

## Microwave Dielectric Properties of $\text{LaPO}_4$ Ceramics Synthesized by a Hydrothermal Method

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**Abstract:** Lanthanum orthophosphate ( $\text{LaPO}_4$ ) ceramics were obtained by using hydrothermal prepared powders and solid-state reaction prepared powders in a sintering temperature range of 1030–1340°C and 1300–1460°C, respectively. The sintering and microwave dielectric properties of hydrothermal processed  $\text{LaPO}_4$  ceramics were compared with those of solid-state reaction processed  $\text{LaPO}_4$ . The results showed that hydrothermal processed  $\text{LaPO}_4$  had a higher sinterability and better microwave dielectric properties due to its much finer particle size when compared with solid-state reaction processed  $\text{LaPO}_4$ . The best microwave dielectric properties of the hydrothermal processed  $\text{LaPO}_4$  ceramics were obtained when the ceramics sintered at 1260°C for 2 h with a permittivity  $\sim 10.2$ , a  $Q \times f$  value about 129704 GHz (at 10.2 GHz) and a temperature coefficient value of  $-58.6 \times 10^{-6}/^\circ\text{C}$ . The  $Q \times f$  value of hydrothermal processed  $\text{LaPO}_4$  ceramics was 2.47 times greater than that of solid-state reaction processed  $\text{LaPO}_4$  ceramics, while the sintering temperature of the former was 140°C lower than that of the latter in the literature.

**Key words:** microwave dielectric properties; hydrothermal synthesis; lanthanum orthophosphate; sintering behavior

With the rapid development of the wireless communications, the requirements for the properties of the microwave devices grow rapidly, which in turn stimulate to improve the properties of the microwave dielectric ceramics. Advanced substrate materials for microwave integrated circuits require a low dielectric constant ( $\epsilon_r$ , about 10), a high quality factor ( $Q \times f$ ), and a near-zero temperature coefficient of resonance frequency ( $\tau_f$ )<sup>[1-2]</sup>. In most cases, microwave dielectric materials are produced by a conventional solid-state reaction process. Unfortunately, a fatal shortcoming of this process is that the as-prepared samples are inhomogeneous with large particle size and low surface area due to the high-temperature sintering. Compared with the solid-state method, hydrothermal reactions are usually performed in moderate conditions, do not require expensive precursors or equipment, and may yield homogeneous crystalline powders. Since sintering behavior and dielectric properties partly depend on the crystalline structure, the grain size, and the morphology, the preparation of the powders with nanostructures is of prime importance for microwave ceramics<sup>[3-4]</sup>.

Lanthanum orthophosphate ( $\text{LaPO}_4$ ) is used as a new sensor<sup>[5]</sup>, composite<sup>[6]</sup>, laser host<sup>[7]</sup>, fibre coating<sup>[8]</sup> and phosphor<sup>[9-19]</sup> due to its novel chemical and physical properties. When doped with cerium and terbium<sup>[20-22]</sup>,  $\text{LaPO}_4$

is a commercially applied lamp phosphor. The low frequency ( $10^2$ – $10^7$  Hz) dielectric properties of  $\text{LaPO}_4$  were reported by Narasimha, *et al.*<sup>[23]</sup> early in 1988. Bregiroux, *et al.*<sup>[24]</sup> investigated the effect of  $\text{LaP}_3\text{O}_9$  powder preparation on the sintering behavior and the microstructural structure of  $\text{LaPO}_4$ . Recent study showed that  $\text{LaPO}_4$  ceramics, produced by a conventional solid-state reaction process, had a high  $Q \times f$  value (64556 GHz) and low permittivity ( $\epsilon_r = 10.4$ ), which was suitable for the application of dielectric resonators and substrates for high-temperature superconducting microwave devices<sup>[25]</sup>. However the synthesis temperature and sintering temperature of solid-state reaction processed  $\text{LaPO}_4$  were too high, which were about 1100°C and 1400°C, respectively. As reported, there are several approaches to reduce the sintering temperature of dielectric ceramics: the addition of low melting point compounds such as  $\text{B}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{CaF}_2$  and  $\text{V}_2\text{O}_5$ , the development of new compositions, and chemical processing to produce smaller particle size of starting powders<sup>[26-27]</sup>. To date there are few reports on the  $\text{LaPO}_4$  ceramics using hydrothermal prepared powders. In this present work,  $\text{LaPO}_4$  ceramics was made by hydrothermal processed powders in order to reduce the sintering temperature. The dielectric properties of the hydrothermal processed ceramics were compared with

those of  $\text{LaPO}_4$  prepared by a solid-state reaction method. The sintering and microwave dielectric properties of  $\text{LaPO}_4$  ceramics at various sintering temperatures were studied.

## 1 Experimental procedure

All the reagents used in the experiments are analytically pure without further purification. The typical hydrothermal process was as follows: Lanthanum nitrate ( $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ) and distilled water were put into a beaker at  $20^\circ\text{C}$  under the magnetic stirring until  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  were dissolved. The mixed solution was adjusted to  $\text{pH} = 5.0$  with dilute  $\text{NH}_3$  and dilute  $\text{HNO}_3$  using a pH meter. Then the solution was transferred into a Teflon lined steel autoclave. The autoclave was maintained at  $150^\circ\text{C}$  for about 15 h. After the autoclave was naturally cooled to room temperature, the products were washed several times by water and alcohol. The products were placed in an oven at  $80^\circ\text{C}$  for 8 h and then calcined at  $900^\circ\text{C}$  for 2 h. The as-calcined powders (hereafter denoted as H- $\text{LaPO}_4$ ) were pressed into cylinders (12 mm in diameter and 4 mm in height) in a steel die with 5wt% PVA binder addition under a uniaxial pressure of 15 MPa. The cylinders were sintered in the temperature range from  $1030^\circ\text{C}$  to  $1340^\circ\text{C}$  for 2 h to obtain the H- $\text{LaPO}_4$  ceramics. For comparison,  $\text{LaPO}_4$  ceramics was also prepared by using solid-state reaction processed  $\text{LaPO}_4$  powders: Stoichiometric mixtures of  $\text{La}_2\text{O}_3$  and  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  were put into an agate mortar, grounded in ethanol for 2 h, and then calcined at  $1025^\circ\text{C}$  for 2 h. The as-calcined powders were re-grounded and re-calcined at  $1025^\circ\text{C}$  for 2 h (hereafter denoted as SSR- $\text{LaPO}_4$ ). The SSR- $\text{LaPO}_4$  powders were used to prepared ceramics using a similar process to the H- $\text{LaPO}_4$  ceramics except the sintering temperature.

Powder X-ray diffraction (XRD) patterns were taken at

room temperature by using a Bruker D8 Advance diffractometer with  $\text{Cu K}\alpha$  radiation. Microstructures of sintered ceramics were observed on the fractured surface with scanning electron microscopy (SEM) (JSM-6390A, JEOL, Japan). The size and morphology of hydrothermal nanoparticles were determined by a transmission electron microscope (TEM) (JEM-3010, JEOL, Japan) at 300 kV and the chemical composition of the material was analyzed by energy dispersive X-ray analysis (EDAX). The apparent densities of sintered ceramics were measured by Archimedes' method. The relative densities were calculated to be the ratio of the apparent densities and the theoretical densities. Dielectric behaviors at microwave frequency were measured with the  $\text{TE}_{01\delta}$  shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA) in the temperature range from  $25^\circ\text{C}$  to  $85^\circ\text{C}$ . The temperature coefficient of resonant frequency  $\tau_f$  (TCF) was calculated with the following formula:

$$\text{TCF} = \frac{f_{85} - f_{25}}{f_{25}(85 - 25)} \text{ ppm}/^\circ\text{C} \quad (1)$$

Where  $f_{85}$  and  $f_{25}$  were the  $\text{TE}_{01\delta}$  resonant frequencies at  $85^\circ\text{C}$  and  $25^\circ\text{C}$ , respectively.

## 2 Results and discussion

Figure 1 showed TEM, high-resolution TEM images and EDAX spectrum of the H- $\text{LaPO}_4$  powders. As shown in Fig. 1(a), the product was primarily composed of nanoparticles ranging in size from about 10 nm to 200 nm, with mean widths of 20 nm and lengths of up to about 200 nm. The high-resolution TEM image in Fig. 1(b) showed that the nanoparticles were structurally uniform with interplanar spacing of about 0.522 nm, 0.351 nm, which corresponded to the (101) and (020) lattice spacing of monoclinic  $\text{LaPO}_4$ . The particles showed well-defined lattice fringes with different spacing, indicating that hydrothermal methods yield materials of high crystallinity. EDAX re

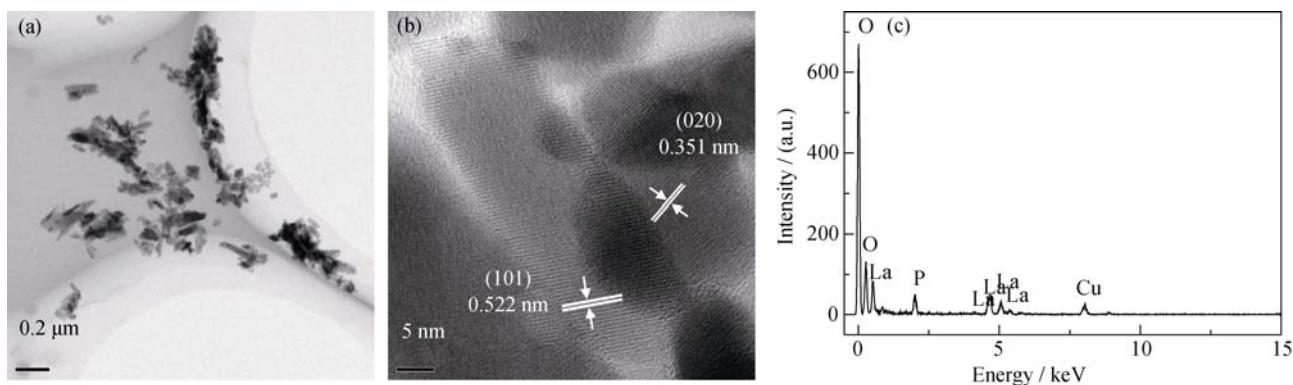


Fig. 1 TEM, high-resolution TEM images and EDAX spectrum of the H- $\text{LaPO}_4$  powders  
(a) TEM images; (b) High-resolution TEM images; (c) EDAX spectrum

sults in Fig. 1(c) gave the atomic ratio of 14.04:14.28:71.28 (1.0:1.017:5.077) for La:P:O, which was close to the ideal value of 1:1:4.

Figure 2 showed the XRD patterns of the  $\text{LaPO}_4$  powders and ceramics under different conditions. All reflection peaks of the hydrothermal processed powders in Fig. 1(a) showed a single phase of  $\text{LaPO}_4$  and could be indexed to the monoclinic  $\text{LaPO}_4$  (space group:  $P2_1/n$ , No. 14) with cell parameters  $a = 0.6837$  nm,  $b = 0.7077$  nm, and  $c = 0.651$  nm (JCPDS 32-0493). The peaks were broadened, indicating that the H- $\text{LaPO}_4$  particles were nanosized which was in good agreement with the results of Curve 2(a). The crystallite size was calculated from the XRD line broadening using Scherrer relationship,  $D_{hkl} = 0.89\lambda / (\beta_{hkl} \cos\theta)$ , where  $hkl$  was the index of the diffracting plane,  $D_{hkl}$  was the average thickness of the crystal in a direction normal to the diffracting plane  $hkl$  in nm,  $\beta_{hkl}$  was the crystallite size contribution to the peak width (full width at half maximum) in radians,  $\lambda$  was the wavelength of X-rays. The crystallite sizes,  $D_{101}$ ,  $D_{200}$ , and  $D_{120}$  were calculated to be 17 nm, 27 nm, and 29 nm, respectively. For SSR- $\text{LaPO}_4$  powders calcined at  $1025^\circ\text{C}$ , major phase of  $\text{LaPO}_4$  with impurities phase of the  $\text{LaP}_3\text{O}_9$  (JCPDS 33-0717, denoted by the asterisk) were observed, as shown in Curve 2(b). The behavior of SSR- $\text{LaPO}_4$  was similar to that of the samples prepared by an aqueous precipitation method. The phase  $\text{LaP}_3\text{O}_9$  was formed at about  $950^\circ\text{C}$  from a reaction between  $\text{LaPO}_4$  and  $(\text{NH}_4)_2\text{HPO}_4$  residual species adsorbed at the particle surface, which decomposed by incongruent melting in the  $1050\text{--}1235^\circ\text{C}$  temperature range<sup>[28-29]</sup>. Curve 2c-d showed the XRD patterns of the H- $\text{LaPO}_4$  ceramics at  $1260^\circ\text{C}$  and SSR- $\text{LaPO}_4$  ceramics at  $1300^\circ\text{C}$ . Both the two ceramics showed a single phase of  $\text{LaPO}_4$  and the intensities were strong which meant high crystallinity. No additional peaks were found in the patterns, indicating that there were no other impurity phases in the  $\text{LaPO}_4$  ceramics synthesized by two methods. Single

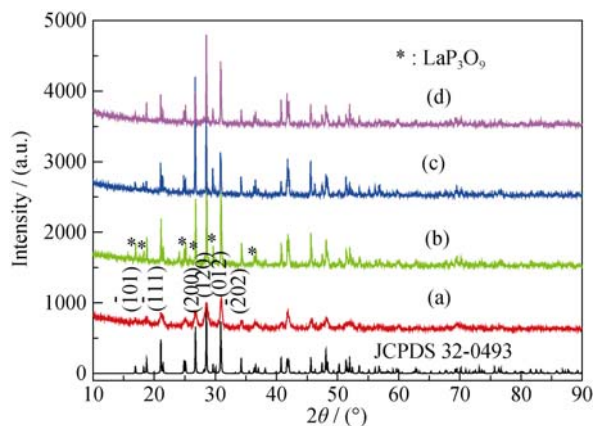


Fig. 2 XRD patterns of the  $\text{LaPO}_4$  powders and ceramics (a) H- $\text{LaPO}_4$  powders; (b) SSR- $\text{LaPO}_4$  powders calcined at  $1025^\circ\text{C}$ ; (c) H- $\text{LaPO}_4$  ceramics sintered at  $1260^\circ\text{C}$ ; (d) SSR- $\text{LaPO}_4$  ceramics sintered at  $1300^\circ\text{C}$

phase of  $\text{LaPO}_4$  can be synthesized by solid-state method when the temperature was  $1235^\circ\text{C}$ , which was  $335^\circ\text{C}$  higher than that in the hydrothermal process.

Figure 3 showed the SEM photos of fractured surfaces of the H- $\text{LaPO}_4$  ceramics sintered from  $1140^\circ\text{C}$  to  $1340^\circ\text{C}$  for 2 h. At all temperatures, dense microstructures with almost no pores in the grain boundary were revealed in the samples, indicating that  $\text{LaPO}_4$  was easy to be densified. The increase of sintering temperature seemed to promote the grain growth and the density of the samples. The grain size, which was several tens of microns, was not homogeneous in all cases. Many pits with 1-2 microns or less were systematically found in the samples sintered from  $1140^\circ\text{C}$  to  $1340^\circ\text{C}$ , as shown in Fig. 3(a)-(e), which might be due to intergranular pores<sup>[24]</sup>. When the temperature reached  $1340^\circ\text{C}$ , relative fine grains were grown, as shown in Fig. 3(f).

Figure 4 showed the relative densities of  $\text{LaPO}_4$  ceramics by the two methods as a function of sintering temperature. In all cases, the relative densities were greater than 92%, indicating that  $\text{LaPO}_4$  was easy to be densified when the temperature between  $1100^\circ\text{C}$  and  $1460^\circ\text{C}$ . As can be seen, the relative densities of H- $\text{LaPO}_4$  ceramics increased to a maximum of 97.1% at  $1300^\circ\text{C}$  and thereafter it decreased with increasing sintering temperature. This sintering temperature was very close to the  $\text{LaPO}_4$  prepared by a precipitation method<sup>[30]</sup>. The relative densities of SSR- $\text{LaPO}_4$  ceramics slightly decreased from 95.8% at  $1300^\circ\text{C}$  to 92.1% at  $1460^\circ\text{C}$  with increasing sintering temperature.

The microwave dielectric properties of  $\text{LaPO}_4$  ceramics by the two methods were compared in Fig. 5. Since

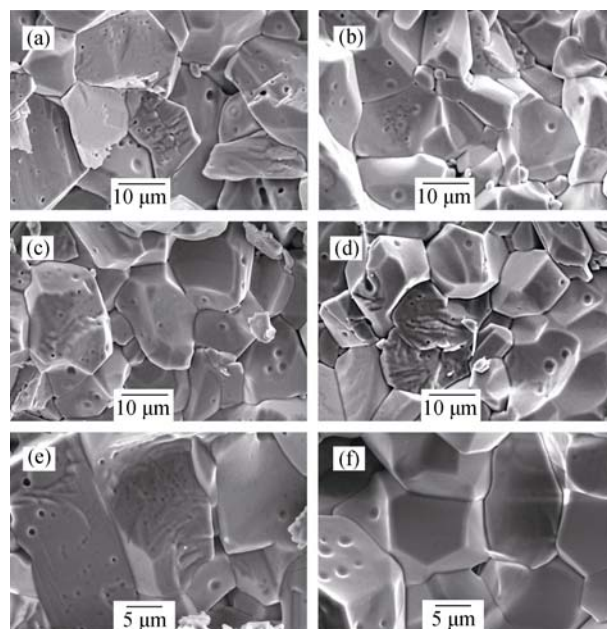


Fig. 3 SEM images of fractured surfaces of the H- $\text{LaPO}_4$  ceramics sintered at different temperatures (a)  $1140^\circ\text{C}$ ; (b)  $1180^\circ\text{C}$ ; (c)  $1220^\circ\text{C}$ ; (d)  $1260^\circ\text{C}$ ; (e)  $1300^\circ\text{C}$ ; (f)  $1340^\circ\text{C}$

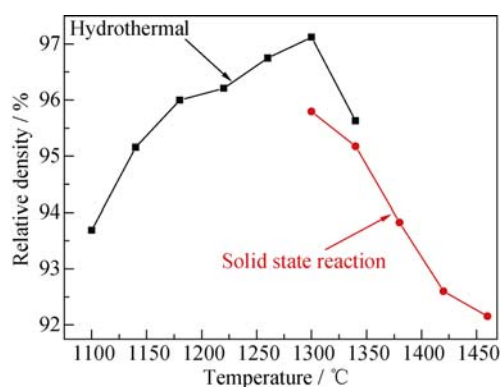


Fig. 4 Relative densities of H- $\text{LaPO}_4$  ceramics and SSR- $\text{LaPO}_4$  ceramics

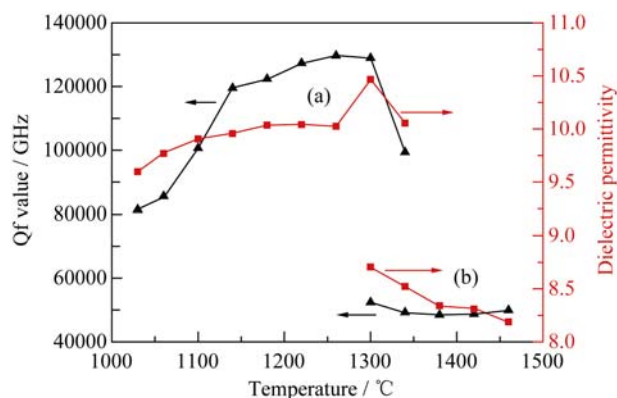


Fig. 5 Microwave dielectric properties (permittivity,  $Q \times f$  value) of H- $\text{LaPO}_4$  ceramics and SSR- $\text{LaPO}_4$  ceramics as a function of sintering temperature  
(a) H- $\text{LaPO}_4$  ceramics; (b) SSR- $\text{LaPO}_4$  ceramics

permittivity was related to density, almost same trend of the density was observed for the permittivity. The permittivity of H- $\text{LaPO}_4$  ceramics firstly increased to a maximum of 10.47 at 1300°C and thereafter it decreased with increasing the sintering temperature. The permittivity of SSR- $\text{LaPO}_4$  ceramics decreased with increasing sintering temperature. In addition, the  $Q \times f$  values at different sintering temperatures also showed a slightly different but similar trend with that of the density. The maximum  $Q \times f$  value of the H- $\text{LaPO}_4$  ceramics was found at 1260°C, which was 129704 GHz (at 10.2 GHz). The degradation of  $Q \times f$  when the temperature was higher than 1260°C might be attributed to the rapid grain growth as observed in Fig. 3(e)-(f). Therefore, the optimum sintering temperature of H- $\text{LaPO}_4$  ceramic was 1260°C. The temperature coefficient value of H- $\text{LaPO}_4$  ceramic sintered at 1260°C was measured to be  $-58.6 \times 10^{-6}/^\circ\text{C}$ . Compared with the H- $\text{LaPO}_4$  ceramics, the SSR- $\text{LaPO}_4$  ceramics had a smaller permittivity and an obvious smaller  $Q \times f$  value, which were  $\epsilon_r = 8.7$  and  $Q \times f = 52421$  GHz (at 10.6 GHz) at maximum, respectively. The temperature coefficient value of SSR- $\text{LaPO}_4$  ceramics sintered at 1300°C was measured to be  $-62.7 \times 10^{-6}/^\circ\text{C}$ . The  $\tau_f$  values of the ceramics by the two methods and the

literature were similar and the difference was not significant. The difference of the dielectric properties between the H- $\text{LaPO}_4$  ceramics and SSR- $\text{LaPO}_4$  ceramics might be attributed to the different size of the two powders. Due to the finer nanoparticle size of the H- $\text{LaPO}_4$  powders, the H- $\text{LaPO}_4$  ceramics showed much higher sinterability than the SSR- $\text{LaPO}_4$  ceramics. Compared with the results of Cho, *et al.*<sup>[25]</sup>, the  $Q \times f$  value of SSR- $\text{LaPO}_4$  ceramics in this work was slight less. However the  $Q \times f$  value of H- $\text{LaPO}_4$  ceramics in this work was nearly 2 times than that of Cho, *et al.*, and the sintering temperature was 140°C lower. Therefore the hydrothermal method was undoubtedly a useful process for producing powders with fine particle size in the manufacturing the  $\text{LaPO}_4$  ceramics.

### 3 Conclusion

Single phase of  $\text{LaPO}_4$  powders was synthesized by a hydrothermal method. The properties of H- $\text{LaPO}_4$  ceramics are better than that of SSR- $\text{LaPO}_4$  ceramics. The best properties of the H- $\text{LaPO}_4$  ceramics with  $\epsilon_r = 10.2$ , and  $Q \times f = 129,704$  (at 10.2 GHz) were obtained at sintering temperature 1260°C for 2 h. The  $Q \times f$  value of H- $\text{LaPO}_4$  ceramics was 2.47 times more than that of SSR- $\text{LaPO}_4$  ceramics. In addition, the H- $\text{LaPO}_4$  powders had a higher sinterability than that of the SSR- $\text{LaPO}_4$  powders. The sintering temperature of H- $\text{LaPO}_4$  ceramics was 140°C lower than that of SSR- $\text{LaPO}_4$  ceramics. The hydrothermal method was considered to be an appropriate method in the manufacture of materials for microwave applications.

### References:

- [1] WU S P, CHEN D F, JIANG C, *et al.* Synthesis of monoclinic  $\text{CaSnSiO}_5$  ceramics and their microwave dielectric properties. *Mater. Lett.*, 2013, **91**: 239–241.
- [2] LI Z F, WU W J, LIU F, *et al.* Microwave dielectric properties of  $\text{La}_4\text{Ti}_3\text{O}_{12}$  ceramics. *Mater. Lett.*, 2014, **118**: 24–26.
- [3] BANG J. Microwave dielectric properties of  $\text{MgCo}_2(\text{VO}_4)_2$  ceramics synthesized by a Sol-Gel method. *J. Eur. Ceram. Soc.*, 2007, **27(13/14/15)**: 3855–3859.
- [4] HUANG C L, WANG J J, HUANG C Y. Sintering behavior and microwave dielectric properties of nano  $\alpha$ -alumina. *Mater. Lett.*, 2005, **59(28)**: 3746–3749.
- [5] ZHOU Y Z, ZHANG H Y, XIE H D, *et al.* A novel sensor based on  $\text{LaPO}_4$  nanowires modified electrode for sensitive simultaneous determination of dopamine and uric acid. *Electrochim. Acta*, 2012, **75**: 360–365.
- [6] WANG R G, PAN W, CHEN J, *et al.* Synthesis and sintering of  $\text{LaPO}_4$  powder and its application. *Mater. Chem. Phys.*, 2003, **79(1)**: 30–36.
- [7] GUO D L, HU C G, XI Y. Synthesis and magnetic property of Fe doped  $\text{LaPO}_4$  nanorods. *Appl. Surf. Sci.*, 2013, **268**: 458–463.



- [8] CHEN P, MAH T I. Synthesis and characterization of lanthanum phosphate sol for fibre coating. *J. Mater. Sci.*, 1997, **32(14)**: 3863–3867.
- [9] MI K, NI Y H, XU Y W, *et al.* A simple mixed-solvothermal route for LaPO<sub>4</sub> nanorods: synthesis, characterization, affecting factors and PL properties of LaPO<sub>4</sub>:Ce<sup>3+</sup>. *J. Colloid. Interf. Sci.*, 2011, **356(2)**: 490–495.
- [10] VISTOVSKYY V, MITINA N, SHAPOVAL A, *et al.* Luminescence properties of LaPO<sub>4</sub>-Eu nanoparticles synthesized in the presence of surface active oligoperoxide as template. *Opt. Mater.*, 2012, **34(12)**: 2066–2070.
- [11] JUNG H K, OH J S, SEOK S I, *et al.* Preparation and luminescence properties of LaPO<sub>4</sub>:Er,Yb nanoparticles. *J. Lumin.*, 2005, **114(3/4)**: 307–313.
- [12] PARK S M, ZHEN Z, PARK D H. Preparation of Eu-doped LaPO<sub>4</sub> films using successive-ionic-layer-adsorption-and-reaction. *Mater. Lett.*, 2010, **64(16)**: 1861–1864.
- [13] YANG Y. Synthesis and luminescent properties of LaPO<sub>4</sub>:Eu<sup>3+</sup> microspheres. *Mater. Sci. Eng. B*, 2013, **178(11)**: 807–810.
- [14] LI Y, ZHENG Y H, WANG Q M, *et al.* LaPO<sub>4</sub>:Eu<sup>3+</sup> *in situ* formed in polymeric gels and its photophysical properties. *Opt. Mater.*, 2012, **34(7)**: 1019–1022.
- [15] GAO R, QIAN D, LI W. Sol-Gel synthesis and photoluminescence of LaPO<sub>4</sub>:Eu<sup>3+</sup> nanorods. *Trans. Nonferrous Met. Soc. China*, 2010, **20(3)**: 432–436.
- [16] LI G H, LI L L, LI M M, *et al.* Facile synthesis and luminescent properties of LaPO<sub>4</sub>:Eu<sup>3+</sup>, Sm<sup>3+</sup> nanorods via a designed two-step hydrothermal method. *Mater. Chem. Phys.*, 2012, **133(1)**: 263–268.
- [17] YANG M, YOU H P, LIANG Y L, *et al.* Morphology controllable and highly luminescent monoclinic LaPO<sub>4</sub>:Eu<sup>3+</sup> microspheres. *J. Alloys Compd.*, 2014, **582**: 603–608.
- [18] FANG Y P, XU A W, SONG R Q, *et al.* Systematic synthesis and characterization of single-crystal lanthanide orthophosphate nanowires. *J. Am. Chem. Soc.*, 2003, **125(51)**: 16025–16034.
- [19] BYRAPPA K, DEVARAJU M K, PARAMESH J R, *et al.* Hydrothermal synthesis and characterization of LaPO<sub>4</sub> for bio-imaging phosphors. *J. Mater. Sci.*, 2008, **43(7)**: 2229–2233.
- [20] NIU N, YANG P P, WANG Y, *et al.* LaPO<sub>4</sub>:Eu<sup>3+</sup>, LaPO<sub>4</sub>:Ce<sup>3+</sup>, and LaPO<sub>4</sub>:Ce<sup>3+</sup>, Tb<sup>3+</sup> nanocrystals: Oleic acid assisted solvothermal synthesis, characterization, and luminescent properties. *J. Alloys Compd.*, 2011, **509(6)**: 3096–3102.
- [21] YANG P P, QUAN Z W, LI C X, *et al.* Solvothermal synthesis and luminescent properties of monodisperse LaPO<sub>4</sub>:Ln (Ln = Eu<sup>3+</sup>, Ce<sup>3+</sup>, Tb<sup>3+</sup>) particles. *J. Solid State Chem.*, 2009, **182(5)**: 1045–1054.
- [22] MEYSSAMY H, RIWOTZKI K, KORNOWSKI A, *et al.* Wet-chemical synthesis of doped colloidal nanomaterials: particles and fibers of LaPO<sub>4</sub>:Eu, LaPO<sub>4</sub>:Ce, and LaPO<sub>4</sub>:Ce,Tb. *Adv. Mater.*, 1999, **11(10)**: 840–844.
- [23] NARASIMHA B, CHOUDHARY R N P, RAO K V. Dielectric properties of LaPO<sub>4</sub> ceramics. *J. Mater. Sci.*, 1988, **23(4)**: 1416–1418.
- [24] BREGIROUX D, LUCAS S, CHAMPION E, *et al.* Sintering and microstructure of rare earth phosphate ceramics REPO<sub>4</sub> with RE = La, Ce or Y. *J. Eur. Ceram. Soc.*, 2006, **26(3)**: 279–287.
- [25] CHO I S, CHOI G K, AN J S, *et al.* Sintering, microstructure and microwave dielectric properties of rare earth orthophosphates, RePO<sub>4</sub> (Re = La, Ce, Nd, Sm, Tb, Dy, Y, Yb). *Mater. Res. Bull.*, 2009, **44(1)**: 173–178.
- [26] ZHOU H F, LIU X B, CHEN X L, *et al.* Preparation, phase structure and microwave dielectric properties of CoLi<sub>2/3</sub>Ti<sub>4/3</sub>O<sub>4</sub> ceramic. *Mater. Res. Bull.*, 2012, **47(5)**: 1278–1280.
- [27] XIA W S, LI L X, ZHANG P, *et al.* Effects of CaF<sub>2</sub> addition on sintering behavior and microwave dielectric properties of ZnTa<sub>2</sub>O<sub>6</sub> ceramics. *Mater. Lett.*, 2011, **65(21/22)**: 3317–3319.
- [28] LUCAS S, CHAMPION E, BREGIROUX D, *et al.* Rare earth phosphate powders RePO<sub>4</sub>·nH<sub>2</sub>O (Re=La, Ce or Y)—Part I. Synthesis and characterization. *J. Solid State Chem.*, 2004, **177**: 1302–1311.
- [29] HATADA N, NAGAI T, NOSE Y, *et al.* Reinvestigation of the phase equilibria in the La<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> system. *J. Phase Equilib. Diff.*, 2013, **34(3)**: 196–201.
- [30] RAJESH K, SIVAKUMAR B, KRISHNA PILLAI P, *et al.* Synthesis of nanocrystalline lanthanum phosphate for low temperature densification to monazite ceramics. *Mater. Lett.* 2004, **58(11)**: 1687–1691.

## 水热法合成陶瓷 LaPO<sub>4</sub> 的微波介电性能

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**摘 要:** 通过水热法和固相反应法制备了 LaPO<sub>4</sub> 粉体, 分别在 1030~1340℃ 和 1300~1460℃ 范围内对粉体进行了烧结, 得到了 LaPO<sub>4</sub> 陶瓷, 研究对比了两种方法得到的陶瓷的烧结行为和微波介电性能。结果表明: 和固相法相比, 水热法得到的陶瓷由于粉体粒径小更易于烧结, 微波介电性能更优; 在 1260℃ 条件下烧结 2 h 得到的水热法陶瓷具有最好的微波介电性能: 介电常数为 10.2,  $Q \times f$  值为 129704 GHz ( $f = 10.2$  GHz), 谐振频率温度系数值为 -58.6 ppm/℃; 水热法陶瓷的  $Q \times f$  值为固相法的 2.47 倍, 烧结温度比固相法低 140℃。

**关 键 词:** 微波介电性质; 水热合成; LaPO<sub>4</sub>; 烧结性

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