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# Structure and microwave dielectric properties of $La_{(2-x)/3}Na_x(Mg_{1/2}W_{1/2})O_3$

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## Abstract

The structure evolution, sintering behavior and microwave dielectric properties of $La_{(2-x)/3}Na_x(Mg_{1/2}W_{1/2})O_3$ ($x = 0$–$0.5$) were investigated in this paper. The X-ray diffraction (XRD) results show that all samples exhibit single phase, and the structure changed from orthorhombic when $0 \le x < 0.3$ to monoclinic phase when $0.3 \le x \le 0.5$. The size and ordering degree of A/B-site domains decrease with the increase in $x$ value. The sintering temperature of the Na-doped samples increased compared to the pure $La_{2/3}(Mg_{1/2}W_{1/2})O_3$ (LMW) due to the estimated decrease in the concentration of A-site vacancies. The addition of $Na^+$ ion does not affect the dielectric permittivity greatly. The $Q \times f$ value decreases with the increase in $x$ value, although the estimated concentration of A-site vacancies decreases with increasing $x$, which may be ascribed to the decrease of A/B-site ordering and domain size with the increase in $x$. The temperature coefficient of resonant frequency changed from negative values into positive values with the increase in $x$ value.

*Keywords:* Dielectric properties; Complex perovskite

## 1. Introduction

Complex perovskites with general formula $A^{2+}(B^{2+}_{1/3}B^{5+}_{2/3})O_3$ have received widespread interest in the wireless microwave communications community. Previous researches have demonstrated that the microwave dielectric properties of these ceramics are closely related to the degree of cation ordering on the B-site position, given that all other factors are equal.[1,2] Compared to the numerous examples of B-site ordered system, A-site ordered perovskites are relatively rare. Most examples are found in non-stoichiometric, oxygen-deficient perovskites such as $La_{2/3}TiO_{3-x}$.[3] Park et al. reported on the synthesis and structure of several new stoichiometric A-site systems.[4,5] A-site order–disorder reaction can play a critical role in affecting the properties of perovskites. Several studies have focused on the ionically conducting perovskites $(RE_{2/3-x}Li_{3x})TiO_3$ (RE: rare earth).[6,7] Recently, another complex perovskite both with A- and B-site cation ordering, $La_{2/3}(Mg_{1/2}W_{1/2})O_3$ (LMW), was reported to have good microwave dielectric properties ($\varepsilon_r = 23.6$, $Q \times f = 32{,}500$, and $\tau_f = -43$ ppm/°C).[8] Its high $Q$ value was considered to be mainly related to the A-site vacancies ordering.[8] On the other hand, the existence of high concentration of vacancies is a detrimental factor for further increase in its $Q$ value. The distribution (order–disorder) and concentration of vacancies, which may be interrelated, are expected to have considerable effect on the microwave dielectric properties of $La_{2/3}(Mg_{1/2}W_{1/2})O_3$. Therefore, the effect of the coupled A-site substitution of Na–La on the cation order and microwave dielectric properties of the tungsten complex perovskite system, $La_{(2-x)/3}Na_x(Mg_{1/2}W_{1/2})O_3$ ($0 \le x \le 0.5$), was investigated in this paper.

## 2. Experiment

$La_{(2-x)/3}Na_x(Mg_{1/2}W_{1/2})O_3$ ($0 \le x \le 0.5$) ceramic samples were prepared by conventional solid-state reaction process from the starting materials including MgO (99.5%), $WO_3$ (99.96%), $Na_2CO_3$ (99.9%) and $La_2O_3$ (99.99%). The $La_{(2-x)/3}Na_x(Mg_{1/2}W_{1/2})O_3$ ($0 < x \le 0.5$) compounds were weighed and mixed with $ZrO_2$ balls in ethanol for 24 h, dried and calcined at the temperature of 1200 °C for 2 h in an alumina crucible. The calcined powders were grounded, dried and mixed with 7 mass% PVA. The mixtures were pressed into pellets. The compacts were sintered between 1400 and 1500 °C for 2 h. In order to prevent the sodium evaporation loss, the compacts were

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covered with powder of the same composition in an MgO crucible.

The phase constitutes of the sintered samples were identified by X-ray powder diffraction (XRD) with Ni-filtered Cu Kα radiation (Model Dmax-RC, Japan). Bulk density of the sintered specimens was identified by the 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 1000 $\mathrm{cm}^{-1}$. 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 ($\varepsilon_r$) was measured according to the Hakki–Coleman method using the $\mathrm{TE}_{011}$ 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 discussion

Fig. 1 shows the XRD patterns of synthesized Na-doped LMW. The examination of the patterns shows that they are all in single phase of perovskite type. In pure LMW ($x = 0$) the A-site cations exhibit the usual (0 0 1) ordered structure with one layer of vacancies alternating with a second that contains an apparently random distribution of 1/3 La and 2/3 vacancies.[9] Orthorhombic structure (S.G.: I222) with doubled $c$ value is adopted due to the ordering of A-site vacancies.[9] For comparison, the XRD pattern of pure LMW ($x = 0$) is also presented here.[8] It shows that the intensity and width of the superstructure reflection peak produced by A-site ordering (marked with asterisk) become decreased with the increase in $\mathrm{Na}^+$ addition. It seems to indicate the decrease of A-site cation ordering degree. It is also confirmed by the diminish of weak addition reflections marked by filled diamond, which are caused by the anti-parallel displacement of B-site cations along $c$-axis produced by the ordering of A-site vacancies along the $c$-direction in addition to the B-site 1:1 ordering (marked with solid circles).[9] The XRD patterns of the samples with $x = 0.5$ are in good agreement with the pattern in JCPDS card (37-0243) which adopted monoclinic structure (S.G. $P2_1$). However, with the decrease in $x$ value the reflection peaks shift to lower degree when $0.3 \leq x \leq 0.5$ and shift to higher degree when $0 \leq x < 0.3$, which seems to indicate the abrupt structure change began at $x = 0.3$. The structure changed from orthorhombic when $0 \leq x < 0.3$ to monoclinic phase when $0.3 \leq x \leq 0.5$, which may be related to the tilt of oxygen octahedron. It is noted that the experimental peak intensity associated with the B-site ordering (marked with solid circle) also becomes decreased as the doping of $\mathrm{Na}^+$ ion, which implies that the microstructure is comprised of small domains of various orientational and anti-phase variants of the 1:1 ordered structure, although the ionic charge difference between $\mathrm{Mg}^{2+}$ and $\mathrm{W}^{6+}$ is large. The samples ($x = 0.1$ and 0.2) sintered 1400 °C/2 h and the samples ($x = 0.3$, 0.4 and 0.5) sintered at 1450 °C/2 h exhibit the same phase as their calcined powders, respectively (Fig. 2). For the sample, $x = 0.5$ unknown second phase(s), which is marked by open triangles, appeared after it was sintered at 1500 °C/2 h, which may be caused by the evaporation of Na at high temperatures. Compared to the pure LMW, the sintering temperature of Na-doped samples increased greatly due to the estimated decrease of A-site vacancies concentration, because the diffusion coefficients of A-site cations might be decreased by the decrease in A-site vacancies concentrations.

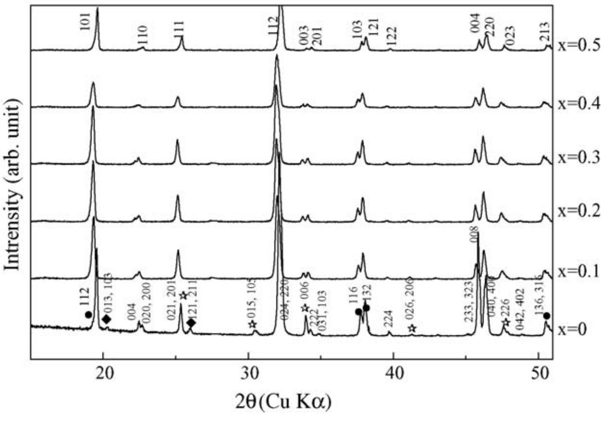

Fig. 1. XRD patterns of synthesized $\mathrm{La}_{(2-x)/3}\mathrm{Na}_x(\mathrm{Mg}_{1/2}\mathrm{W}_{1/2})\mathrm{O}_3$.

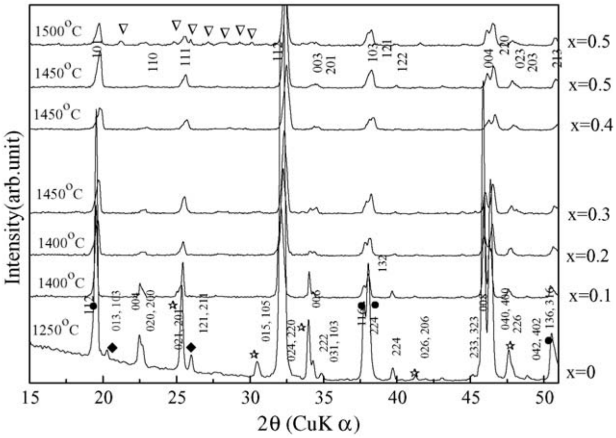

Fig. 2. XRD patterns of sintered $\mathrm{La}_{(2-x)/3}\mathrm{Na}_x(\mathrm{Mg}_{1/2}\mathrm{W}_{1/2})\mathrm{O}_3$.

Raman spectroscopy was considered to be an ideal tool for probing the degree of cation ordering. Narrow and intense peaks are usually observed for well-ordered structures, and generally sharpness and intensity of the Raman lines may be taken as a measure of the degree of ordering. Four mode bands are active in Raman scattering for cubic phase of complex perovskite: $\mathrm{A}_{1g} + \mathrm{E}_g + 2\mathrm{F}_g$. The existence of ordered regions with particular symmetry allows additional Raman scattering.[10] Fig. 3 shows the Raman scattering spectrum of Na-doped LMW. It shows four main band modes, which correspond to $\mathrm{A}_{1g}$, $\mathrm{E}_g$ and $2\mathrm{F}_g$ ($\mathrm{F}_{1g}$ and $\mathrm{F}_{2g}$), respectively. $\mathrm{A}_{1g}$ and the $\mathrm{F}_{2g}$ mode bands near 425 $\mathrm{cm}^{-1}$ were considered to be very sensitive to the long range ordering of B-site cations, and were only present due to B-site and not A-site ordering.[11] In terms of the line width of $\mathrm{A}_{1g}$ and $\mathrm{F}_{2g}$ shown in Fig. 3, it seems that the B-site domain size decreases with the increase in Na addition when $x \leq 0.4$ and slightly increases again

Table 1
Microwave dielectric properties of sintered $La_{(2-x)/3}Na_x(Mg_{1/2}W_{1/2})O_3$ ceramics sintered at different temperatures

| Composition | S.T. (°C) | Bulk density (g/cm$^3$) | $\varepsilon_\gamma$ | $Q \times f$ (GHz) | $\tau_f$ (ppm/°C) |
|---|---|---|---|---|---|
| $x = 0$ | 1250 | 6.65 | 23.6 | 32500 | −43 |
| $x = 0.1$ | 1400 | 6.30 | 22.6 | 19738 | −33.9 |
| | 1450 | 6.28 | 21.9 | 12591 | |
| $x = 0.2$ | 1400 | 6.23 | 22.6 | 16667 | −26.6 |
| | 1400 | 6.20 | 22.08 | 9550 | |
| $x = 0.3$ | 1450 | 6.22 | 22.88 | 11509 | 45.3 |
| | 1500 | 6.18 | 20.69 | 7749 | |
| | 1400 | 6.10 | 20.9 | 4428 | |
| $x = 0.4$ | 1450 | 6.14 | 22.06 | 5456 | 46.7 |
| | 1500 | 6.03 | 21.1 | 3734 | |
| | 1400 | 5.92 | 20.35 | 4500 | |
| $x = 0.5$ | 1450 | 6.01 | 20.76 | 5693 | 47 |
| | 1500 | 5.98 | 18.6 | 5400 | |

when $x = 0.5$, which is in agreement with the XRD results. The low frequency $F_{1g}$ mode, which was predominantly caused by the motion of A-site ions against the oxygen octahedron should increase with the increase in lighter $Na^+$ ion. This is consistent with the experimental results. It is noted that the lower frequency band near by $F_{1g}$ mode marked with arrow on the Raman scattering of pure LMW ($x = 0$), which is due to the long range ordering of A-site cations, diminishes when $x \geq 0.1$. It may be related to the decrease of long range ordering of A-site cation and ordered domain size with the increase in Na addition, which is in agreement with the XRD analysis. The $E_g$ mode bands centered at about 300 cm$^{-1}$ corresponding to the internal vibration of oxygen octahedron is observed to split when $x \geq 0.3$, which is due to lowering of the symmetry in some region. This is in agreement with the XRD analysis that the structure is changed from orthorhombic to monoclinic phase at $x = 0.3$. Further structure analysis should be taken by TEM.

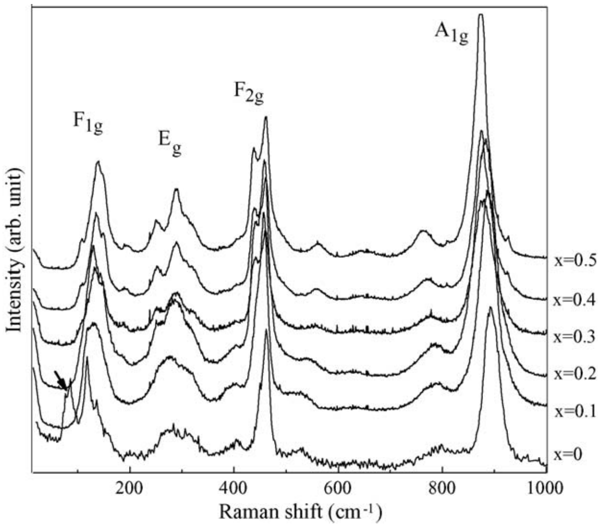

Fig. 3. Raman spectrum of sintered $La_{(2-x)/3}Na_x(Mg_{1/2}W_{1/2})O_3$ ceramics.

Table 1 illustrates the microwave dielectric properties of Na-doped samples. For comparison the microwave dielectric properties of pure LMW are also presented.[8] It shows that the addition of $Na^+$ does not affect the dielectric permittivity greatly except for the sample with $x = 0.5$ sintered at 1500 °C/2 h. The slight change of dielectric permittivity with $x$ value is mainly caused by the variation of bulk density. The relatively lower dielectric permittivity for sample with $x = 0.5$ sintered at 1500 °C/2 h is mainly caused by the appearance of second phase (Fig. 2) and low bulk density (93.1% TD). The $Q \times f$ values of Na-doped samples are affected greatly by the sintering temperature. The maximum $Q \times f$ value of each doped sample corresponding to the sample with highest bulk density decreases with the $x$ value. This is mainly related to the decrease of A/B-site cations ordering degree and domain size, although the concentration of A-site vacancies decreases with the $x$ value. For the sample with $x = 0.5$, its $Q \times f$ value increases slightly although the A/B-site ordering degree increases compared to the sample with $x = 0.4$. This may be related to its low bulk density. The temperature coefficient of resonant frequency $\tau_f$ is negative when $0 \leq x < 0.3$ and changed into positive value when $0.3 \leq x < 0.5$, which may have been originated from changes in structure that might accompany the ordering state reactions. This interpretation is in agreement with the references.[12]

## 4. Conclusions

The structure and microwave dielectric properties of the Na-doped $La_{(2-x)/3}Na_x(Mg_{1/2}W_{1/2})O_3$ ($x = 0$–$0.5$) system have been invested. The structure changed from orthorhombic when $0 \leq x < 0.3$ to monoclinic phase when $0.3 \leq x \leq 0.5$. The doping of Na does not cause great alteration in the dielectric constant. The $Q \times f$ value of the Na-doped sample is sensitive to processing conditions, and decreases with the increase in $x$ value, although the concentration of A-site vacancies decreases with increasing $x$, which may be ascribed to the decrease of A/B-site ordering degree with the increase in $x$. The temperature coefficient of resonant frequency changed from negative values into positive values with the increase in $x$ value.

## References

1. Desu, S. B. and O'Bryan, H. M., Microwave loss quality of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics. *J. Am. Ceram. Soc.*, 1985, **68**(10), 546–551.
2. Davies, P. K., Tong, J. and Negas, T., Effect of ordering-induced domain boundaries on low loss $Ba(Zn_{1/3}Ta_{2/3})O_3$–$BaZrO_3$. *J. Am. Ceram. Soc.*, 1997, **80**(7), 1727–1740.
3. Kim, I. S., Jung, W. H., Inaguma, Y., Nakamira, T. and Itoh, M., Dielectric properties of A-site deficient perovskite-type lanthanum–calcium–titanium oxide solid solution system $(1-x)La_{2/3}TiO_3$–$x$$CaTiO_3$ $(0.1<x<0.96)$. *Mater. Res. Bull.*, 1995, **30**, 307–316.
4. Park, J. H., Woodward, P. M. and Parise, J. B., Predictive modeling and high pressure-high temperature synthesis of perovskites containing monovalent silver. *Chem. Mater.*, 1998, **10**, 3092–3100.
5. Park, J. H., Woodward, P. M., Parise, J. B. and Reeder, R. J., Synthesis, structure, and dielectric properties of $(Bi_{1/2}Ag_{1/2})TiO_3$. *Chem. Mater.*, 1999, **11**, 177–183.
6. Laguna M. A., Sanjuan M. L. Varez A. and Sanz J., Lithium dynamics and disorder effects in the Raman spectrum of $La_{(2-x)/3}Li_xTiO_3$, *Phys. Rev.*, 2002, **B66**, 054301-1–054301-7.
7. Inaguma, Y., Katsumata, T., Itoh, M. and Morii, Y., Crystal structure of a Lithium ion-conducting perovskite $La_{(2-x)/3}Li_xTiO_3$ $(x=0.05)$. *J. Solid State Chem.*, 2002, **166**, 67–72.
8. Bian, J. J., Gao, H. B. and Wang, X. W., Microwave dielectric properties of $(Pb_{(1-3x)/2}La_x)(Mg_{1/2}W_{1/2})O_3$. *Mater. Res. Bull.*, 2004, **39**(13), 2127–2135.
9. Torii, Y. and Sekiya, T., Crystallographic and dielectric properties of the $Pb_2(MgW)O_6$–$La_{1.33}$ $(MgW)O_6$ solid solution. *Mater. Res. Bull.*, 1981, **16**, 1153–1158.
10. Siny, I. G., Tao, R. S. and Bahalla, A. S., Raman spectroscopy of Mg–Ta order–disorder in $Ba(Mg_{1/3}Ta_{2/3})O_3$. *J Phys. Chem. Solids*, 1998, **59**, 181–195.
11. Zheng, H., Reanney, I. M., Csete de Gyorgfalva, G. D. C., Ubic, R., Yarwood, J., Seabra, M. P. and Ferreura, V. M., Raman spectroscopy of $CaTiO_3$-based perovskite solid solution. *J. Mater. Res.*, 2004, **19**(2), 488–495.
12. Colla, E. L., Reanney, I. M. and Setter, N., Effect of structural changes in complex perovskites on the temperature coefficient of the relative permittivty. *J. Appl. Phys.*, 1993, **75**(5), 3414–3425.