

# Structure and microwave dielectric properties of $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$

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**Abstract** The structure evolution, and microwave dielectric properties of  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$  Ceramics ( $x = 0.02 \leq x \leq 0.5$ ) were investigated in this paper. X-ray diffraction (XRD) and scanning electron microscopy (SEM) results show that all samples exhibit single phase. The concentration and ordering degree of A-site vacancies decrease with the increase of  $x$  value, and no A-site ordering exists when  $x > 0.2$ . The dielectric constant decreases with the decrease of  $x$  value. The  $Q \times f$  value increases up to  $x = 0.1$  and then decreases with the further increase of  $x$  value. A maximum  $Q \times f$  value of 18,826 GHz is obtained when  $x = 0.06$ . The temperature coefficient of resonant frequency exhibits positive value and decreases greatly with the decrease of  $x$  value.

**Keywords** A-site deficient perovskite · Order–disorder · Microwave dielectric properties

## 1 Introduction

Complex perovskites with general formula  $\text{A}^{2+}(\text{B}^{2+}_{1/3}\text{B}^{5+}_{2/3})\text{O}_3$  have received widespread interest in the wireless microwave communications community. Compared to the numerous examples of B-site ordered system, A-site ordered perovskites are relatively rare. A-site order–disorder reaction can play a critical role in affecting the properties of perovskites. Several studies have focused on the ionic conducting perovskites,  $(\text{La}_{2/3-x}\text{Li}_{3x})\text{TiO}_3$  [1–3]. The

ionic conductivities of the ordered A-site samples were approximately an order of magnitude lower than their disordered counterparts [1]. The A-site ordering degree of  $(\text{La}_{(2-x)/3}\text{Li}_x\text{TiO}_3)$  was governed by the Li content and thermal treatment [3, 4]. In Li poor compounds the A-site cations adopt usual (001) ordered structure, and in Li rich compounds ( $x \geq 0.25$ ) or quenched samples a disordered A-site structure was adopted. The precise crystal structures for different  $x$  values have not been well established until now and controversial results have been reported in the literature [5–7]. By contrast, the analogous sodium series,  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$ , which exhibit dielectric properties, seem to be much less studied. Ruiz et al. have investigated the structure characteristics of this perovskite-type series ( $x = 0.165, 0.24, 0.42$ ), in particular the cation order–disorder phenomena on the A-site and  $\text{BO}_6$  distortion and tilting [8]. However there are few reports on the microwave dielectric properties of  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$  except that Takahashi et al. have studied the microwave dielectric properties of  $(\text{La}_{0.5}\text{Na}_{0.5})\text{TiO}_3$  to the best of our knowledge [9]. The distribution (order–disorder) and concentration of vacancies, which may be interrelated, are expected to have considerable effect on the microwave dielectric properties of  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$ . Therefore the purpose of this paper is to systematically investigate the structure evolution and microwave dielectric properties of  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$  Ceramics ( $x = 0.02 \leq x \leq 0.5$ ).

## 2 Experiment

$\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$  ( $0.02 \leq x \leq 0.5$ ) ceramic samples were prepared by conventional solid-state reaction process from the starting materials including  $\text{TiO}_2$  (99.9%),  $\text{NaCO}_3$  (99.9%) and  $\text{La}_2\text{O}_3$  (99.99%). The  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$  ( $0.02 \leq x \leq 0.5$ )

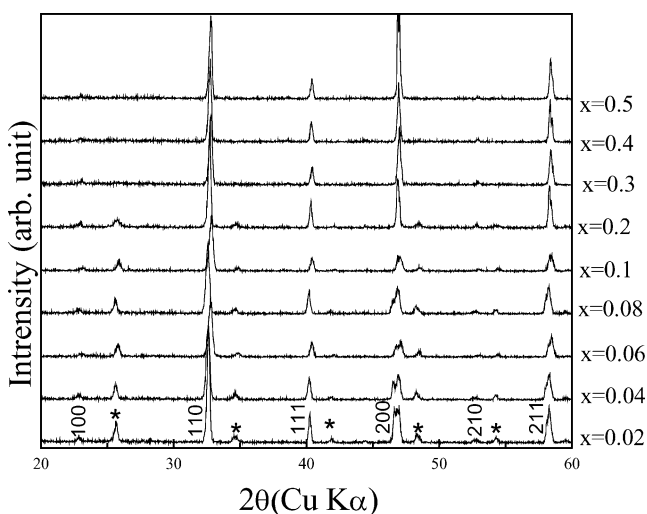
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compounds were weighed and mixed with  $ZrO_2$  balls in ethanol for 24 h, dried and calcined at the temperature of 1,100 °C for 2 h in a alumina crucible. The calcined powders were grounded, dried and mixed with 7 wt.% PVA. The mixtures were pressed into pellets. The compacts were sintered between 1,300–1,400 °C for 2 h.

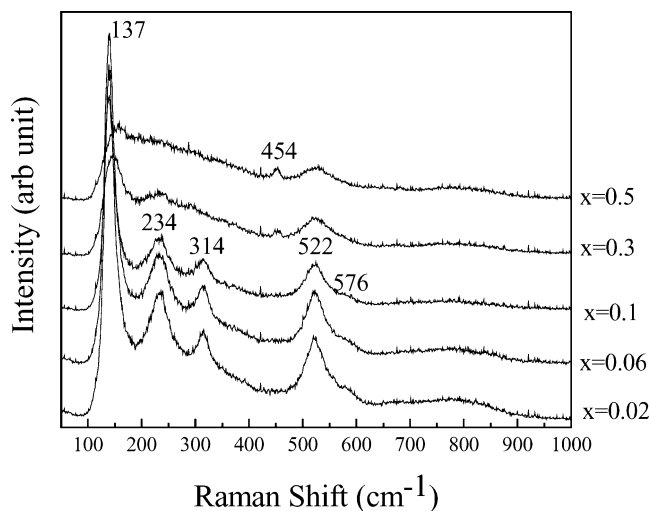
The phase constitutes of the sintered samples were identified by X-ray powder diffraction (XRD) with Ni-filtered  $CuK\alpha$  radiation (Model Dmax-RC, Japan). Bulk density of the sintered specimens was identified by Archimedes' method. The Raman experiments were carried out for the sintered samples (Model Jobin Y'von U1000). A laser line of 532 nm and 500 mW average power was used. The spectra were recorded from 0 to 1,000  $cm^{-1}$ . The microstructure of the sintered sample was characterized by scanning electron microscopy (SEM)(Model XL20, Philips Instruments, Netherlands). All samples were polished and thermal etched at the temperature which was 70–100 °C lower than its sintering temperature. Microwave dielectric properties of the sintered samples were measured between 7 and 8 GHz using network analyzer (Hewlett Packard, Model HP8720C, USA). The quality factor was measured by the transmission cavity method. The relative dielectric constant ( $\epsilon_r$ ) was measured according to the Hakki–Coleman method using the  $TE_{011}$  resonant mode, and the temperature coefficient of the resonator frequency ( $\tau_f$ ) was measured using invar cavity in the temperature range from –20 to 80 °C.

### 3 Results and discussions

Figure 1 shows the XRD patterns of sintered  $La_{(2-x)/3}Na_xTiO_3$  ( $0.02 \leq x \leq 0.5$ ) samples, in which the Bragg reflections



**Fig. 1** XRD patterns of  $La_{(2-x)/3}Na_xTiO_3$  ( $0.02 \leq x \leq 0.5$ ) sintered at 1,350 °C/2 h for  $x < 0.1$  and 1,400 °C/2 h for  $x \geq 0.1$ , respectively (The reflections marked by asterisk are superstructure lines caused by A-site ordering)

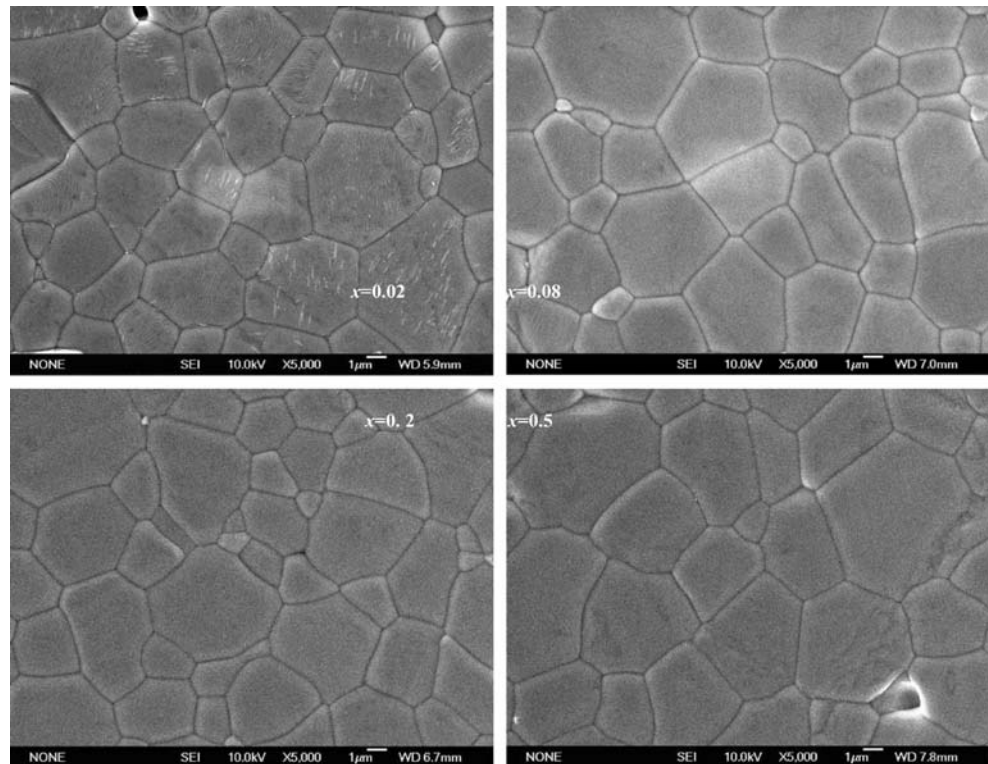


**Fig. 2** Raman spectrum of the sintered  $La_{(2-x)/3}Na_xTiO_3$  ceramics with different  $x$  values

tions have been indexed to the parent cubic cell. All samples exhibit single perovskite-type phase. However some differences are clearly observed as the function of sodium content,  $x$ . The samples with  $x \leq 0.2$  exhibit similar XRD pattern to the sodium free  $La_{2/3}TiO_{3-x}$  ( $x \leq 0.07$ ) [10], in which the A-site cations exhibit ordered alternative arrangement of La and Na ions and vacant sites along the c-axis. The superstructure reflections produced by A-site ordering (marked with asterisk) become decreased with the addition of  $Na^+$ , and disappear when  $x > 0.2$ . It indicates the A-site cation ordering degree decrease with the increase of sodium content and becomes disorder for A-site cations distribution when  $x > 0.2$ , which is agreement with that of Ruiz et al. [8] and also with that of analogous lithium series,  $La_{(2-x)/3}Li_xTiO_3$  [11]. It is noted that the profiles of the fundamental (200) peak is splitted when  $x \leq 0.2$ , which indicates the lower symmetry of the structure, while no splitting occurs when  $x > 0.2$ . It seems to imply some relevance between the peak splitting and the A-site ordering state. In the well-ordered system, the La(1) site is almost fully occupied by La while the La(2) site accommodates the remaining La/Na atoms and vacancies [5]. Due to this charge unbalance,  $Ti^{4+}$  shift away from the center of the oxygen octahedral toward the La(2) plane, while equatorial oxygens shift toward the La(1) plane, which results in  $TiO_6$  octahedra distortion. This picture only applies to sodium poor compounds [4]. Beyond  $x = 0.2$  the A-site cations distribution becomes disorder,  $Ti^{4+}$  shifts toward the center of the octahedron, and symmetry evolves from orthorhombic one to an almost cubic cell [5]. Therefore the splitting of (200) peak is caused by the distortion of  $TiO_6$  octahedron which is resulted from the A-site ordering.

A room temperature Raman spectra of the samples with different Na content are shown in Fig. 2. For the orthorhombic structure (Pnma), a total 24 modes are Raman

**Fig. 3** SEM photographs of  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$  ceramic sintered at 1,350 °C/2 h for  $x=0.02, 0.08$  and 1,400 °C/2 h for  $x=0.2$  and 0.5, respectively

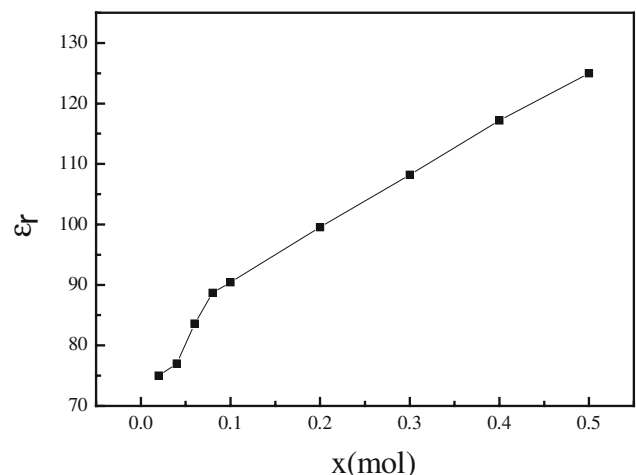


active according to the factor group analysis [12]. However, in reality not all of these bands can be observed due to bands overlap or low changes in polarizability. The Raman spectrum of  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$  ( $0.02 \leq x \leq 0.5$ ) in Fig. 2 shows only five bands, which is in good agreement with that of  $\text{La}_{(2-x)/3}\text{Li}_x\text{TiO}_3$  reported by Sanjuan et al. who interpreted their results within the tetragonal instead of orthorhombic approach [3]. Although the symmetry of  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$  ( $x=0.165, 0.24, 0.42$ ) has been unambiguously described as orthorhombic [8], the assumption of tetragonal approach is reasonable [3]. According to the tetragonal approach the 137, 234 and  $522 \text{ cm}^{-1}$  band can be assigned to be  $E_g$  symmetry species, while the 314 and  $576 \text{ cm}^{-1}$  band behave like  $A_{1g}$  modes. Some qualitative trend can be observed that all bands are broadened and the intensities are decreased with the increase of sodium content. Especially the  $A_{1g}$  mode close to  $314 \text{ cm}^{-1}$  caused by Ti vibration along the  $c$ -axis disappears when  $x \geq 0.3$ . This may be related to the disappearance of  $\text{TiO}_6$  distortion resulted from the A-site disordering, which is good agreement with the XRD results. It is noted that for sodium rich ( $x \geq 0.3$ ) samples another weak band near  $454 \text{ cm}^{-1}$  appears, which may be due to the tilting of  $\text{TiO}_6$ . The tilt angle of  $\text{TiO}_6$  was considered to be increased as the vacant A-sites decrease for  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$  [8]. The tilting of oxygen octahedra in perovskites should cause superstructure reflections which is difficult to detect by XRD due to the weakness of reflections associated with small displacement of the oxygen

atoms, while can be apparently detected by Raman scattering.

Figure 3 shows the SEM photographs for the samples sintered at 1,350 °C/2 h for  $x=0.02$ , and 1,400 °C/2 h for  $x=0.1, 0.2$  and 0.5, respectively. All sintered samples exhibit dense single phase microstructure.

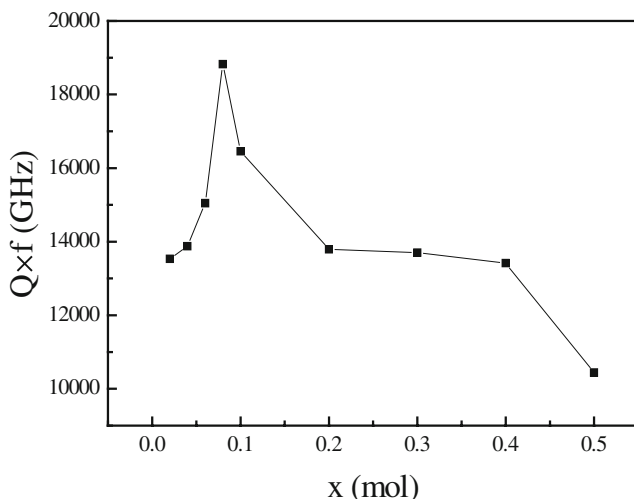
Figure 4 shows the variation of dielectric constants measured at microwave frequency as a function of  $x$  value for  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$ . The dielectric constant increases with the increase of sodium content. According to the equation



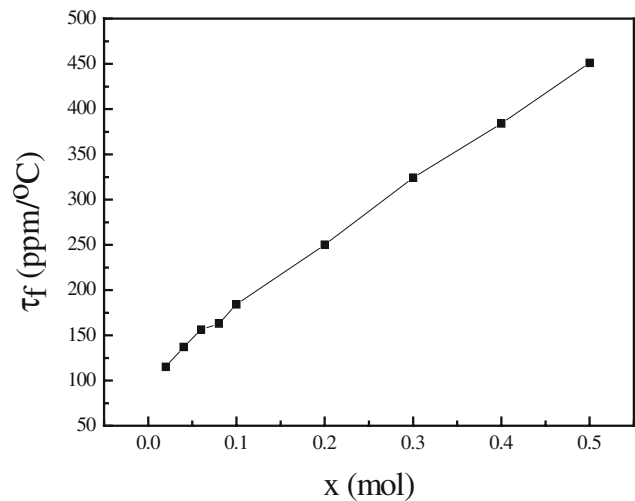
**Fig. 4** Variation of dielectric constants as a function of  $x$  value for  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$

of Clausius–Mossotti (C–M), the dielectric constant increases with increasing total dielectric polarizability  $\alpha_D$  and decreasing unit-cell volume. However  $\alpha_D$  in one primitive cell decreases with increasing sodium content due to the fact that the ionic polarizability of  $\text{Na}^+$  is much lower than that of  $\text{La}^{3+}$  ( $\alpha_{\text{La}^{3+}}^3: 6.07 \text{ \AA}^3$  and  $\alpha_{\text{Na}^+}^3: 1.8 \text{ \AA}^3$ ). And the unit cell volume changes slightly with the variation of sodium content due to the similar ionic radii between  $\text{La}^{3+}$  and  $\text{Na}^+$  ( $R_{\text{La}^{3+}}^3: 1.50 \text{ \AA}$  and  $R_{\text{Na}^+}^3: 1.53 \text{ \AA}$ ). So the dielectric constant should be decreased with increasing sodium content, which is contradicted with the results in Fig. 4. Further more the calculated dielectric polarizability  $\alpha_D$  for the sample with  $x=0.5$  is about 12.89, which is lower than the measured one (13.54). This seems to indicate the existence of “rattling” cations in this structure. Although in  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$  the A-cations exhibit quite distorted cuboctahedral coordination as a consequence of the displacement of oxygen anions, the mean La/Na–O and Ti–O distance are in good agreement with the Shannon ionic radii sums and keep almost no variation with the sodium content [8]. Therefore the “rattling” assumption seems to be inappropriate here. The explanation of dielectric permittivity behavior for the title compounds should be further studied.

The variation of  $Q \times f$  values as a function of sodium content is shown in Fig. 5. The  $Q \times f$  increases dramatically as the sodium content increases from  $x=0.02$  to  $x=0.06$ , which is mainly caused by the decrease of A-site vacancy concentration with the addition of  $\text{Na}^+$ , and then decreases with the further increase of sodium content, which is mainly due to the decrease of A-site ordering as discussed above. The maximum  $Q \times f$  value of 18,826 GHz is obtained when  $x=0.06$ . It seems to indicate that A-site vacancy concentration and its ordering degree have opposite effect on the  $Q \times f$



**Fig. 5** Variation of  $Q \times f$  value as a function of  $x$  value for  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$



**Fig. 6** Variation of  $\tau_f$  value as a function of  $x$  value for  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$

value. Figure 6 shows the change of temperature coefficient of resonant frequency  $\tau_f$  as a function of sodium content. All samples exhibit positive  $\tau_f$  value, and decreases almost linearly from 451 to 115 ppm/°C as the sodium content decreases from  $x=0.5$  to  $x=0.02$ . This may be related to the decrease of tilting angle of  $\text{TiO}_6$ -octahedra with the decrease of sodium content [8, 13].

#### 4 Conclusions

The microstructure and microwave dielectric properties of  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$  Ceramics ( $0.02 \leq x \leq 0.5$ ) have been studied in this paper. In conclusion, all sintered samples exhibit single phase and dense microstructure. The A-site ordering degree decreases with the increase of sodium content and becomes disorder when  $x > 0.2$ . The distribution (order–disorder) and concentration of vacancies, which is interrelated, have considerable effect on the microstructure and microwave dielectric properties of  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$ . The  $\text{TiO}_6$ -octahedra distortion due to A-site ordering is alleviated as the A-site ordering is decreased. A-site vacancy concentration and its ordering degree have opposite effect on the  $Q \times f$  value. For  $\text{La}_{(2-x)/3}\text{Na}_x\text{TiO}_3$  a maximum  $Q \times f$  value of 18,826 GHz is obtained when  $x=0.06$ . The dielectric constant decreases with the decrease of sodium content. The  $\tau_f$  decreases almost linearly with the decrease of sodium content due to the decrease of tilting angle of  $\text{TiO}_6$ -octahedra.

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