Bohdan Lyshchenko DP-82 Variant №4

## VI. High permittivity microwave dielectrics

Microwave (MW) dielectric ceramics have been used in mobile communications, satellite television broadcasts, radar, Global Position System (GPS), Wireless Fidelity (WiFi) and other modern communication systems as dielectric resonator (DR), filters, duplexers and substrates, for almost half a century due to their high dielectric permittivity ($\varepsilon_r$), high Qf (Q $\sim$ MW quality factor and f $\sim$ resonant frequency) and small temperature coefficient of resonant frequency (TCF). Since the first report of MW dielectrics in the $BaO - TiO_2$ binary system, ceramics with a range of $\varepsilon_r$, high Qf and near-zero TCF such as the $Ba(Zn, Mg, Co)_{1/3}(Nb, Ta)_{2/3}O_3$, $(Sr, Ca)TiO_3 - LnAlO_3$ $(Ln = La, Nd, Sm)$, $(Zr, Sn)TiO_4$ and $BaO-Ln_2O_3-TiO_2$ have been developed for use from 300MHz $\sim$ 40GHz by leading corporations such as Murata, Kyocera, EPCOS and Trans-Tech. In general, the roadmap for the development of MW dielectric materials [2–4,6] may be separated into the following key target areas where there is a technology pull from systems engineers and the absence suitable materials: 1) Expanding the range of $\varepsilon_r$. Currently, most high Qf, zero TCF materials have $20 < \varepsilon_r < 50$ (base station resonators/antenna substrates) but there is a strong technology pull for $5 < \varepsilon_r < 20$ (higher bandwidth antenna substrates), $60 < \varepsilon_r < 70$ (base station resonators) and $\varepsilon_r > 120$ (ultra-small GPS antenna substrates).

2) Low sintering temperature technology. The drive is to create a range of low temperature co-fired ceramics (LTCC) compatible with Ag electrodes (sintering temperature 960°) or ultra-low temperature co-fired ceramics (ULTCC) compatible with Al as inner electrodes (sintering temperature $<$ 660°C).

3) Ultrahigh Qf ceramics (>200,000 GHz).The focus here is to optimize Qf to achieve better selectivity to a specific frequency, critical for the transition from 4G to 5G technology in mobile telecommunications.

4) Compositions based on low cost, abundant constituents. Here, the technology is driven by scarcity, environmental concerns and geopolitical uncertainty surrounding raw materials such as $Ta_2O_5, Nb_2O_5$, and $Ln_2O_3$(Ln = lanthanide).

Generically, MW dielectric ceramics are oxides, principallydue to the large ionic polarizability of the $O^2$ -ion. Binary compounds, such as $MgO, TiO_2, Bi_2O_3, TeO_2$ , $Al_2O_3$ and $CeO_2$, possess high Qf and in some cases useful $\varepsilon_r$ but invariably have large positive/negative TCF. Hence, ternary and higher compounds or compositesare often explored to obtain temperature stable microwave dielectric ceramics with high Qf[1–15] The key to success in MW ceramicdevelopment is therefore in choosing,either an adaptable crystal structure to form solid solutions or immiscible end members to form composites that have no or limited interaction. Perovskite is the mostadaptable crystal structure to form solid solution for MW ceramics ($ABO_3$) since a large number of metallic elements may occupy the A and B sites in accordance with the Goldschmidt tolerance factor, $t = (R_A + R_B) / \sqrt{(R_B + R_O)}$ where $R_A, R_B$ and $R_O$ are the ionic radii of the A − B - and O -site. Perovskitesdominate medium and high permittivity commercial MW dielectrics in the range $25 < \varepsilon_r < 60$ and $\varepsilon_r > 90$[8–13] Althoughefforts have been made to explore novel complex perovskite-structured microwave dielectrics with $\varepsilon_r \sim 65$, only limited progress has been achieved with Qf $<$ 12,500GHz. [28] Moreover, it is difficult to lower the sintering temperatures of perovskites and related microwave dielectrics to meet the requirements of LTCC technology. For example, commercial tungsten bronze structured compounds achieve $70 < \varepsilon_r < 90$ and $8,000 <$ Qf $< 12,000$GHz when sintered to full density. If the sintering temperature is lowered to $\sim 900°C$ by the addition of glass, $\varepsilon_r$ and Qf decrease to $\sim 65$ and $< 6,000$GHz, respectively. Despite the great potential of LTCC technology and a substantial body of work in thescientific literature, suppliers such as Dupont and Ferro offer only a limited range of commercial LTCC materials.

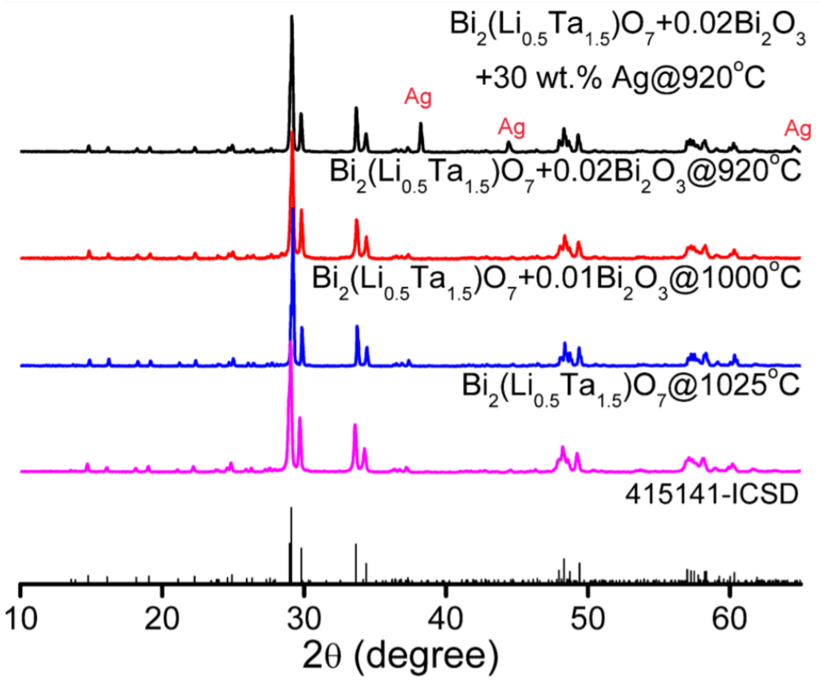


Рис. 1: XRD patterns of the $Bi_2(Li_{0.5}Ta_{1.5})O_7+xBi_2O_3(x = 0, 0.01$ and $0.02)$ ceramics sintered at different temperatures and co-fired with $Bi_2(Li_{0.5}Ta_{1.5})O_7+0.02Bi_2O_3$ and 30 wt. % silver powders

Figure 1 shows the XRD patterns of $Bi_2(Li_{0.5}Ta_{1.5})O_7 + xBi_2O_3(x = 0, 0.01$ and $0.02)$ ceramics sintered at different temperatures and co-fired with 30 wt. % silver powder. As reported by Muktha et al., [32] undoped $Bi_2(Li_{0.5}Ta_{1.5})O_7$ crystalize in a variant of the Aurivillius structure with a monoclinic, C2/c space group. The diffraction peaksfrom 415141 -ICSD (Inorganic Crystal Structure Database) are also plotted in Figure 1. All peaks were attributed to a single $Bi_2(Li_{0.5}Ta_{1.5})O_7$ phase when sintered at their optimal temperatures with no evidence of second phase, despite the addition of excess $Bi_2O_3$. Although it is possible that excess $Bi_2O_3$ becomes incorporated in the lattice, Bi-rich phases may also exsits but below the detectionlimit of the XRD equipment used within this study. Results from Rietveld structural refinements are shown in Figure S1 of the supplementary material.