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Letter

New temperature stable and low loss materials of $(Nd_{0.97}Mn_{0.045})_{1.02}Nb_{0.988}O_4$ ceramics by La^{3+} substitution

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A B S T R A C T

$(Nd_{0.97}Mn_{0.045})_{1.02}Nb_{0.988}O_4$ ceramics based on La^{3+} substitution were prepared via a conventional solid−state reaction method. The effects of La^{3+} substitution for Nd^{3+} on microwave dielectric properties of the $(Nd_{0.97}Mn_{0.045})_{1.02}Nb_{0.988}O_4$ ceramics were investigated. The X-ray patterns showed that the specimens presented single $NdNbO_4$ phase with the monoclinic fergusonite structure in the range of x = 0.0 −0.05, with a further increase of the amount of substitution ions, $LaNb_7O_{19}$ phase appeared in this system. For the main phase, the increase of dielectric constant could be attributed to the increase in the Nd-site bond ionicity. The Q × f value and τ_f value were correlated to lattice energy and bond energy, respectively. Moreover, at 1250 °C, the $((Nd_{0.97}Mn_{0.045})_{1-x}La_x)_{1.02}Nb_{0.988}O_4$ ceramics with x = 0.05 possessed excellent microwave dielectric properties: ε_r = 21.93, Q × f = 66 700 GHz and τ_f = −1.08 ppm/°C.

1. Introduction

Microwave dielectric materials play a key role in global society, which have a wide range of applications form terrestrial and satellite communication including software radio, GPS, and TV to environmental monitoring via satellites [1]. In order to meet the specifications of the current and future systems, improved microwave dielectric materials are required. The key properties required for the microwave devices are high relative permittivity (ε_r), high quality factor (Q) and near zero temperature coefficient of resonant frequency (τ_f) [2,3]. However, with only a limited number of useful dielectric ceramic materials to choose from, numerous works have focused on developing excellent microwave dielectric materials that are easily affordable for manufacture.

The monoclinic fergusonite structure of $NdNbO_4$ ceramics with ε_r of 19.6, Q × f of 33, 000 GHz and τ_f of −24 ppm/°C are firstly reported by *Kim* et al. [4]. Then many works have been done on the $NdNbO_4$ ceramics. For example, *Zhang* et al. [5]. reported that the microwave dielectric properties of $NdNbO_4$ doping with 2.0 wt.% CaF_2 sintered at 1225 °C for 4 h shows excellent microwave dielectric properties with ε_r ~20.1, Q × f ~75, 000 GHz and τ_f ~ −19.16 ppm/°C. Doping with 0.6 wt.% $CaTiO_3$ the a high Q × f value can be obtained for the $NdNbO_4$ ceramics sintered at 1275 °C for 4 h [6]. Recently, the effects of Mn^{2+} substitution on the microwave dielectric properties of $(Nd_{1-x}Mn_{1.5x})_{1.02}Nb_{0.988}O_4$ ceramics are investigated, with x = 0.03 Mn^{2+} addition the maximum Q × f values 80 000 GHz of $NdNbO_4$ ceramics can be obtained [7], and it possesses a big τ_f value of −22.5 ppm/°C. The effects of Ta^{5+} and Sb^{5+} ions substitution for the $NdNbO_4$ ceramics are also investigated, both of them have a big τ_f value of −45.6 and −23.1 ppm/°C [8,9]. The methods to achieve temperature stable microwave dielectric materials are combining two component materials with opposite τ_f values or ions substitution, the first method usually can destroy the microwave dielectric properties of the ceramics [6]. *Kim* et al. [4] also have reported that $LaNbO_4$ possesses ε_r of 19.3, Q × f of 54 400 GHz and τ_f of 9 ppm/°C sintered at 1250 °C. In addition, since $LaNbO_4$ and $NdNbO_4$ ceramics both have the same monoclinic fergusonite structure, a high Q × f value and near zero τ_f value of $(Nd_{1-x}Mn_{1.5x})_{1.02}Nb_{0.988}O_4$ ceramics could be obtained by carefully adjusting the substitution of La^{3+} content.

Therefore, in this paper, the $(Nd_{1-x}Mn_{1.5x})_{1.02}Nb_{0.988}O_4$ ($0 \le x \le 0.07$) ceramics at x = 0.05 with excellent microwave properties (ε ~ 21.93, Qf ~ 63 400 GHz, τ_f ~ −1.08 ppm/°C) were synthesized. The bond ionicity, lattice energy and bond energy were calculated. Moreover, an available method based on the Rietveld refinement of X-ray techniques was used to analyze the structure of the crystalline phases.

2. Experimental procedure

$((Nd_{0.97}Mn_{0.045})_{1-x}La_x)_{1.02}Nb_{0.988}O_4$ microwave dielectric ceramics were prepared by a conventional solid−state reaction from oxide powders (Nd_2O_3 (99%), $MnCO_3$(99.99%), La_2O_3(99.99%) and Nb_2O_5(99.99%)) method. The raw materials were mixed according to the formula of $((Nd_{0.97}Mn_{0.045})_{1-x}La_x)_{1.02}Nb_{0.988}O_4$ (x = 0.0, 0.01, 0.02, 0.03, 0.05, 0.07) based on the results of our previous study [7], we got single phase $NdNbO_4$ according to stoichiometry of $Nd_{1+y}Nb_{1-0.6y}O_4$ (the ions of Nd and Nb as oxides are

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positive 3 and 5 values, respectively.) at y = 0.02 based on the balance of the chemical valence. Therefore, in this paper we chose the stoichiometry of $((Nd_{0.97}Mn_{0.045})_{1-x}La_x)_{1.02}Nb_{0.988}O_4$. Then the mixed powders were milled for 6 h with distilled water in a nylon container with ZrO_2 balls. All the slurries were dried and pre-sintered at 900 °C for 4 h. The pre-sintered powders were re-milled for 6 h. After drying and sieving, the powders were pressed into pellets with 10 mm diameter and 5 mm thickness. Then these pellets were sintered at temperatures of 1225–1275 °C for 4 h.

The crystalline phases of the sintered samples were identified by X-ray diffraction (XRD, Rigaku D/max 2550 PC, Tokyo, Japan) with Cu Kα radiation generated at 40 kV and 40 mA. The microstructure of the ceramic surfaces were performed and analyzed by a scanning electron microscopy (SEM, MERLIN Compact, Germany). The microwave dielectric properties were measured in the frequency range of 8–12 GHz using a HP8720ES network analyzer. The temperature coefficients of resonant frequency (τ_f) were measured in the temperature range from 25 °C to 85 °C. The τ_f (ppm/°C) was calculated by noting the change in resonant frequency (Δf)

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 is resonant frequency at T_1 and f_2 is the resonant frequency at T_2.

The apparent densities of the sintered pellets were measured use the Archimedes method (Mettler ToledoXS64). To study the relative density of the sample, the theoretical density was obtained from the crystal structure and atomic weight by the Eq. (2) [10]:

$$\rho\text{theory} = \frac{ZA}{V_C N_A} \quad (2)$$

where V_C, N_A, Z, and A are volume of unit cell (cm^3), avogadro number (mol^{-1}), number of atoms in unit cell, and atomic weight (g/mol), respectively. The relative density was obtained by the Eq. (3):

$$\rho relative = \frac{\rho bulk}{\rho theory} \times 100\% \quad (3)$$

3. Results and discussion

The X-ray diffraction patterns of $((Nd_{0.97}Mn_{0.045})_{1-x}La_x)_{1.02}Nb_{0.988}O_4$ ($0 \le x \le 0.07$) ceramics sintered at 1250 °C for 4 h are given in Fig. 1. Single phase $NdNbO_4$ (PDF #32-0680) without any secondary phase was obtained in the range of x = 0–0.05, $NdNbO_4$ performed monoclinic fergusonite structure and belonged to the space group I2/a (no. 15) and Z = 4. The lattice parameters from Rietveld refinement are calculated as a = 5.148 Å, b = 11.265 Å, and c = 5.459 Å. With the substitution content increased, the $LaNb_7O_{19}$ peaks (indexed as $LaNb_5O_{14}$, PDF #48-0595) can be detected when x = 0.07. The lattice parameters of $LaNb_7O_{19}$ phase are $a = b$ = 6.2531 Å, c = 20.0685 Å and Z = 2 [11]. The formation of $LaNb_7O_{19}$ could be attributed to the reaction of the Nb^{5+} with the excess La^{3+}. The crystallographic data from Rietveld refinement showed in Table 1, and with increasing of La^{3+} substitution, the unit cell volume increased. This could be due to the bigger ionic radius of La^{3+} (1.16 Å, CN = 8) than Nd^{3+}(1.109 Å,CN = 8).

Fig. 2 shows the SEM photographs of $((Nd_{0.97}Mn_{0.045})_{1-x}La_x)_{1.02}Nb_{0.988}O_4$ ($0 \le x \le 0.07$) ceramics sintered at 1250 °C for 4 h. As shown in Fig. 2a–e, the grains are homogeneous and the surface is smooth. Moreover, the grain sizes have insignificant change, all in the range of 4–6 μm. It demonstrated that La^{3+} substitution have no obvious change for SEM patterns of the $(Nd_{0.97}Mn_{0.045})_{1.02}Nb_{0.988}O_4$ ceramics. However, when x = 0.07, abnormal grain is found, as shown in Fig. 2f.

The relative density and dielectric constant of $((Nd_{0.97}Mn_{0.045})_{1-x}La_x)_{1.02}Nb_{0.988}O_4$ ($0 \le x \le 0.07$) ceramics are presented in Fig. 3. The dielectric constant is dependent on the relative density, dielectric polarizabilities and structural characteristics such as the distortion, tilting and rattling spaces of oxygen octahedron in the unit cell [12,13]. In our experiments, ε_r has no direct relationship with the relative density, which is because that the relative densities of all the specimens are higher than 94%. Therefore the ε_r is dependent on the dielectric polarizabilities and structural characteristics. *Batsanov* et al. [14] have reported that the dielectric constant has the close relationship with the bond ionicity. Their relationship could be described as follows:

$$\varepsilon_r = \frac{n^2 - 1}{1 - f_i} + 1 \quad (4)$$

where n was the refractive index. It indicates that the dielectric constant decreased with the bond ionicity decreasing. The bond ionicity can be calculated using the generalized P–V-L dielectric theory as follows [15]:

$$f_i^{\mu} = \frac{(C^{\mu})^2}{\left(E_g^{\mu}\right)^2} \quad (5)$$

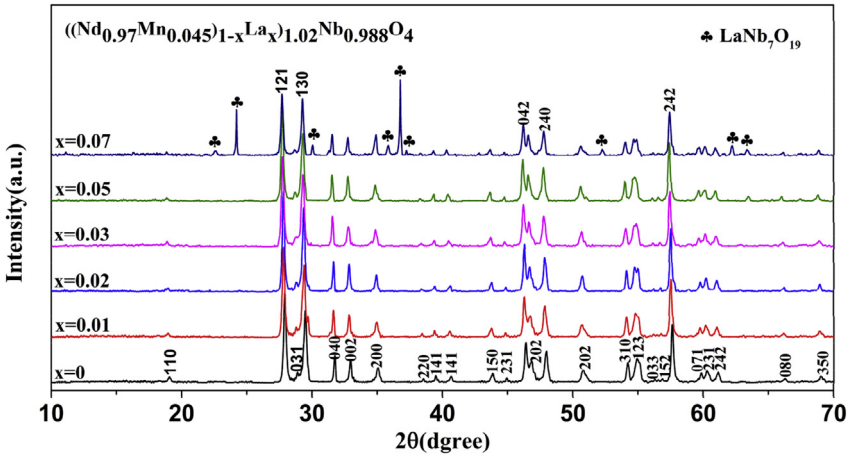

Fig. 1. The X-ray diffraction patterns of $((Nd_{0.97}Mn_{0.045})_{1-x}La_x)_{1.02}Nb_{0.988}O_4$ ($0 \le x \le 0.07$) ceramics sintered at 1250 °C for 4 h.