Journal of the European Ceramic Society 21 (2001) 1719–1722

www.elsevier.com/locate/jeurceramsoc

# Microwave dielectric properties of $Li_{1+x-y}M_{1-x-3y}Ti_{x+4y}O_3$ ($M = Nb^{5+}$, $Ta^{5+}$) solid solutions

Albina Borisevich *, Peter K. Davies

*Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA, USA*

Received 4 September 2000; received in revised form 23 October 2000; accepted 1 November 2000

**Abstract**

A series of new low sintering temperature microwave resonator ceramics were investigated in the $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ solid solution system. Ceramics with high relative permittivities (78–55), $Q \times f$ values up to 9000 (6 GHz), and zero temperature coefficients in the microwave region could be obtained via sintering at 1100°C. Similar phases were identified in the $Li_2O$–$Ta_2O_5$–$TiO_2$ system and their stability region at 1100°C was determined. The microwave dielectric properties of the tantalates were similar to those of their Nb counterparts. The addition of $\geqslant$ 2 mol% $V_2O_5$ to the Nb solid solutions was effective in producing a large reduction in the sintering $T$ and dense ceramics could be prepared at $T \leqslant 900$°C. The addition of V did not induce any significant degradation of the microwave properties and their apparent compatibility with Ag powder may indicate potential applications as co-fired circuit components. 

*Keywords:* Dielectric properties; Microwave dielectrics; Niobates; Sintering; Tantalates

## 1. Introduction

The rapid growth of the wireless communication industry has created a high demand for microwave ceramic components. In addition to the materials requirements of high dielectric constant, low dielectric loss, and a zero temperature coefficient of resonant frequency, low cost — of individual components and processing/sintering — is a critical requirement for commercial application. Because contemporary commercial resonator materials have processing temperatures of 1300° C and higher,[1] there is considerable interest in the development of new materials with low sintering temperatures. One favoured approach has involved investigations of the effect of eutectic or glass-forming additives on the properties of established microwave materials. Another approach involves studies of new systems with lower melting points. This research exploits the latter method and focuses on the so-called "*M*-phase" solid solutions, $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$, that can be formed in the $Li_2O$–$Nb_2O_5$–$TiO_2$ system at 1100°C. These solid solutions were first described by Villafuerte-Castrejon et al. in 1987,[2] however, there have been no reports on their dielectric properties.

To modify the properties of the "*M*-phase" niobate we also explored several routes of chemical substitution. One involved complete substitution of Nb for Ta, and the formation of analogous solid solution in the $Li_2O$–$Ta_2O_5$–$TiO_2$ system. The second approach utilised low melting point additives such as $V_2O_5$ in an attempt to prepare ceramics with sintering temperatures close to 900°C that could have potential applications as co-fired circuit components.

## 2. Experimental

The samples were synthesised from dried $Li_2CO_3$ (Baker, 99.0%), $Nb_2O_5$ (Cerac, 99.95%), $Ta_2O_5$ (Cerac, 99.99%), $TiO_2$ (Cerac, 99.9%), and $V_2O_5$ (Baker, 99.6%) powders. After mixing under acetone, the powders were pre-annealed at 700°C to drive off $CO_2$, then reground and annealed in Pt crucibles at 1100°C for 10 h with subsequent ball-milling in ethanol with YTZ® zirconia balls. The annealing and ball-milling was

* Corresponding author. Tel.: +1-215-898-7968; fax: +1-215-573-2128.

*E-mail address:* albinab@seas.upenn.edu (A. Borisevich).

0955-2219/01/$ - see front matter 
PII: S0955-2219(01)00101-7

repeated until the XRD patterns of the resultant powders were free of impurity peaks (2–7 times depending on the composition). Pellets were formed from isostatically pressed powders by sintering at 1100°C for 1 h in closed Pt envelopes to prevent the loss of Li. For the $V_2O_5$-containing samples lower annealing and sintering temperatures were used, 850–925°C depending on the additive content.

XRD patterns were collected on Rigaku DMaxB diffractometer using Cu$K_\alpha$ radiation generated at 45 kV and 30 mA. The relative permittivity, $\varepsilon_r$, and dielectric loss tangent, tan $\delta$, were measured in the 100 Hz to 1 MHz frequency range and from −100 to 200°C by the parallel-plate method using a Delta 9920 environmental chamber and an HP 4284A precision LCR meter. Microwave measurements were performed via the cavity reflection method using an HP 8719C network analyser.

## 3. Results and discussion

### 3.1. Nb "M-phase"

The "*M*-phase" solid solutions with $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ were prepared according to the formalism described in reference,[3] where $y$ is the direction of site-balanced substitution ($Li^+ + 3\ Nb^{5+} \leftrightarrow 4\ Ti^{4+}$), and $x$ the direction of site-imbalanced substitution ($Nb^{5+} \leftrightarrow Li^+ + Ti^{4+}$). The observed phase stability region was in close agreement with[3] with the exception of some compositions close to the $Li_2TiO_3$ side of $LiNbO_3$–$Li_2TiO_3$ join. The observed diffraction patterns were in good agreement with those reported previously in.[2–4]

The temperature dependence of the dielectric permittivity was registered for frequencies 100 Hz to 1 MHz between −100 and 200°C. The values of the relative permittivity at 1 MHz were quite high, ranging from 84 to 61. The contour map in Fig. 1 illustrates that the dielectric constant exhibits a well-defined compositional trend and generally decreases in the $y$ direction. To analyse this variation polarizability was calculated using the Clausius–Mossotti equation $\alpha_D = (3/4\pi)V_m(\varepsilon_r - 1)/(\varepsilon_r + 2)$, where $V_m$ is the molar volume ($V_m = V_{unitcell}/Z$). The compositional dependence of the polarizability is almost linear (Fig. 2) suggesting that it can be described within a homogeneous model proposed by Shannon.[5] Thus systematic changes in dielectric properties are induced by variations in Li/Ti/Nb ratio within the phase field rather than by more complicated structural effects. This conjecture is reinforced by the behaviour of the temperature coefficient of the relative permittivity $\tau_\varepsilon$ (Fig. 3). The temperature coefficients exhibit high tunability, varying linearly with composition with extremes of 185 and −100 ppm/°C. The dielectric losses observed at 1 MHz were generally low ($\sim 10^{-4}$) and often beyond the precision of experiment and are thus not discussed.

Data on microwave dielectric properties was collected for selected single-phase samples from the "*M*-phase" solid solution field (Table 1). The permittivities are high (78–55) and in good agreement with those observed at 1 MHz. As expected from the 1 MHz data the temperature coefficient of resonant frequency $\tau_f$ also demonstrates

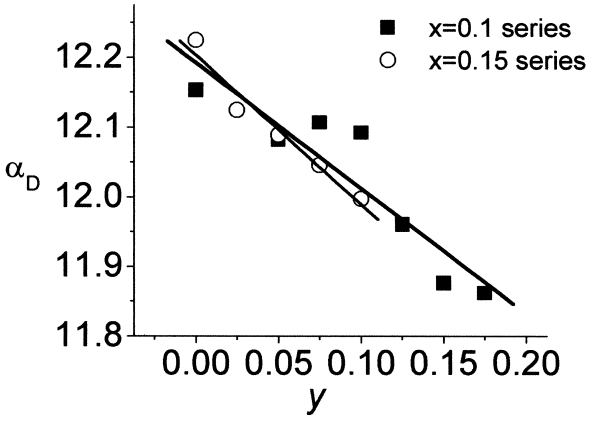


Fig. 2. Dielectric polarizability vs. composition for Nb "*M*-phase".

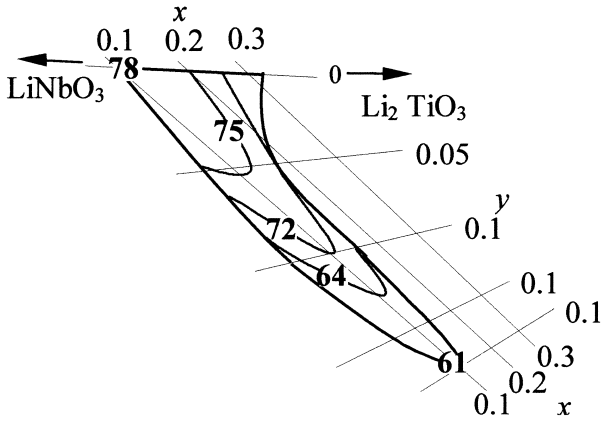


Fig. 1. Contour map of relative permittivity of Nb "*M*-phase" at 1 MHz and 25°C.

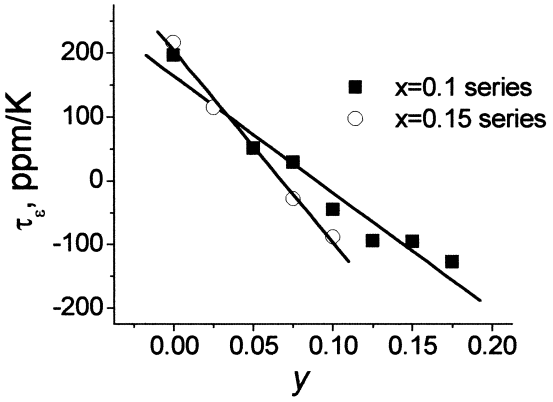


Fig. 3. Temperature coefficient of permittivity vs. composition for Nb "*M*-phase".

tunability. The $Q$ values, which are the reciprocal of the dielectric loss, reach values as high as 1700 at 6 GHz for $x=0.1$, $y=0.175$, and increase in $y$ direction again demonstrating uniform compositional tuning.

### 3.2. Ta "M-phase"

Similar solid solutions were discovered in the $Li_2O$–$Ta_2O_5$–$TiO_2$ system, though the region of stability was more limited than that for the niobates (Fig. 4). The XRD patterns of the tantalates were identical to their Nb counterparts with the same $x$ and $y$ values.

The dielectric properties of the Ta solid solutions at 1 MHz are comparable to the niobates; the relative permittivity decreases with the Ti content, while $\tau_\varepsilon$ remains negative for all compositions (Fig. 5). The microwave data (Table 2) is again consistent with the 1 MHz values and the Q values were similar to those obtained for the Nb compounds.

### 3.3. $V_2O_5$-doped "M-phase"

In an attempt to lower the sintering temperature to 900°C and below, samples of the Nb solid solutions were doped with small levels of $V_2O_5$. This additive was chosen because $Nb^{5+}$ and $V^{5+}$ are relatively similar in their chemistry and some degree of homogeneous substitution can be expected; in addition $V_2O_5$ itself has a low melting point (680°C).

Additions of just 2% of $V_2O_5$ were found to be effective in inducing very large reductions in the sintering conditions required to induce densification. At 900°C uniform microstructures with densities in the range of 92–96% of theoretical were produced. The dielectric properties of the V-substituted ceramics were very similar to those of the pure niobate solid solutions and for the 2% doped sample ceramics with $\varepsilon_r=66$, $Q\times f=3800$ (5.6 GHz) and a tunable $\tau_f$ could be prepared at $T_{sint}=900$°C (Fig. 6). Minor degradation of dielectric properties on V addition was observed: ~2% per 1% additive for permittivity and ~17% per 1% additive for dielectric loss. These values are very small for the case of liquid-phase doping, especially taking into account low doping levels (2%) necessary to achieve $T_{sint}=$ 900°C.

Preliminary investigations of the potential of these systems for co-fired circuit applications were made by examining the XRD patterns of $Ag/V_2O_5$-"$M$-phase" mixtures before and after sintering at 900°C. No third-phase peaks were observed after the thermal treatment suggesting that the doped material does not react with silver under the sintering conditions.

Table 1
Microwave dielectric properties of the selected Nb "$M$-phase" samples

| $x$ | $y$ | $f$, GHz | $\varepsilon_r$ (25°C) | $\tau_f$, ppm/K | Q | $Q\times f$ (GHz) |
|---|---|---|---|---|---|---|
| 0.15 | 0 | 5.321 | 76.21 | −62 | 187 | 997 |
| 0.05 | 0.05 | 5.206 | 77.76 | −42 | 419 | 2184 |
| 0.1 | 0.05 | 6.009 | 62.38 | −53 | 657 | 3949 |
| 0.1 | 0.075 | 5.917 | 64.04 | −15 | 779 | 4612 |
| 0.05 | 0.1 | 6.312 | 58.45 | −31 | 987 | 6233 |
| 0.1 | 0.1 | 5.660 | 64.79 | +8 | 1128 | 6385 |
| 0.1 | 0.125 | 6.052 | 59.16 | +22 | 1250 | 7565 |
| 0.1 | 0.15 | 6.029 | 56.19 | +15 | 1384 | 8345 |
| 0.1 | 0.175 | 6.153 | 54.88 | +28 | 1446 | 8896 |

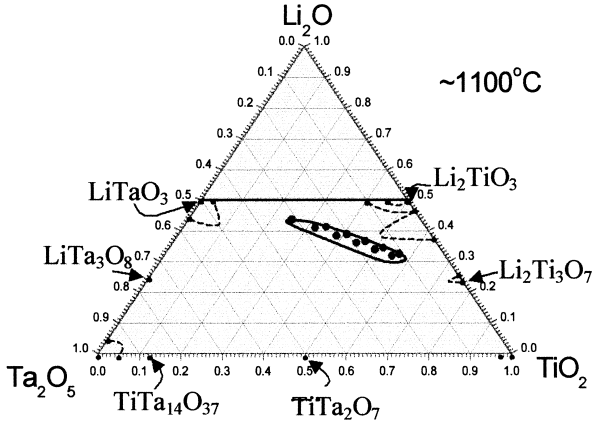


Fig. 4. Schematic phase diagram for the $Li_2O$–$TiO_2$–$Ta_2O_5$ system at 1100°C with the "$M$-phase" field highlighted.

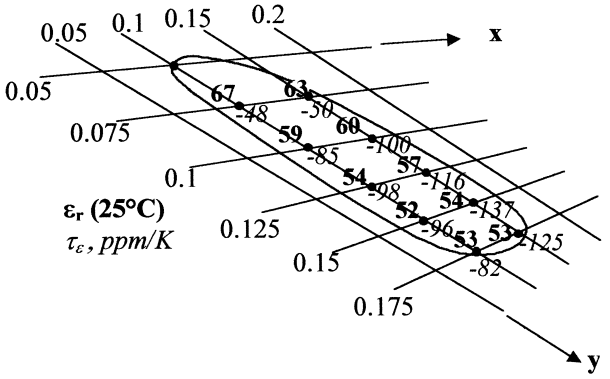


Fig. 5. Dielectric properties of Ta "$M$-phase" at 1 MHz for different compositions.

Table 2
Microwave dielectric properties of the selected Ta "$M$-phase" samples

| $x$ | $y$ | $f$, GHz | $\varepsilon_r$ | $\tau_f$, ppm/K | $Q$ | $Q\times f$(GHz) |
|---|---|---|---|---|---|---|
| 0.1 | 0.075 | 6.167 | 60.49 | −5 | 813 | 5014 |
| 0.15 | 0.075 | 6.141 | 62.12 | 13 | 1008 | 6190 |
| 0.1 | 0.1 | 6.203 | 58.97 | 26 | 1282 | 7721 |
| 0.15 | 0.1 | 6.349 | 59.65 | 42 | 1435 | 9111 |
| 0.1 | 0.15 | 6.419 | 54.78 | 34 | 1621 | 10,405 |
| 0.1 | 0.175 | 6.672 | 49.82 | 32 | 1578 | 10,528 |

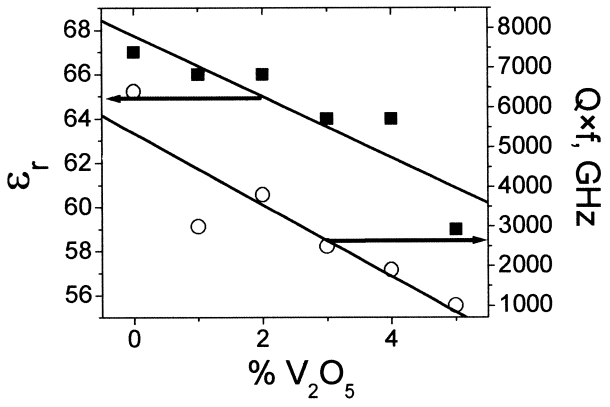


Fig. 6. Microwave dielectric properties of $V_2O_5$-doped Nb "*M*-phase" ceramics ($x=0.1$, $y=0.1$ sample) vs. amount of additive.

## 4. Conclusions

1. "*M*-phase" solid solutions in the $Li_2O$–$TiO_2$–$Nb_2O_5$ system have promising microwave dielectric properties: $\varepsilon_r$ 78–55, a tunable $\tau_f$, $Q\times f$ up to 9000 (6 GHz), and a sintering temperature close to 1100°C.
2. Similar phases identified in the $Li_2O$–$TiO_2$–$Ta_2O_5$ system have comparable microwave properties.
3. The addition of 2% of $V_2O_5$ to the niobate "*M*-phase" ceramics decreases their sintering temperature to $\leqslant$ 900°C and induce a small degradation in $Q$ ($\varepsilon_r=66$, $Q\times f=3800$ at 5.6 GHz; $\tau_f$ of 11). The low fire ceramics also exhibit compatibility with silver under sintering conditions suggesting possible applications as low temperature co-fired ceramics.

## Acknowledgements

We thank D. Lisjak and M. Valant (IJS, Ljubljana, Slovenia). This work was supported by National Science Foundation.

## References

1. Davies, P. K., Influence of structural defects on the dielectric properties of ceramic microwave resonators. In *Ceramic Transactions, Vol. 53, Materials and Processes for Wireless Communications*, ed. T. Negas and H. Ling. American Ceramic Society, Westerville, OH, 1995, pp. 137–151.
2. Villafuerte-Castrejon, M. E., Aragon-Pina, A., Valenzuela, R. and West, A. R., Compound and solid solution formation in the system $Li_2O$–$Nb_2O_5$–$TiO_2$. *J. Solid State Chem.*, 1987, **71**, 103–108.
3. Smith, R. I. and West, A. R., Characterization of an incommensurate LiTiNb oxide. *Mater. Res. Bull.*, 1992, **27**, 277–285.
4. Roth, R. S. and Davis, K. L., Incommensurate solid solution in $TiO_2$ doped $LiNbO_3$ and $LiTaO_3$. In *Am. Ceram. Soc. Ann. Meet., 89th*, The American Ceramic Society, Westerville, OH, 1987, p.88; also in *Phase Equilibria Diagrams: Vol. XI*, ed. R. S. Roth, The American Ceramic Society, Westerville, OH, 1995, pp. 231–232.
5. Shannon, R. D., Dielectric polarizability of ions in oxides and fluorides. *J. Appl. Phys.*, 1993, **73**(1), 348–366.