

Effect of La^{3+} substitution on microwave dielectric properties of $(\text{Pb}_{0.5}\text{Ca}_{0.5})(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ ceramics

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Abstract Microwave dielectric properties of the $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_{2x/3}](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ and $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_x](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ ceramics were investigated as a function of La^{3+} content ($0.0 \leq x \leq 0.2$). A single perovskite phase was detected in $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_{2x/3}](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$, while $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ were detected as a secondary phase in $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_x](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ beyond $x=0.05$ due to the excess of unbalanced charge. The amount of $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ was proportional to the unbalanced charge. Qf value of $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_{2x/3}](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ decreased remarkably with La^{3+} substitution due to the increase of oxygen vacancy. For $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_x](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ ceramics, dielectric constant and Qf value increased with La^{3+} content up to $x=0.03$ due to an increase of density and grain size. Temperature coefficient of resonant frequency (TCF) was depended on B-site bond valence in single perovskite phase.

Keywords Microwave dielectric properties · $(\text{Pb}_{0.5}\text{Ca}_{0.5})(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ · $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ · Phase stability · Bond valence

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1 Introduction

Recently, much attention has been paid to the Pb-based ceramics [1, 2], due to the high dielectric constant (K) and small temperature coefficient of resonant frequency (TCF). In particular, $(\text{Pb,Ca})(\text{Fe,Nb})\text{O}_3$ system shows good microwave dielectric properties by the substitution of Ca^{2+} for Pb^{2+} . With an increase of Ca content in the system, TCF and Qf values were improved, while the dielectric constant significantly decreased. Typically, K of 104, Qf of 3,920 GHz, and TCF of +26 ppm/°C were obtained for the specimens of $(\text{Pb}_{0.5}\text{Ca}_{0.5})(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ [1].

For the ABO_3 perovskite compound, TCF and K of the specimens closely related with effective ionic radii and polarizabilities, respectively [3]. Because of smaller ionic radius (1.36 Å) and larger polarizability (6.07 Å) of La^{3+} than the average ionic radius (1.415 Å) and the polarizability (4.87 Å) of $(\text{Pb}_{0.5}\text{Ca}_{0.5})^{2+}$, respectively [4, 5], TCF and K could be controlled by the substitution of La^{3+} for A site of $(\text{Pb}_{0.5}\text{Ca}_{0.5})(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$. Also, it has been reported that TCF was affected by the interaction between the composing ions of the compound which could be evaluated by the bond valence [6].

In this study, the microwave dielectric properties and phase stability of $(\text{Pb}_{0.5}\text{Ca}_{0.5})(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ were investigated as a function of balanced and/or unbalanced substitution of La^{3+} for A site. Effect of bond valence and unbalanced charge on the microwave dielectric properties and phase stability were also discussed.

2 Experimental procedures

$(\text{Pb}_{0.5}\text{Ca}_{0.5})(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ ceramics with La^{3+} substitution were prepared by the conventional mixed oxide method

with high purity oxides (>99.9%) via the columbite route. The starting materials were mixed according to the desired compositions and ground with ZrO_2 ball for 24 h in distilled water. The mixtures were dried and calcined at 900 °C for 4 h, and then isostatically pressed into pellets under a pressure of 1,450 kg/cm² and sintered at 1200 °C for 3 h. To inhibit the loss of PbO, the specimens were buried in powder of the same composition and placed into a platinum crucible by using $PbZrO_3$ powder as atmosphere powder.

Crystalline phases of the specimens were identified by the powder X-ray diffraction analyses (D/Max-3C, Rigaku, Japan). Microstructure was observed by a scanning electron microscope (JSM 6500F, JEOL, Japan). Dielectric constant and unloaded Q value were measured by Hakki-Coleman's method at 5~6 GHz [7]. TCF was measured by the cavity method [8] in the temperature range from 25 to 80 °C.

3 Results and discussion

Figure 1 shows the X-ray diffraction patterns of $[(Pb_{0.5}Ca_{0.5})_{1-x}La_{2x/3}](Fe_{0.5}Nb_{0.5})O_3$ and $[(Pb_{0.5}Ca_{0.5})_{1-x}La_x](Fe_{0.5}Nb_{0.5})O_3$ specimens as a function of La^{3+} content. A single perovskite phase was obtained through the entire composition range of the $[(Pb_{0.5}Ca_{0.5})_{1-x}La_{2x/3}](Fe_{0.5}Nb_{0.5})O_3$ system [Fig. 1(a)]. However, $Pb_3Nb_4O_{13}$ phase as a secondary phase was detected beyond $x=0.050$ [Fig. 1(b)]. With an increase of La^{3+} content, lattice parameters of the $[(Pb_{0.5}Ca_{0.5})_{1-x}La_x](Fe_{0.5}Nb_{0.5})O_3$ system were decreased up to $x=0.030$. These results are due to the smaller ionic

radius of La^{3+} (1.36 Å³) than that of $(Pb_{0.5}Ca_{0.5})^{2+}$ (1.415 Å³) [5].

The phase stabilities of the perovskite compounds were affected from tolerance factor and electrical neutrality [9, 10]. With an increase of La^{3+} content, there was no significant change of tolerance factors from 0.9978 to 0.9939 for $[(Pb_{0.5}Ca_{0.5})_{1-x}La_x](Fe_{0.5}Nb_{0.5})O_3$, while those for $[(Pb_{0.5}Ca_{0.5})_{1-x}La_{2x/3}](Fe_{0.5}Nb_{0.5})O_3$ were changes from 0.9978 to 0.9393. However, the pyrochlore phase ($Pb_3Nb_4O_{13}$) was detected above $x=0.050$ of $[(Pb_{0.5}Ca_{0.5})_{1-x}La_x](Fe_{0.5}Nb_{0.5})O_3$. Therefore, pyrochlore phase was formed due to the unbalanced charge of A-site by the substitution of La^{3+} ion. A relative amount of pyrochlore phase could be evaluated from Eq. 1 [1]:

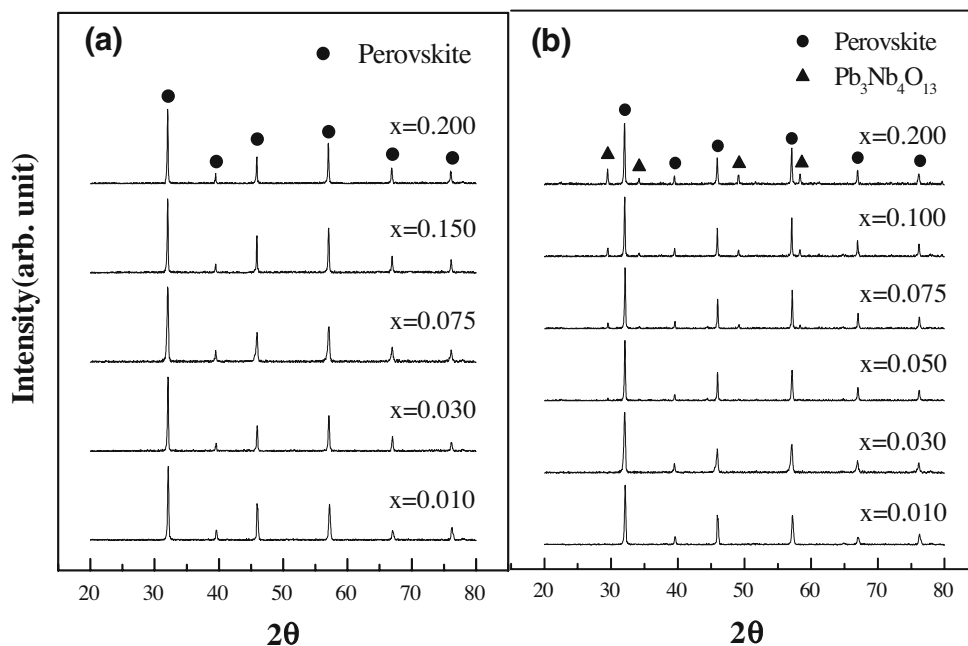
$$\text{Pyrochlore phase(\%)} = \frac{I_{\text{pyro.}}}{I_{\text{perov.}} + I_{\text{pyro.}}} \quad (1)$$

where, $I_{\text{pyro.}}$ and $I_{\text{perov.}}$ are the relative integral intensity of main peak on pyrochlore and perovskite phase, respectively. The relative amount of pyrochlore phase was increased with the unbalanced charges in $[(Pb_{0.5}Ca_{0.5})_{1-x}La_x](Fe_{0.5}Nb_{0.5})O_3$, as shown in Fig. 2.

The relative density of $[(Pb_{0.5}Ca_{0.5})_{1-x}La_x](Fe_{0.5}Nb_{0.5})O_3$ increased up to $x=0.030$, and then decreased. These results could be confirmed by SEM micrographs of specimens in Fig. 3. Grain size increased with an increase of La^{3+} content up to $x=0.030$, and then decreased for further substitution of La^{3+} .

In general, the dielectric constant (K) was depended on the relative density and the dielectric polarizability at microwave frequencies [11]. Even though the dielectric

Fig. 1 X-ray diffraction patterns of (a) $[(Pb_{0.5}Ca_{0.5})_{1-x}La_{2x/3}](Fe_{0.5}Nb_{0.5})O_3$ and (b) $[(Pb_{0.5}Ca_{0.5})_{1-x}La_x](Fe_{0.5}Nb_{0.5})O_3$ specimens sintered at 1200 °C for 3 h



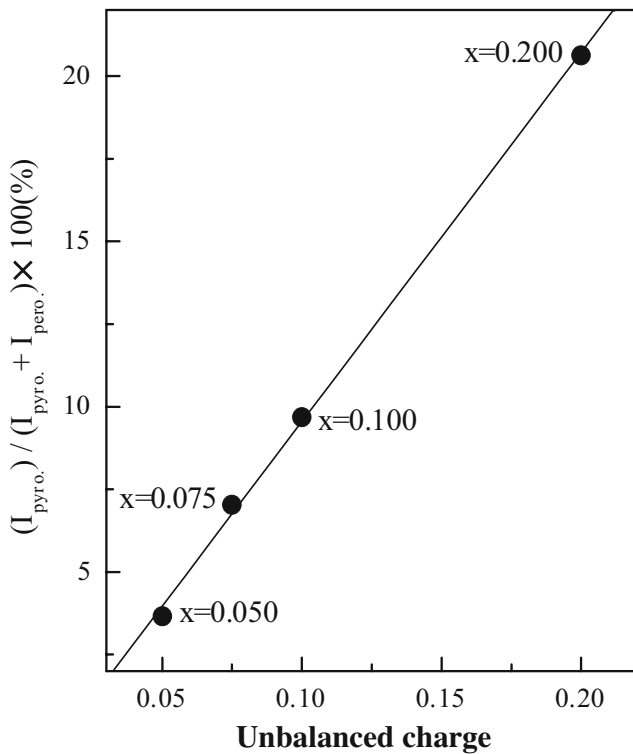
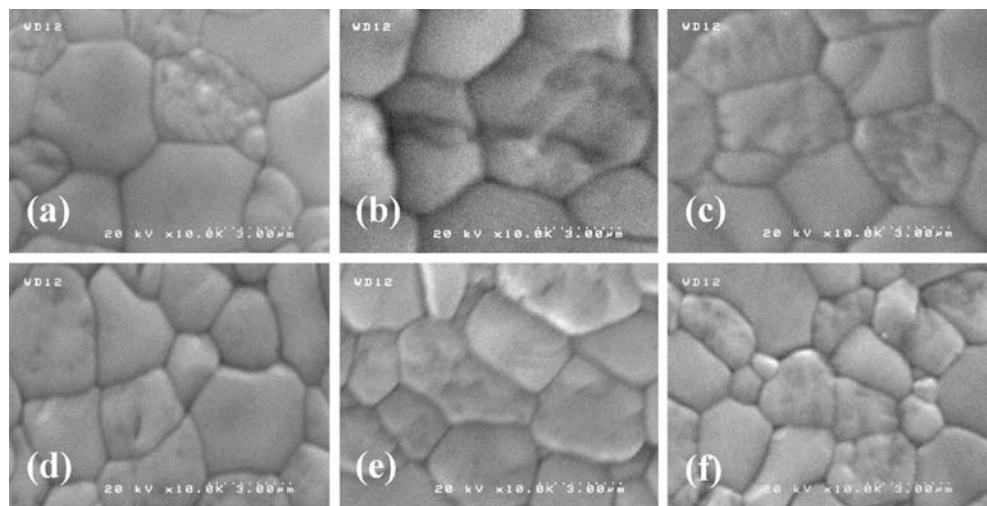


Fig. 2 Pyrochlore phase (%) of $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_x](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ specimens sintered at 1200 °C for 3 h with unbalanced charges

polarizability of La^{3+} (6.07\AA^3) is larger than that of $(\text{Pb}_{0.5}\text{Ca}_{0.5})^{2+}$ (4.87\AA^3) [3], the dielectric constant (K) of $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_x](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ was increased up to $x=0.030$, and then decreased, as shown in Fig. 4. These results were due to the changes of density of the specimens.

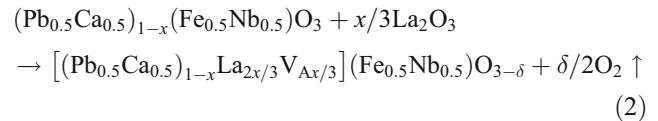
It has reported that Qf value was depended on the grain size, relative density, and secondary phases of the specimens [12]. The change of Qf value was consistent with the relative density and grain size, and the maximum Qf value of 5,200 GHz was obtained at $x=0.030$.

Fig. 3 SEM photographs of the $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_x](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ specimens sintered at 1200 °C for 3 h; (a) $x=0.010$, (b) $x=0.030$, (c) $x=0.050$, (d) $x=0.075$, (e) $x=0.150$, (f) $x=0.200$



For $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_{2x/3}](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$, the specimens with $x=0.01$ showed Qf value of 725 GHz, and Qf value could not be measured for the specimens with further La^{3+} content.

It has been reported that the formation of oxygen vacancy by substitution of trivalent ion for A-site in ABO_3 perovskite [10, 13]. The substitution of La^{3+} for $(\text{Pb}_{0.5}\text{Ca}_{0.5})^{2+}$ in $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_{2x/3}](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ could be expressed by Eq. 2:



where, $\text{V}_{Ax/3}$ is A-site vacancy resulted from the substitution of La^{3+} for Pb^{2+} and Ca^{2+} in ABO_3 perovskite compounds. As confirmed in Eq. 2, oxygen vacancy was increased by the substitution of La^{3+} . Therefore, Qf value of $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_{2x/3}](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ decreased remarkably with La^{3+} content due to the increase of oxygen vacancy [10].

Figure 5 shows TCF of $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_x](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ sintered at 1200 °C for 3 h. With an increase of La^{3+} content, TCF decreased up to $x=0.030$, and then increased. These results could be explained by the changes of B-site bond valence and the formation of $\text{Pb}_3\text{Nb}_4\text{O}_{13}$, respectively. TCF showed the lowest value of -0.7 ppm/°C at $x=0.030$. For the single perovskite structure, TCF was closely related with structural characteristics of oxygen octahedra, such as tolerance factor and bond valence [5, 14]. However, the tolerance factor could not fully explain the change of TCF, because structural characteristics changed with not only ionic radius, but also bond strength between cation and anion. Therefore, the change of TCF could be explained by B-site bond valence in ABO_3 perovskite.

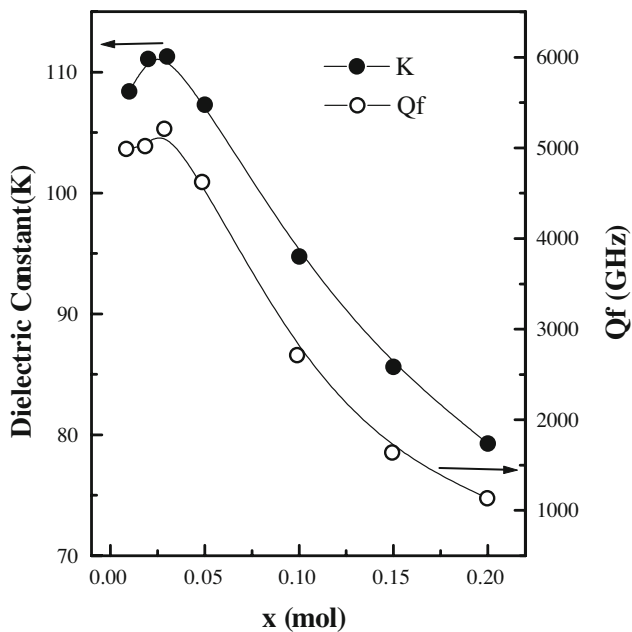


Fig. 4 Microwave dielectric properties of $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_x](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ specimens sintered at 1200°C for 3 h

B-site bond valences of $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_x](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ were increased due to the decrease of lattice parameters by substitution of La^{3+} (1.36\AA , C.N.=12) which had smaller ionic radius than $(\text{Pb}_{0.5}\text{Ca}_{0.5})^{2+}$ (1.415\AA , C.N.=12) [5]. Therefore, TCF was decreased with La^{3+} content

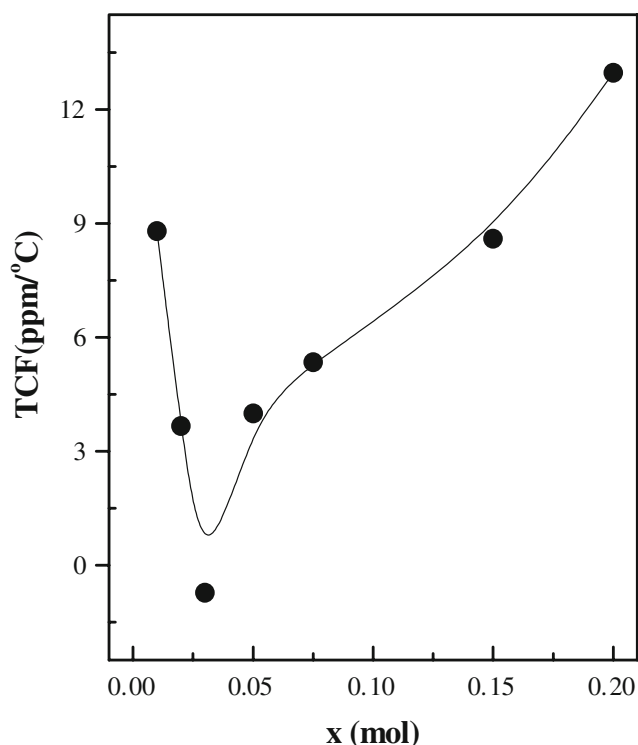


Fig. 5 TCF of $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_x](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ specimens sintered at 1200°C for 3 h

up to $x=0.030$ due to an increase of B-site bond valence, as shown in Fig. 6.

4 Conclusion

A single perovskite phase was obtained up to $x=0.03$ in $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_{2x/3}](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$, while $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ was detected as a secondary phase in $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_x](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ beyond $x=0.050$, and the amount of $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ was proportional to the unbalanced charge.

Dielectric constant (K) of the $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_x](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ increased up to $x=0.030$ due to an increase of the relative density, and then decreased. Qf value of $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_x](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ was dependent on the relative density and grain size, and showed maximum value of 5,200 GHz at $x=0.030$, while that of $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_{2x/3}](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ decreased remarkably with La^{3+} substitution, due to an increase of oxygen vacancy. TCF could be controlled from $+26\text{ ppm}/^\circ\text{C}$ to $-0.7\text{ ppm}/^\circ\text{C}$ due to an increase of B-site bond valence in the single perovskite structure.

The specimens of $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{0.97}\text{La}_{0.03}](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ sintered at 1200°C for 3 h, showed good microwave dielectric properties of $K=110$, $Qf=5,200\text{ GHz}$, $\text{TCF}=-0.7\text{ ppm}/^\circ\text{C}$.

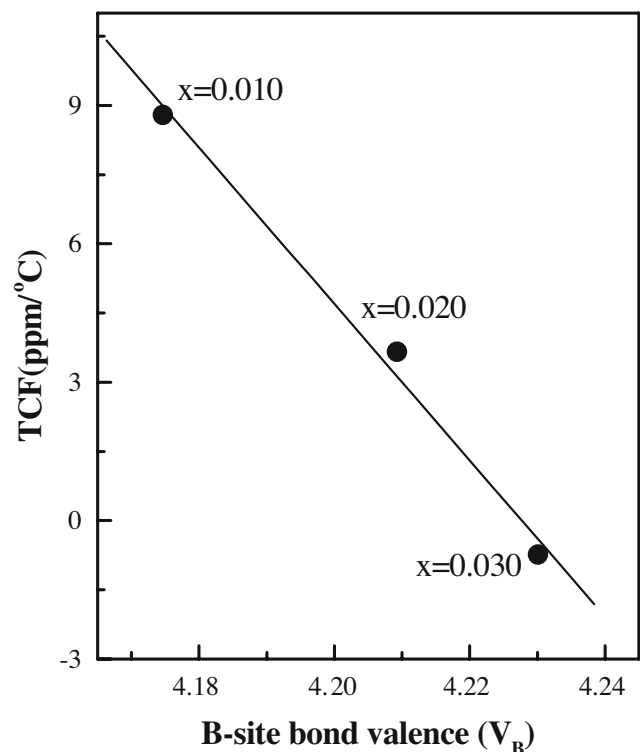


Fig. 6 TCF and B-site bond valence of $[(\text{Pb}_{0.5}\text{Ca}_{0.5})_{1-x}\text{La}_x](\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$ specimens sintered at 1200°C for 3 h

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