Effect of La$^{3+}$ on Microwave Dielectric Properties of (Pb$_{0.45}$Ca$_{0.55}$)(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ Ceramics

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Abstract: In this work, microwave dielectric properties of A-site substitution by La$^{3+}$ in (Pb$_{0.45}$Ca$_{0.55}$)(Fe$_{0.5}$Nb$_{0.5}$)O$_3$ system were investigated. Microwave dielectric properties of A-site charge unbalance substitution of [(Pb$_{0.45}$Ca$_{0.55}$)$_{1-x}$La$_x$] (Fe$_{0.5}$Nb$_{0.5}$)O$_3$+δ (P45CLFN) were improved because the solid solution of small amount of surplus La$^{3+}$ with (Pb, Ca)$_{2+}$ could eliminate oxygen vacancies, and the formation of secondary phase (pyrochlore) was also caused by surplus La$^{3+}$. The decreasing of dielectric constant with the increase of La$^{3+}$ content is due to the formation of pyrochlore. The grain size is changed slightly and $Q_t$ values (7000~7300 GHz) are almost unchanged at $x = 0.02$~0.10, but the temperature coefficient of resonant frequency (TCF) are increased and changed from negative to positive. TCF is zero at $x = 0.075$ with $Q_t = 7267$ GHz and $K = 89$. TCF of all specimens are within $\pm 5 \times 10^{-6}$ ℃$^{-1}$.

Key words: (Pb$_{0.45}$Ca$_{0.55}$)(Fe$_{0.5}$Nb$_{0.5}$)O$_3$; microwave dielectric properties; oxygen vacancy; A-site substitution; rare earths

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The development of microwave communication systems requires materials which can be used at microwave frequencies as resonators in filters or oscillators in radar detectors, cellular telephone and global positioning satellite devices[6,7]. In order to meet this particular demand, these materials are required to have high dielectric constant $K$, low dielectric loss tanδ (high quality factor $Q_t$, where $Q$ is equal to 1/tanδ and $f$ is measuring frequency) and near zero temperature coefficient of resonant frequency (TCF)[8]. Pb-based perovskites of A-site substitution by Ca$^{2+}$ have high dielectric constant over 90 with high $Q_t$ values and small TCF[4,5]. In particular, (Pb$_{0.45}$Ca$_{0.55}$) (Fe$_{0.5}$Nb$_{0.5}$)O$_3$ (PCFN) has high $K = 91$, small TCF = +2.2 $\times 10^{-6}$ ℃$^{-1}$ and $Q_t = 4950$ GHz (at 3 GHz). But the $Q_t$ value is still relatively low. B-site substitution by Ti$^{4+}$ or Sn$^{4+}$ improved its microwave dielectric properties[6,7].

In this paper, the microwave dielectric properties of A-site charge unbalance substitution by La$^{3+}$ in [(Pb$_{0.45}$Ca$_{0.55}$)$_{1-x}$La$_x$] (Fe$_{0.5}$Nb$_{0.5}$)O$_3$+δ (P45CLFN) system were investigated as a function of $x$ content.

1 Experimental

The starting materials PbO, CaCO$_3$, La$_2$O$_3$, Fe$_2$O$_3$ and Nb$_2$O$_5$ powders with purity of 99.9% were weighed according to the desired compositions and mixed in distilled water for 24 h with zirconia balls. Specimens were synthesized by conventional solid-state synthesis processing, calcined at 900 ℃for 4 h. Disks with 10 mm in diameter and 5~6 mm in thickness isostatically pressed at 145 MPa were sintered at 1150 ℃ at 1300 ℃ for 3 h in double Pt crucibles by using a PbZrO$_3$ powder as bed powder to prevent PbO evaporation. Sintered pellets were examined by X-ray diffraction (XRD) analysis with Cu Kα radiation. Microstructures of the specimens were observed by scanning electron microscope (SEM). Dielectric constant $K$ and $Q_t$ values of the specimens were measured on TE011 mode at 5~6 GHz by Hakki-Coleman’s method. TCF at microwave frequencies was measured from 25 to 80 ℃ by cavity method.

2 Results and Discussion

Fig. 1 shows the XRD patterns of P45CLFN specimens sintered at 1250 ℃ for 3 h with variation of La$^{3+}$ content. Besides the main (Pb, Ca, La) (Fe, Nb)O$_3$ perovskite phase, a small amount of secondary phase (pyrochlore) was detected during the whole compositional range. In P45CLFN system, A-site substitution...
of (Pb, Ca)\(^{2+}\) by La\(^{3+}\) is charge unbalance substitution, the unbalanced charge structure is unstable and easy to form secondary phase. The amount of pyrochlore is proportional to the surplus La\(^{3+}\) content.

Figs. 2 and 3 show the dielectric constant \(\varepsilon\) and \(Q_f\) values of P45C-LFN specimens as a function of La\(^{3+}\) content, respectively. \(\varepsilon\) decreased with the increase of La\(^{3+}\) content, because the amount of secondary phase was increased with the increase of La\(^{3+}\) content and pyrochlore has relative low dielectric constant that caused the total dielectric constant decreasing. \(Q_f\) values (7000\(\sim\)7300 GHz) were nearly unchanged at \(x = 0.02\), 0.10 and this is higher than 4950 GHz of the undoped PCFN specimen.

In \([\ (\text{Pb}_{0.45} \text{Ca}_{0.55})_{1-x} \text{La}_x \ (\text{Fe}_{0.3} \text{Nb}_{0.7}) \text{O}_{3+\delta}]\ (\text{P45C-LFN})\) system, \(2x/3\) mole La\(^{3+}\) substituting \(x\) mole (Pb, Ca)\(^{2+}\) would keep the same perovskite structure, since it is charge balance substitution. Another \(x/3\) mole surplus La\(^{3+}\) may result in the formation of secondary phase. But when \(x\) is small enough, the surplus La\(^{3+}\) occupied Pb\(^{2+}\) site and eliminated oxygen vacancies caused in the ceramics sintering process.

\[
\text{La}_2\text{O}_3 + \text{V}_0 \xrightarrow{2\text{PbO}} 2\text{LaPb} + 3\text{O}_3
\]

So La\(_2\)O\(_3\) not only is the substitution element, but also the donor additive. Suitable donor additives could eliminate oxygen vacancies and improve its dielectric properties [8].

In the following experiment, 0.0068 mol La\(^{3+}\) was added to (Pb\(_{0.45}\)Ca\(_{0.55}\)) (Fe\(_{0.3}\)Nb\(_{0.7}\)) O\(_3\) system. Besides the main (Pb, Ca) (Fe, Nb) O\(_3\) perovskite phase, no secondary phase was detected as shown in Fig. 4, this time La\(_2\)O\(_3\) is only the donor additive and we got good microwave dielectric properties of \(\varepsilon = 96.5\), \(Q_f = 6804\) GHz and \(\text{TCF} = -4.99 \times 10^{-6} \degree\text{C}^{-1}\). So it is clear that the solid solution of small amount of surplus La\(^{3+}\) with (Pb, Ca)\(^{2+}\) could eliminate oxygen vacancies and improved their microwave dielectric properties. The TCF of P45C-LFN specimens increased with the increase of La\(^{3+}\) content, changed from negative to positive, as shown in Fig. 5. TCF is zero at \(x = 0.075\) with \(Q_f = 7267\) GHz and \(\varepsilon = 89\). The TCF of all specimens are within \(\pm 5 \times 10^{-6} \degree\text{C}^{-1}\). The microstructures of P45C-LFN specimens are observed by SEM. The grain size was changed slightly and in the range of 3\(\sim\)6\(\mu\)m as shown in Fig. 6. So the grain boundaries are not so important to affect the microwave dielectric properties and the \(Q_f\) values were almost unchanged.
Conclusion

A-site charge unbalance substitution of \[ (\text{Pb}_{0.45} \text{Ca}_{0.55})_{1-x} \text{La}_x (\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_{3.46} \] improved the microwave dielectric properties because the solid-solution of small amount of surplus \(\text{La}^{3+}\) with \((\text{Pb}_x\text{Ca})^{2+}\) could eliminate oxygen vacancies. Surplus \(\text{La}^{3+}\) cause the formation of secondary phase. The decrease of dielectric constant with the increase of \(\text{La}^{3+}\) content is due to the formation of pyrochlore. The grain size is changed slightly and \(Q_f\) values (7000\(\pm\)7300 GHz) are almost unchanged at \(x = 0.02\)\(\pm\)0.10, but the temperature coefficient of resonant frequency (TCF) are increased and changed from negative to positive. TCF is zero at \(x = 0.075\) with \(Q_f = 7267\) GHz and \(K = 89\). TCF of all specimens are within \(\pm5 \times 10^{-6} ^\circ\text{C}^{-1}\).

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