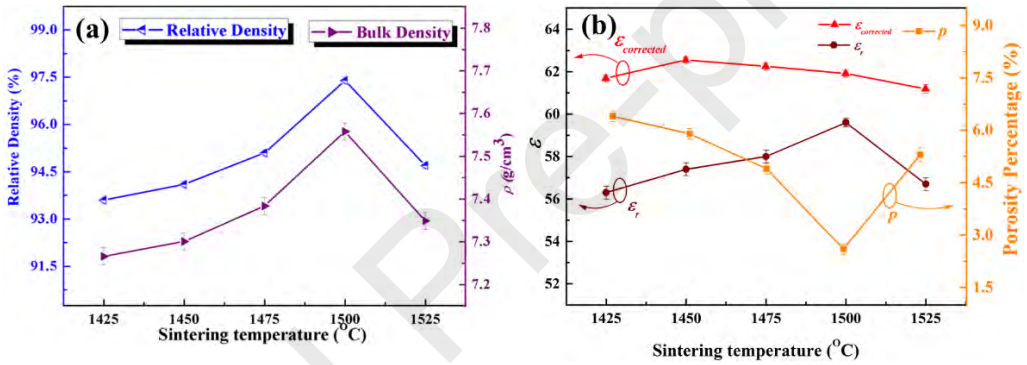

FIG. 3 (a) bulk and relative density, (b) measured and corrected relative permittivity of $LiSmTa_4O_{12}$ ceramics sintered at different temperatures.

To remove the influence of the porosity on the relative permittivity of ceramics, the Bosman and Havinga's correction equation was applied [10,11].

$$\varepsilon_{co} = \varepsilon_m (1 + 1.5p) \quad .(2),$$

$$p = 1 - d. \quad (3),$$

where, ε_{co}, ε_m, p, and d, are the corrected values of relative permittivity, measured values of relative permittivity, porosity percentage, and relative density respectively. The porosity percentage reached the minimum at 1500 °C for 2.6 %. The ε_{co} values of

$LiSmTa_4O_{12}$ ceramic higher than the measured, and more stable along with change of sintering temperature as shown in FIG. 3(b). This result means that the change of porosity is supposed to be the most critical factor for the variation of permittivity of ceramics.

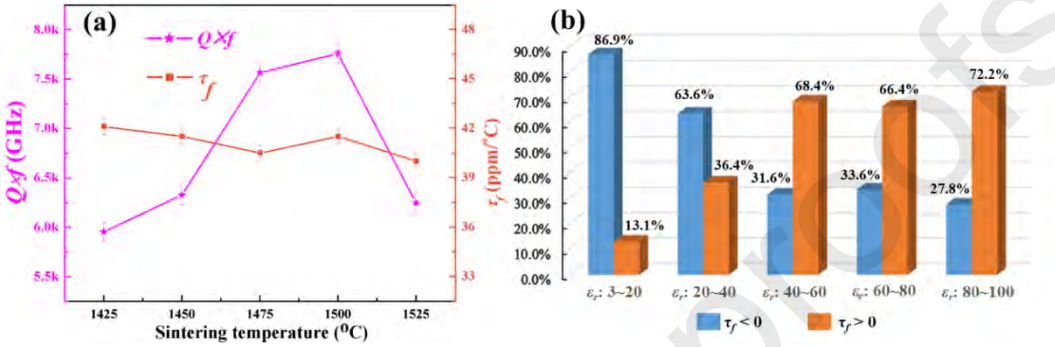

FIG. 4 (a) $Q\times f$ and τ_f values of $LiSmTa_4O_{12}$ ceramics sintered at different temperatures, (b) the relationship between the ε_r and τ_f for the different material systems.

FIG. 4(a) demonstrates the trend of $Q\times f$ and τ_f values for $LiSmTa_4O_{12}$ ceramics sintered at various temperatures. Usually, lattice phonon energy, vibrations in crystal, porosity, morphology and secondary phases will affect the $Q\times f$ values of microwave ceramics [12,13]. At the best densified temperature of 1500 °C, the $LiSmTa_4O_{12}$ ceramic exhibited a maximum $Q\times f$ value of 7,760 GHz at a low frequency of 5.065 GHz. When the dielectric resonator operates in TE_{01} mode, the resonant frequency f_0 was according with the equation:

$$f_0 = \frac{c}{l\sqrt{\varepsilon}} \qquad .(3),$$

where c and l are the light speed and dimensions of resonators. Hence, under the condition of constant test and use environment, high relative permittivity systems will tend to be a low f_0 and $Q\times f$ value.

It's well known that the contribution of porous rate to τ_f values of ceramics is very tiny [14]. Hence, τ_f values of $LiSmTa_4O_{12}$ ceramics maintain a stable value between +40.0 ppm/°C and +42.1 ppm/°C with changing the sintering temperature because of the invariant phase composition. FIG. 4(b) shows the relationship between the permittivity and temperature coefficient of frequency for the different material systems. Microwave dielectric ceramic systems with high relative permittivity are more likely to have positive than low relative permittivity. Roberts [15] summarized that the τ_f of the samples will be increased by diluting the polarization concentration of ions. The ionic polarization is the key factor to determine relative permittivity of ceramic system. Unfortunately, no literature can clearly indicate that how relative permittivity of microwave dielectric ceramics influence the temperature coefficient of resonance frequency.

4. Conclusion

The microwave dielectric properties of A-site deficient perovskite $LiSmTa_4O_{12}$ ceramics have been investigated. The ceramics displayed a single tetragonal $LiSmTa_4O_{12}$ phase, and the best microwave dielectric properties of ε_r = 59.60, $Q \times f$ = 7,760 GHz, and τ_f = +40.0 ppm/°C appeared at 1500 °C. The advantage of high relative permittivity makes it suitable for small communication devices.

Acknowledgments

This work was supported by the Natural Science Foundation of China (Nos. 61761015 and 11664008).

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Highlights

1. $LiSmTa_4O_{12}$ ceramics displayed A-site deficient perovskite structure which is similar to $La_{1/3}TaO_3$.

2.$LiSmTa_4O_{12}$ ceramics exhibited a high relative permittivity and good microwave dielectric properties.

3.The high relative permittivity makes $LiSmTa_4O_{12}$ ceramics suitable for small communication devices.

Conflicts of interest

The authors declared that they have no conflicts of interest to this work.

Authors' contributions

Huanfu Zhou and Kangguo Wang conceived and designed the study. Kangguo Wang synthesized and prepared the samples. Huanfu Zhou and Kangguo Wang wrote the paper. Shixuan Li and Jiji Deng tested the samples for XRD, Xiaowen Luan tested the samples for microwave dielectric properties and Xianjie Zhou and Sang Hu tested the samples for SEM, Huanfu Zhou and Kangguo Wang reviewed and edited the manuscript. All authors read and approved the manuscript.

Conflicts of interest

There are no conflicts to declare.