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Temperature tunable photonic bandgap in PLZT inverse opals

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Abstract Three-dimensional periodic microstructure of air spheres in (Pb,La)(Zr,Ti)O_3 (PLZT) matrix were synthesized by sol–gel process using synthetic opals as template. The micro-region optical reflection spectra of PLZT inverse opal photonic crystals have been on-line measured continuously with treating temperature increasing. It demonstrates that the bandgap blue-shifts with treating temperature increasing based on the diminishment of periodical size in sintering process. The tunable band gap in PLZT inverse opals should be of high interest in device application.

Keywords PLZT · Temperature · Photonic crystal · Tunable

1 Introduction

There is currently a great interest in the three-dimensional photonic crystals due to their potential applications in the area of manipulating photonics [1–5]. For many applications it is advantageous to obtain some degree of tunability of the photonic bandgap structure, so tunable PCs is proposed as a important concept [6–9], in which the photonic band gap can be tuned as desired by controlling parameters such as the refractive index, periodicity, or space filling factor through the change of electric filed [8–10], magnetic field [11], temperature [12, 13], and the deformation of shape [14]. Some groups demonstrated that it was possible to fine-tune the bandgap properties of synthetic opal photonic crystals of silica or polymer colloids by sintering or annealing the samples at elevated temperature [15–17]. But there is no report about the shifts of bandgap with treating temperature increasing measured in real-time.

On the other hand, Lead Lanthanum Zirconate Titanate (PLZT) Ceramics are transparent ferroelectrics with strong electro-optic effects and possesses a high refractive index (2.4–2.6) in visible wavelength. PLZT materials are of great interest for the fabrication of electric devices such as non-volatile memories, piezoelectric resonators, pyroelectric detectors and electro-optic devices [18, 19]. Recently, the PLZT were used as matrix to fabricate inverse opal photonic crystals [20] and a photonic bandgap was found in this system [21, 22].

Herein, we measured the reflective spectra of the PLZT inverse opals on line at different temperature in the whole continuous heating process. The main aim of this study is to investigate the influence of sintering temperatures on photonic crystals' band gaps in a whole heat-treating process. Our study showed the peaks of reflective spectra are blue-shifted continuously with sintering temperature increasing.

2 Experimental procedure

2.1 Samples preparation

PLZT inverse opals were synthesized by sol–gel process using synthetic opals as it was reported before [20]. In this approach, monodispersed polystyrene microspheres (Bangs Lab, USA) are first assembled into a face-center-cubic array (opals) with the (111) plane parallel to the substrate by

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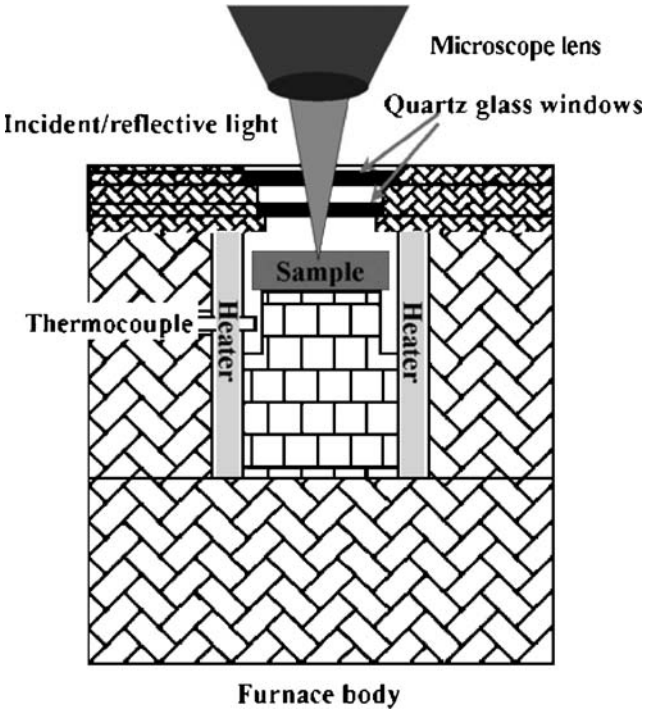

Fig. 1 Experimental setup for the measurement of reflective spectrum of PLZT inverse opals versus the temperature

gravitational sedimentation. In the second step, the PLZT precursor was prepared by sol–gel method according to the formula $Pb_{0.91}La_{0.09}(Zr_{0.65}Ti_{0.35})_{0.9775}O_3$. The starting raw materials were zirconium propoxide ($Zr(OC_3H_7)_4$, Aldrich Chemical Company, Inc.), titanium butoxide ($Ti(OC_4H_9)_4$ Beijing JinLong chemical Reagents Company), lead acetate ($Pb(C_2H_3O_2)_2{\cdot}3H_2O$, Beijing Chemical factory), lanthanum nitrate ($La(NO_3)_3{\cdot}6H_2O$ Beijing chemical factory). The PLZT precursor was used to infiltrate into the voids of the template due to capillary force. After infiltration, the specimens were placed in the humidity chamber to let the sol react with water vapor through hydrolysis and condensation. In the finial stage, the polystyrene spheres were removed by heating samples in a rate of 50 °C/h to sintering temperature (between 400 and 900 °C) and being kept for 3 h.

2.2 Characterization

The microstructure of the PLZT inverse opals was investigated by field emission scanning electron microscopy (FESEM JEOS 6301F). The temperature depended reflective spectra of the PLZT inverse opals were measured using micro-region UV-visible spectroscopy consisting of an optical microscope (Olympus BX50) and an ultraviolet-visible spectrometer (Ocean Optics USB2000). Because we hope to measured the reflective spectra of the PLZT inverse opals on line in the whole heating process, a pint-sized furnace was designed and set under the object lens of microscope, as it was shown in Fig. 1. The PLZT inverse opal sample is placed at the center of the furnace. The incident and reflect light form/to the object lens can travel through the double-layer quartz glass windows without block. To modulate the temperature, the heating power is controlled by alternating current transformer.

3 Results and discussion

3.1 Gelation and sintering

After the PLZT sol was filled in the opal template, the samples were placed in the humidity chamber to let the precursor react with water vapor. In this process, the precursor was gelated through hydrolysis and poly-condensation process at proper conditions with reactions below:

$$\chi\mathrm{HOAc} + \mathrm{Ti(OR)_4} \rightarrow \mathrm{Ti(Zr)Ac_\chi(OR)_{8-\chi}} \quad (1)$$

$$\mathrm{Ti(Zr)Ac_\chi(OR)_{8-\chi}} + \mathrm{H_2O} \xrightarrow{\text{hydrolysis}} \mathrm{Ti(Zr)Ac_\chi(OH)_{8-\chi}} \quad (2)$$

$$\mathrm{Ti(Zr)Ac_\chi(OH)_{8-\chi}} \xrightarrow{\text{polycondensation}} \text{gel} \quad (3)$$

The PLZT Gel was sintered after gelation. It is amorphous when heat-treated at below 400 °C while it formed the desirable perovskite phase heat-treated at 600 °C [20]. The

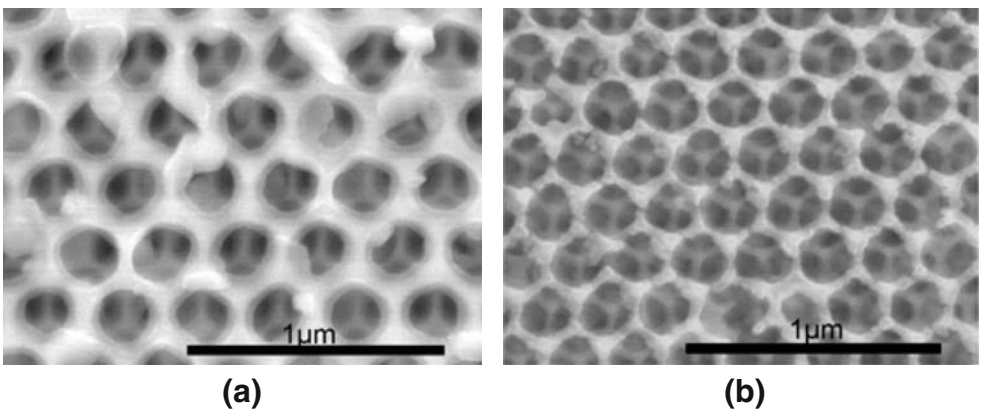

Fig. 2 SEM images of the same samples sintered at 400 °C (**a**) and 750 °C (**b**) respectively

reflective light of our PLZT inverse opal sample is easy to be observed by naked eye. The samples exhibit shiny yellow color sintered at 450 °C and green-yellow light sintered at 750 °C. The bright colors are caused by the optical Bragg diffraction from the crystal planes.

3.2 Microstructure of PLZT inverse opals

Figure 2 shows SEM images of the PLZT inverse opals sintered at 400 and 750 °C respectively. There are hexagonal domains where hollow regions of air spheres are very well ordered in a triangular lattice. There are three dark regions inside each hollow region, which are corresponded to the air spheres of the underlying layer. The SEM images show that the PLZT inverse opals sintered at 400 °C [Fig. 2(a)] and 750 °C [Fig. 2 (b)] have different lattice parameters, the center-to-center distance between the air spheres are about 300 and 250 nm respectively. To compare the Center-to-center distances of PLZT inverse opals sintered at different temperatures, the samples were sintered at 400, 500, 600, 700 and 750 °C respectively, and the distances were measured in SEM images. All of the results were list in Table 1. This demonstrates that a significant shrink occur in sintering process.

As we known, the optical properties of the PLZT inverse opals is determined by the controlling parameters such as the refractive index, periodicity, and space filling factor. The change of sintering temperature can tune all of these parameters at the fabrication process without reversibility. Between 400 and 750 °C, the PLZT inverse opals are densified by the crystallization and grain growth together with the consolidation of nano-pores and the removal of internal hydroxyl species. The integrate effect of all above factors leads to the change of refractive index, periodicity, and space filling factor in PLZT inverse opals. In the sintering process, the shrinking is the determinant factor resulting in the color of reflective light shifts from yellow to blue.

3.3 Temperature tunable reflective spectra of PLZT inverse opals

Figure 3 gives the reflective spectra of PLZT inverse opals measured in the sintering process from 100 to 1000 °C. The

Table 1 The center-to-center distance of the PLZT inverse opals treated at different temperature.

Sintering temperature (°C)	Center-to-center distance (nm)
400	301
500	293
600	275
700	266
750	250

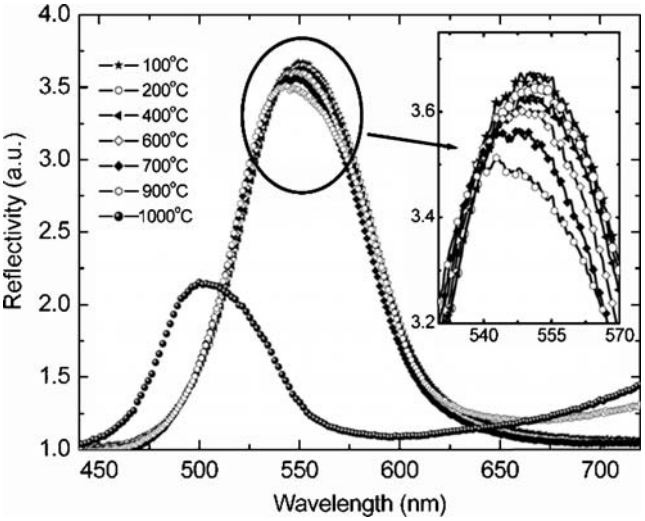

Fig. 3 Reflective spectra of the samples (c) heat-treated from 100 to 1000 °C

PLZT sample was pre-calcined at 500 °C to remove the opal template before it was set in the furnace for micro-region reflective spectra measurement. Clear bandgaps in reflective spectra were detected in both of the PLZT inverse opals treated at different temperature. As the sintering temperature increased, the bandgap properties of the photonic crystals displayed obvious changes: (1) between 100 and 400 °C, the bandgap position is stable at 550 nm. With temperature increasing from 400 to 900 °C, its bandgap position shifted towards shorter wavelengths continuously (blueshift) from 550 to 540 nm. When the sintering temperature increases from 900 to 1000 °C, a significant shift of bandgap position was observed from 540 to 500 nm, and the intensity of reflective peak at 1000 °C distinctly decreased to half of that at 900 °C. The giant shift of bandgap positions and drop of reflective intensity is corresponding with a rapid shrinking process between 900 and 1000 °C. We suppose this is not only caused by the densifying process with the consolidation of nano-pores and the removal of internal hydroxyl species; but also the inordinate growth of perovskite crystal grains which destroys the order structure of inverse opal in part.

4 Conclusion

The PLZT inverse opals were fabricated as tunable photonic crystals that allowed one to conveniently tune the bandgap properties of the photonic crystal without reversibility by changing sintering temperature. It should be of use in photonic device application. We also supply a on-line method to measure the temperature depended reflective spectrum of photonic crystals.

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