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High dielectric constant low loss microwave dielectric ceramics in the $Ca_5Nb_{2-x}Ta_xTiO_{12}$ system

P.V. Bijumon [a], P. Mohanan [b], M.T. Sebastian [a,*]

[a]Ceramics Division, Regional Research Laboratory, Trivandrum 695 019, India
[b]Department of Electronics, Cochin University of Science and Technology, Kochi 682 022, India

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Abstract

High dielectric constant and low loss ceramics in the system $Ca_5Nb_{2-x}Ta_xTiO_{12}$ $(0 \le x \le 2)$ have been prepared by conventional solid-state ceramic route. The structure was studied by X-ray diffraction and microstructure by SEM techniques. The materials were characterized at microwave frequencies. They show a linear variation of dielectric properties with the value of x. Their dielectric constant varies from 48 to 38, quality factor $Q_u \times f$ from 26 000 to 33 000 GHz and temperature variation of resonant frequency from +40 to +10 ppm/°C as the value of x increases. The microwave dielectric properties of these materials indicate that these low loss ceramics can be used for dielectric resonator (DR) applications.

Keywords: Dielectric materials; Dielectric resonators; Microwave ceramics; Complex perovskites; Microwave resonators

1. Introduction

The recent advances in the telecommunication systems have led to an increasing attention on microwave ceramic dielectric resonators [1]. Dielectric resonators (DRs) are extensively used in microwave devices like filters, oscillators and Dielectric Resonator Antennas. To meet the requirements for use in such wide applications, the materials should possess stringent properties like (a) high dielectric constant (ε_r) for miniaturization, (b) high unloaded quality factor (Q_u) or low dielectric loss for better selectivity and (c) low temperature coefficient of resonant frequency (τ_f) for frequency stability. Although several materials have been reported [2–4] for practical applications, active research is still going on for new ceramics due to the great demand for a variety of materials with varying dielectric constants. Recently, Cava et al. [5] studied the low-frequency (1 MHz) dielectric properties of $Ca_5Nb_2TiO_{12}$ and $Ca_5Ta_2TiO_{12}$ and suggested that these materials will be useful as DRs. More recently, Bijumon et al. [6] investigated the microwave dielectric properties of these compounds. In the present study, we report the effect of synthesizing conditions and microwave dielectric properties of $Ca_5Nb_{2-x}Ta_xTiO_{12}$ $(0 \le x \le 2)$ ceramics.

2. Experimental

The ceramic resonators in the system $Ca_5Nb_{2-x}Ta_xTiO_{12}$ were prepared by the conventional solid-

* Corresponding author. Tel.: +91-471-515294; fax: +91-471-491712.
E-mail address: mailadils@yahoo.com (M.T. Sebastian).

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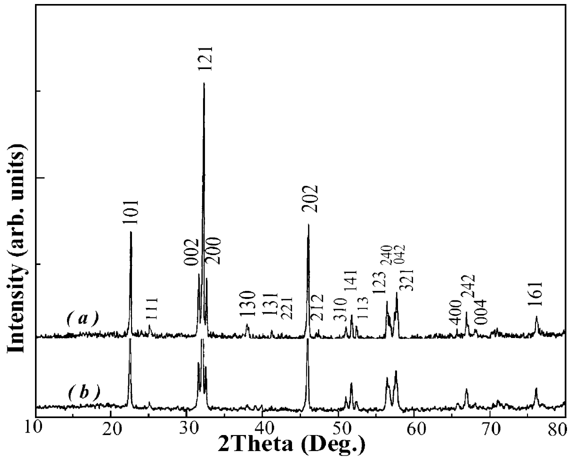

Fig. 1. X-ray diffraction patterns of (a) $Ca_5Nb_2TiO_{12}$ and (b) $Ca_5Ta_2TiO_{12}$ ceramics.

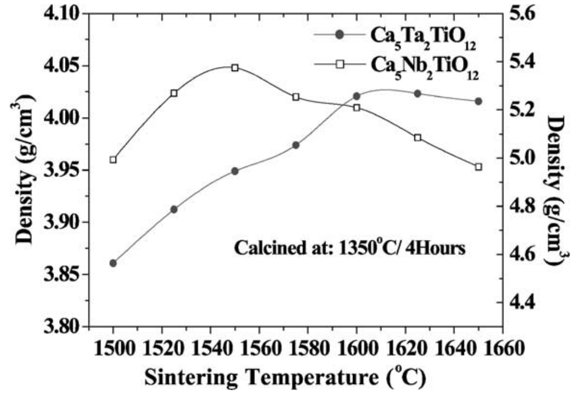

Fig. 3. Variation of density of $Ca_5Nb_2TiO_{12}$ and $Ca_5Ta_2TiO_{12}$ ceramics with sintering temperature.

state ceramic route. High purity (>99%) $CaCO_3$, TiO_2 (Aldrich) and Ta_2O_5, Nb_2O_5 (NFC, India) were used as the starting materials. Stoichiometric amounts of the powders were weighed and ball milled using zirconia balls in plastic containers. $Ca_5Nb_{2-x}Ta_xTiO_{12}$ ($0 \le x \le 2$) was calcined in the range 1200–1400 °C for 4 h. The calcined powders were ground well and mixed with 5 wt.% solution of PVA as the binder. The powders were then uniaxially pressed into cylindrical disks with 14 mm diameter and 7 mm height under a pressure of 250 MPa. The samples were fired at 600 °C for 1 h to remove the organic binder and then sintered in the range 1500–1650 °C for different durations. The sintered samples were well polished and their bulk density was calculated by Archimedes method. The crystal structure and phase purity of the samples were studied by X-ray diffraction techniques. The surface morphology of the samples was examined by SEM.

The microwave dielectric properties such as dielectric constant and unloaded quality factor were measured by using an HP8510C Vector Network Analyzer attached with a sweep oscillator and reflection transmission test unit. The quality factor was measured by cavity method [7]. For the present samples, resonance occurred between 3 and 5 GHz. The dielectric constant was calculated by using TE_{011} resonant mode of the samples keeping it under the end-shorted position by Hakki and Coleman [8] method and later modified by Courtney [9]. The temperature coefficient of res-

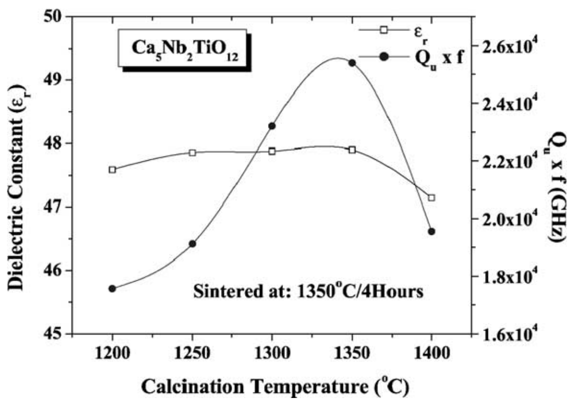

Fig. 2. Variation of dielectric properties of $Ca_5Nb_2TiO_{12}$ ceramics with calcination temperature.

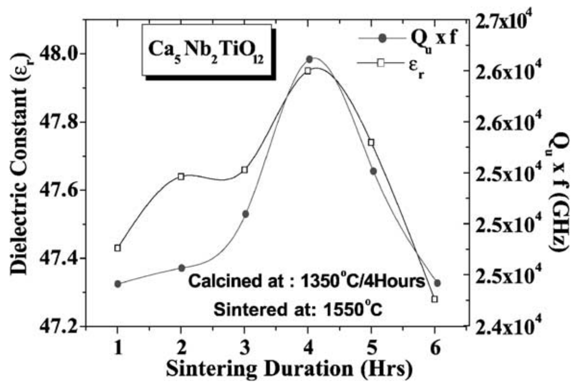

Fig. 4. Variation of dielectric properties of $Ca_5Nb_2TiO_{12}$ ceramics with sintering duration.

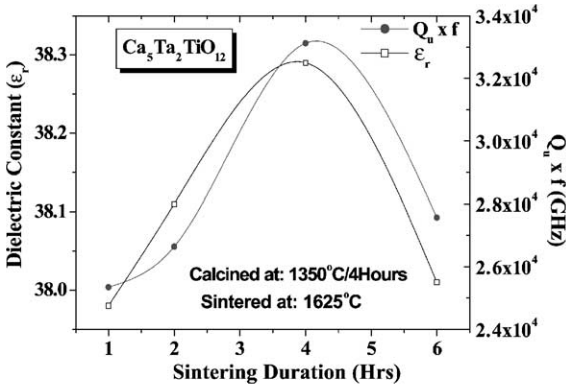

Fig. 5. Variation of dielectric properties of $Ca_5Ta_2TiO_{12}$ ceramics with sintering duration.

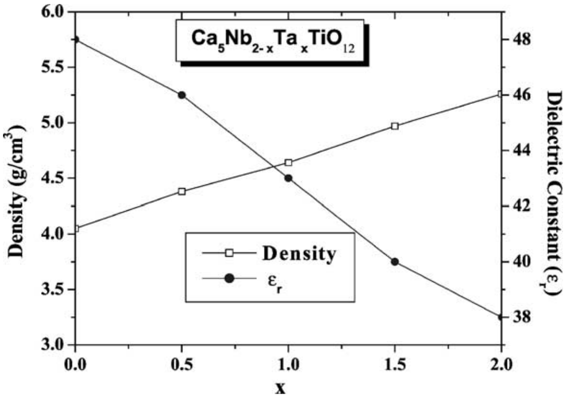

Fig. 7. Variation of density and ε_r of $Ca_5Nb_{2-x}Ta_xTiO_{12}$ ceramics with *x*.

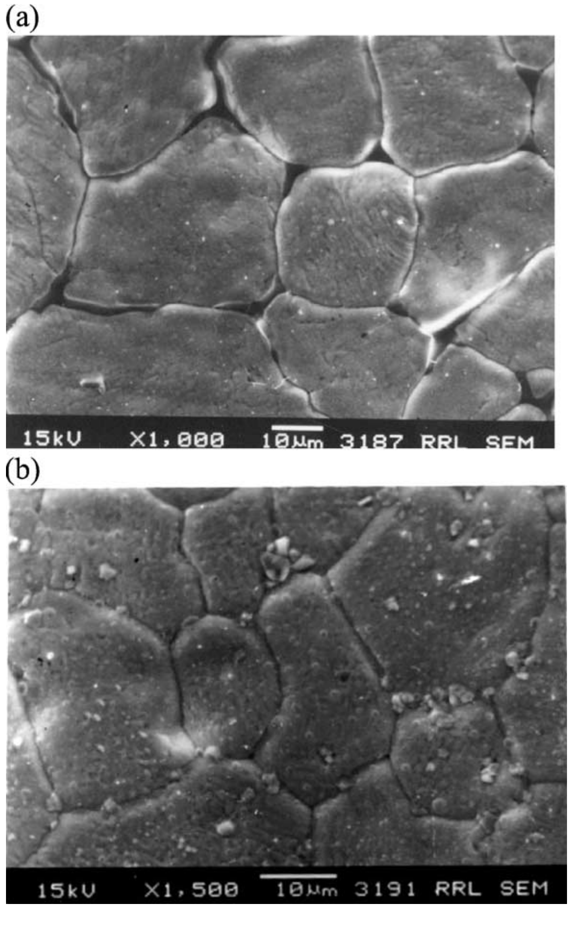

Fig. 6. Typical SEM photographs of (a) $Ca_5Nb_2TiO_{12}$ and (b) $Ca_5Ta_2TiO_{12}$ microwave ceramics.

onant frequency was measured by noting the variation of TE_{011} resonance mode in the temperature range 25–70 °C.

3. Results and discussion

The system $Ca_5A_2TiO_{12}$ (A = Nb, Ta) belongs to the complex perovskite family and can be conveniently written as $Ca(Ca_{1/4}A_{1/2}Ti_{1/4})O_3$. Here the perovskite A-site is occupied by the large atom Ca and Ca, Ti and Nb/Ta occupy B site with 1:2:1 ordering. The X-ray diffraction pattern for both the materials look similar with a slight shift in the position of peaks (Fig. 1). The unit cell has orthorhombic symmetry [10,11]. The microwave dielectric properties of the system strongly

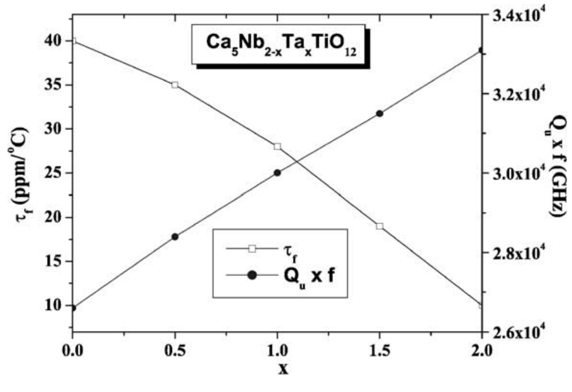

Fig. 8. Variation of τ_f and $Q_u \times f$ of $Ca_5Nb_{2-x}Ta_xTiO_{12}$ ceramics with *x*.

Table 1
Density and microwave dielectric properties of $Ca_5Nb_{2-x}Ta_xTiO_{12}$ ceramics

x	Material	Sintering temperature (°C)	Bulk density (g/cm^3)	Dielectric constant ε_r	$Q_u \times f$ (GHz)	τ_f (ppm/°C)
0.0	$Ca_5Nb_2TiO_{12}$	1550	4.05	48	26 600	+40
0.5	$Ca_5Nb_{1.5}Ta_{0.5}TiO_{12}$	1560	4.38	46	28 400	+35
1.0	$Ca_5NbTaTiO_{12}$	1580	4.64	43	30 000	+28
1.5	$Ca_5Nb_{0.5}Ta_{1.5}TiO_{12}$	1600	4.97	40	31 500	+19
2.0	$Ca_5Ta_2TiO_{12}$	1575	5.26	38	33 100	+10

depend on the synthesizing conditions. We optimized the calcination temperature, sintering temperature and their durations for $Ca_5Nb_2TiO_{12}$ and $Ca_5Ta_2TiO_{12}$ materials. The best density and dielectric properties of $Ca_5Nb_2TiO_{12}$ ceramics are at a calcination temperature of 1350 °C/4 h and sintering temperature of 1550 °C/4 h. In the case of $Ca_5Ta_2TiO_{12}$ ceramics, the calcination temperature is the same as that of the niobates but the sintering temperature is 1625 °C/4 h. The dependence of density and dielectric properties on the synthesizing conditions are depicted in Figs. 2–5. Both these materials were sintered to more than 96% of their theoretical density. The sintered samples were thermally etched and the microstructures examined under SEM. No secondary phases can be observed (Fig. 6). The grains are of relatively large size up to 20 μm.

Under optimum preparation conditions, $Ca_5Nb_2TiO_{12}$ has an ε_r of 48, $Q_u \times f$>26 000 GHz and τ_f= +40 ppm/°C and $Ca_5Ta_2TiO_{12}$ has ε_r=38, $Q_u \times f$>33 000 GHz and τ_f=+10 ppm/°C. The $Ca_5Nb_{2-x}Ta_xTiO_{12}$ $[0 \le x \le 2]$ shows intermediate dielectric properties between the end members $Ca_5Nb_2TiO_{12}$ and $Ca_5Ta_2TiO_{12}$. Since the ionic radii [12] and charge are the same for both Nb and Ta ions, the $Ca_5Nb_{2-x}Ta_xTiO_{12}$ forms a complete solid solution for all values of x with the properties changing linearly with x. Hence, the crystal symmetry was similar for all compositions with the orthorhombic structure like that of $Ca_5Nb_2TiO_{12}$ and $Ca_5Ta_2TiO_{12}$. Density and microwave dielectric properties are varying linearly between the title compounds for x=0 to x=2. Density increased with the amount of tantalum and can be attributed to the high molecular weight of Ta compared with Nb. Dielectric constant and τ_f was decreasing as x increases and the unloaded quality factor was increasing with the value of x (see Figs. 7 and 8). This variation can be attributed to the change in ionic polarizability and cell volume. The density and microwave dielectric properties of $Ca_5Nb_{2-x}Ta_xTiO_{12}$ ceramics for different values of x are given in Table 1.

4. Conclusion

The $Ca_5Nb_{2-x}Ta_xTiO_{12}$ $(0 \le x \le 2)$ has been prepared as single-phase materials by the conventional solid-state ceramic route. The effect of synthesizing conditions on the microwave dielectric properties has been studied. Under optimum preparation conditions, $Ca_5Nb_2TiO_{12}$ has ε_r=48, $Q_u \times f$>26 000 GHz and τ_f=+40 ppm/°C. The $Ca_5Ta_2TiO_{12}$ has ε_r=38, $Q_u \times f$>33 000 GHz and τ_f=+10 ppm/°C. In the $Ca_5Nb_{2-x}Ta_xTiO_{12}$ $[0 \le x \le 2]$ system, the density and dielectric properties shows a linear variation between that of the end members for all compositions.

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