Scaling Behaviour, Optical and Photoluminescence Properties of La$_2$Hf$_2$O Films with Annealing Treatments

Z Li$^{1, a}$, C Y Ma$^{2, b}$ and Q Y Zhang$^2$

$^1$Department of Mechanical Engineering, Dalian University, Dalian 116622, People’s Republic of China
$^2$Key Laboratory of Materials Modification by Laser, Ion and Electron beams (Dalian University of Technology) Ministry of Education, Dalian 116024, People’s Republic of China

Corresponding author Email: $^a$lizhi@dlu.edu.cn; $^b$chunyuma@dlut.edu.cn;

Abstract. The structure, optical and PL characteristics of La$_2$Hf$_2$O$_7$ (LHO) films deposited by rf sputtering and subsequently annealed at 800-950°C are studied by x-ray diffraction (XRD), atomic force microscopy (AFM), UV/VIS spectrophotometry, and photoluminescence (PL) measurements. Structural studies indicate that LHO films with 37% atomic ratio of La/(La+Hf) have shown high crystallization temperature higher than 900°C. The scaling behaviors of AFM topographical profiles were analysed using one-dimensional power spectral density analysis (1DPSD). For as-grown films, only one growth exponent $\alpha$ is evidenced. For annealed films two different slopes $\alpha_1$ and $\alpha_2$ were observed, indicating distinct growth dynamic in LHO films. The estimated optical band gap was found to be in the range of 5.18-5.55 eV. Photoluminescence (PL) spectra of LHO films in visible light range (i.e., at 412~435 nm and 468 nm, respectively) can be attributed to localized states at the band tails and oxygen vacancies, respectively. This PL can be diminished or decreased by adjusting structural properties i.e. the amount of oxygen vacancies or some other kind of structure defects in the films by thermal annealing processing.

1. Introduction

A$_2$B$_2$O$_7$ complex oxides (A is a rare earth cation, B is a transition element such as Hf,Zr,Ti) attract plenty of interests due to their excellent thermo-mechanical stability, good catalytic efficiency, high ionic conductivity, unique magnetic properties, high efficiency as luminescence hosts, along with a strong resistance to amorphization under irradiation. These suitable properties render A$_2$B$_2$O$_7$ materials potentially good prospect for applications such as thermal barrier coating[1,2], electro- and photo-catalysts[3], magnetic materials[4], solid electrolytes for high temperature oxide fuel cells[5], defect-induced fluorescent materials and neutron absorbers in nuclear reactors[6,7], etc.

There exist in two major structures of A$_2$B$_2$O$_7$ complex oxides: the ordered pyrochlore having Fd-3m space group and the disordered fluorite with Fm-3m space group, which depends on ionic radius ratio of $r_A$ and $r_B(r_A/ r_B)$. According to Subramanian et al.[8], pyrochlore structure steadily exists when $r_A/ r_B =1.46$~1.78. The A$_2$B$_2$O$_7$ pyrochlore structure mainly belongs to long range order of cationic positions and anionic vacancies, where the A sites are occupied by trivalent cations located in the centre of distorted cubes of oxygen anions, and the B sites are occupied by tetravalent transition metal ions situated in the centre of oxygen octahedral[9].
Interestingly, La$_2$Hf$_2$O$_7$ ($r_{La}^{3+}/r_{Hf}^{4+}=1.63$) usually existing in just one crystal form of the pyrochlore structure has been considered for the application of novel density radiation detectors due to a high density (7.84 g/cm$^3$) and large effective atomic number (64)[10-12]. Meanwhile, amorphous La$_2$Hf$_2$O$_7$ is widely studied as a promising high-k candidate because of its rather lower defect densities, higher dielectric constant (20-30) and better thermal stability [13, 14]. Here, we focus on the amorphous and pyrochlore forms of La$_2$Hf$_2$O$_7$ films. Several methods have been explored for the formation of La$_2$Hf$_2$O$_7$ films, such as magnetron sputtering [14, 15], atomic layer deposition [16], metal organic chemical vapour deposition [17], pulsed laser deposition and molecular beam epitaxy [13, 18], etc. Among these methods, the sputtering method is a very useful technique because it provides large area coatings with good thickness uniformity, high film quality and strong mechanical durability.

Despite the wide interest for amorphous and pyrochlore La$_2$Hf$_2$O$_7$, the detailed study on structure, optical and PL characteristics of La$_2$Hf$_2$O$_7$ films due to the annealing process has not yet been reported. In this work, we report the observation of room temperature photoluminescence (PL) of La$_2$Hf$_2$O$_7$ films in visible light range (i.e., at 412–435 nm and 468 nm, respectively) due to localized states at the band tails and oxygen vacancies during deposition and possible approaches to decrease or diminish the PL of the films by adjusting structural properties i.e. the amount of oxygen vacancies or some other kind of structure defects in the films by thermal annealing processing. Also, the dynamics of the evolution of the surface morphology due to the annealing process was analysed using the one-dimensional power spectral density method (1DPSD).

2. Experimental details
La$_2$Hf$_2$O$_7$ (LHO) films were deposited onto n-type Si (001) wafers and optical grade quartz substrates by rf magnetron sputtering in an Ar/O$_2$ atmosphere. All the substrates were carefully cleaned by ultrason in sequence in acetone, ethanol, and de-ionized water baths. N-type Si wafers were HF dipped to remove the native silicon oxide layer immediately before deposition, followed by rinsing in de-ionized water and dried under flowing N$_2$ gas. The vacuum chamber was evacuated to 8.0×10$^{-4}$ Pa using a turbomolecular pump. LHO films were deposited by the co-sputtering of La and Hf targets (60 mm diameter, 3 mm thick and purity higher than 99.99%). The two disc-shaped targets are inclined toward the substrate at an angle of about 45$^\circ$. The target to substrate distance is about 80 mm, and the substrate is rotated at 3 rounds / min for uniform film deposition. The flow of the Ar and O$_2$ and their ratio (30:5) was controlled using standard mass flow meters. Before each deposition, the Hf and La targets were presputtered for 10 min using Ar alone with shutter above the targets closed. The RF power of La and Hf targets was fixed at 100 W and 120 W, respectively. The deposition was carried out for 2 hours with sputtering pressure of 0.5 Pa. The substrate was not heated intentionally. Pure HfO$_2$ films were also prepared for comparison. Post-deposition annealing (PDA) was performed in air from 850 to 950$^\circ$C for 30 min.

The composition of LHO films is measured by an energy-dispersive x-ray (EDX) spectrometer. The crystalline structure of the films was analysed by x-ray diffraction (XRD) using unresolved Cu K$\alpha$ radiation (wavelength $\lambda_{x-ray} = 0.1542$ nm, D/Max 2400). A typical 20 scan range of 25-80$^\circ$ and a step size of 0.02$^\circ$ were employed. Atomic force microscopy (AFM) on a CSPM5500 scanning probe microscope was used in contact mode with a scan frequency of 1.0 Hz to measure surface morphologies and roughness of the films. The measurement of transmittance (T) and reflectance (R) at normal incidence of the films deposited on quartz substrates were performed in the wavelength range of 190-1100 nm using a Lambda-35 UV/VIS spectrometer. Photoluminescence (PL) spectra were recorded by using a Fluorescence spectrometer (Edinburgh Instr.Model-FLS920) with a 450W Xenon lamp as excitation source.

3. Results and discussion

3.1. X-ray diffraction
Figure 1 shows XRD patterns for the LHO films with as-grown and after PDA in air from 850 to 950°C for 30 min. EDX analysis (not shown) of the LHO films gave an estimation of 0.37:1 for the atomic ratio of La/(La+Hf). A typical XRD pattern of as grown HfO$_2$ films is also shown. Generally,

![Figure 1 XRD patterns of LHO films.](image)

HfO$_2$ and La$_2$O$_3$ films start to crystalline below 600°C [19, 20], while the incorporation of La in periodic HfO$_2$ shows higher crystallization temperature than pure HfO$_2$ or La$_2$O$_3$. In Figure 1, the XRD curve of the pure HfO$_2$ film indicates the polycrystalline nature of samples. The peaks can be unambiguously assigned to monoclinic HfO$_2$ as labelled in Figure 1 (referenced JCPDS 74-1506). It is clear that as-grown LHO films are amorphous and remain amorphous up to 900°C. This is probably due to the La acting as a network modifier, which stabilizes the amorphous nature of its metal oxide. It is also believed that the incorporation of La breaks the periodicity and/or inhibits the continuous crystal growth of HfO$_2$ during PDA. Increasing the annealing temperature to 950°C, LHO films crystalline to be the cubiclike pyrochlore structure, and this is clearly distinguished from the monoclinic structure of HfO$_2$. A diffraction peak around $2\theta = 29.4^\circ$ has been observed, which is the strongest diffraction peak of pyrochlore structure having Fd-3m space group, corresponding to the (111) planes. The other four weak diffraction peaks at 34.1$^\circ$, 49.1$^\circ$, 58.4$^\circ$ and 61.2$^\circ$ can also be observed, corresponding to the (200), (220), (311) and (222) planes of La$_2$Hf$_2$O$_7$, respectively. This indicates a polycrystalline LHO film with predominant (111) orientation on Si (100) is formed after annealing at 950°C, suggesting that surface and interfacial energy minimization may provide an additional driving force for the preferential growth of the (111) oriented grain.

3.2. Surface morphology and scaling analysis
Figure 2 shows AFM images of the LHO films prepared by rf magnetron sputtering on Si (100) wafers. By visual inspection of these figures two morphological features are recognized. The first feature is that the granules of various scales exist in the films and are distributed evenly in some ranges. The second feature is that the evolution of root mean square roughness (rms) as a function of annealing temperature up to 950°C, where valleys, mountains, and island clusters become bigger as films are annealed. The results (Ra and rms) have been listed in Table 1. It can be see that the average roughness Ra and rms values increased as the annealing temperature is increased. The above analyses indicate average roughness Ra and rms are strongly affected by the degree of aggregation and cluster size of the films.

The surface morphology has an irregular geometry with self-affine structure determined by the thermodynamic environment. Power spectral density (PSD) analysis has been widely used for quantitative surface characterizations with spatial resolution of the roughness and correlations between roughness and specific surface features [21-23]. We analyse the scaling behaviour of the AFM topological profile using the one-dimensional power spectral density (1DPSD).

\[
1DPSD(f) = \frac{1}{L} \left| \int_{L}^{f} y(x) e^{2\pi i x} dx \right|^2
\]  

in units of nm³, where \( y(x) \) is the topographical profile, \( L \) is the scan length, \( f \) is the spatial frequency, and \( x \) is the fast scan direction of an area scan. The scaling behaviour of surfaces can be analysed from their power density spectra. In a finite frequency range, a self-affine structure exhibits the power law decay

\[
1DPSD = K_0 f^{-\gamma}
\]

where \( K_0 \) is a constant dependent on the system and \( \gamma \) is related to the roughness exponent (\( \alpha \)) by \( \alpha = (\gamma - d)/2 \), where the line scan dimension \( d = 1 \).

The log-log 1DPSD plots of AFM topographical morphologies corresponding to the as grown and annealed samples in Figure 2 are presented in Figure 3. The 1DPSD plots exhibit several distinct regions, a frequency-independent region at low frequency (long length scales), and a frequency-dependent region at higher frequency (short length scales). Interestingly, for the annealed LHO films, Figure 3 (b)-(d), this higher frequency behaviour is composed of two constant-slope regions with different roughness exponents. The dependence can be fitted by \( f^{-\gamma_1} \) and \( f^{-\gamma_2} \) power law decays at high and intermediate frequencies, respectively. According to the scaling theory, the appearance of an
intermediate region (\( \gamma_2 \)) indicates a new coarsening mechanism, such as grain growth and oriented growth effects.

The roughness exponents were extracted from the two constant-slope 1DPSD regions based on Eq. (2). As listed in Table 1, the only roughness exponent \( \alpha_1 \) for as grown LHO films is about 0.93, while two roughness exponents with \( \alpha_1 \) (the higher-frequency region) and \( \alpha_2 \) (the intermediate-frequency region) for our annealed LHO films are found. In addition, for amorphous LHO films annealed at 850-900°C, the two roughness exponents \( \alpha_1 \) and \( \alpha_2 \) are nearly constant, with values in the range 1.21~1.23 and 0.2~0.25, respectively. With the films annealed at 950 °C presenting a clear transition from amorphous to crystalline structures, \( \alpha_2 \) decreases from 0.2 to 0.1, while \( \alpha_1 \) increase from 1.21 to 1.39.

These roughness exponents are similar to previous theoretical results that have identified two types of growth front dynamic scaling behaviour. The first type has a self-affine growth morphology characterized by a roughness exponent \( 0<\alpha<1 \). This behaviour has been described as a balance between roughening mechanisms, such as random fluctuations in the depositing flux, and smooth processes, such as diffusion at the growth front so that the local structure remains unchanged. The second type is anomalous dynamic scaling, which gives \( \alpha \geq 1 \). In this situation the roughening fluctuations and the smooth effects cannot quite reach a balance. We suggest that for our annealed LHO films, the intermediate-frequency self-affine region with \( \alpha_2 = 0.1-0.25 \) is characterized by balance between grain and oriented growth induced roughening and longer range diffusion processes so that the local structure remains unchanged, while the high frequency region with \( \alpha_1 =1.21-1.39 \) corresponds to anomalous dynamic scaling behaviour dominated by surface diffusion.

The frequencies of transition marked by arrows in Figure 3 between the various regimes of 1DPSD behaviour are of interest since they infer some physically meaning correlation lengths. The first correlation length (\( L_{C1} \)) is defined by the (inverse) frequency of transition between the high-frequency and intermediate-frequency regions, which marks the beginning of the surface diffusion part of 1DPSD=\( K_0f^{-\gamma} \). For annealed LHO films, the \( L_{C1} \) values (about 150 nm) extracted at points of 1DPSD slope change are approximately constant which represents the minimum lateral feature stable against surface diffusion. Surface features with lateral dimensions smaller than those defined by \( L_{C1} \) will gradually vanish by surface diffusion. Similarly, the second correlation length (\( L_{C2} \)) indicates the transition between the low-frequency plateau and the intermediate-frequency self-affine region in the 1DPSD, which therefore defines the mean lateral extension of a surface feature stable against surface diffusion. \( L_{C2} \) values for LHO films are also listed in Table 1, it can be seen that \( L_{C2} \) values increase with increasing annealing temperature.

**Table1.** Surface roughness (\( R_a \) and \( \text{rms} \)) and morphological characteristics from analysis of 1DPSD plots for LHO films.

| Sample | As-grown | Annealing temp.850°C | Annealing temp.900°C | Annealing temp.950°C |
|--------|----------|---------------------|---------------------|---------------------|
| AFM    | \( R_a \)(nm) | 0.75 | 1.06 | 1.23 | 1.70 |
|        | \( \text{rms} \)(nm) | 1.01 | 1.49 | 1.64 | 2.28 |
|        | \( L_{C1} \)(nm) | - | 148 | 150 | 149 |
|        | \( L_{C2} \)(nm) | 242 | 383 | 452 | 465 |
| \( \gamma_2 \) | - | 1.50±0.1 | 1.40±0.1 | 1.19±0.09 |
| \( \gamma_3 \) | 2.85±0.02 | 3.45±0.05 | 3.41±0.03 | 3.78±0.04 |
| \( \alpha_1 \) | 0.93 | 1.23 | 1.21 | 1.39 |
| \( \alpha_2 \) | - | 0.25 | 0.20 | 0.10 |

3.3. Optical characterizations
Optical transmission spectra of the films were measured using an UV/visible spectrophotometer. As shown in Figure 4 (a), All LHO films exhibit very high transparency in the visible optical region. LHO films exhibits higher transmittance than HfO$_2$ films. This observation indicates the high quality and transparent nature of LHO films with almost zero absorption losses. Moreover, it can be seen that the transmittance maxima of amorphous LHO films annealed at 900 °C are slightly higher than that of pyrochlore LHO films annealed at 950 °C. In comparison with that of pure HfO$_2$ film, it can be found that the absorption edge shifts to the shorter wavelength for annealed LHO, which is correlated to the change in the optical band gap value. The optical absorption coefficient of the films is evaluated using the relation:

$$\alpha = \frac{1}{t} \ln \left[ \frac{T}{(1-R)^2} \right]$$  \hspace{1cm} (3)

where $T$ is the transmittance, $R$ the reflection, and $t$ the film thickness. In the $E_g$ region (high absorption) or above the fundamental absorption edge, the absorption follows a power law of the form

$$\alpha(h\nu) = B(h\nu - E_g)^2$$  \hspace{1cm} (4)

where $h\nu(E)$ is the energy of the incident photon, $B$ the absorption edge width parameter, and $E_g$ the band gap. The $(\alpha h\nu)^{1/2}$ versus $E$ plots for LHO films are shown in Figure 4 (b). The linear fit of the data indicates the characteristic feature of LHO with an indirect band gap. Extrapolation of the linear region of the plot to zero absorption i.e., $(\alpha h\nu)^{1/2} = 0$, provides the value of $E_g$. The extracted band gap of as grown LHO is 5.18 eV, which is close to the band gap value 5.2 eV of pure HfO$_2$ film. The band gap energies of 850°C and 900°C annealed LHO films are 5.43eV and 5.45eV, respectively, and that of pyrochlore LHO films annealed at 950°C increases to 5.55 eV.

An increase in the optical band gap after annealing at 850-900 °C compared to that of as grown LHO is obtained, which can be attributed to a decrease in the density of tail adjacent to the band edge. It is known that dangling bands are formed in amorphous films during deposition and they will lead to the formation of defects which produces localized states in amorphous solids. During the heat treatment, a great fraction of saturated bands are produced. The formed saturated bonds will reduce the number of defects and decrease the density of localized states in the band structure. On the other hand, this study confirms that band gap energy of the pyrochlore LHO films with more long range ordering is larger than that of the amorphous LHO film. XRD measurement clearly indicates that grain growth on LHO films annealed at 950°C. The observed blue shifting of band gap in pyrochlore LHO films can be mainly ascribed to the contribution of quantum confinement.
3.4. Photoluminescence characterization

Photoluminescence (PL) is a very sensitive and effective tool for the investigation of electron structure of defect centers [24, 25]. Figure 5(a) shows the PL spectra recorded at room temperature for LHO films as grown and after annealed at 850 °C and 950°C, respectively, using photoluminescence excitation of 280 nm. A broad ultraviolet PL signal is present with a peak value at 308 nm (4.0 eV) in all LHO samples. This PL is considered to be excited due to the interband absorption. In addition to the ultraviolet PL peak, visible PL peaks in the range 468 nm (2.65 eV) to 412 nm (3.0 eV) are observed for the case of the as grown sample, which can be fitted based on three Gaussian peaks PL peaks at 468 nm (2.65 eV), 435 nm (2.85) and 412 nm (3.0 eV).

The measured intensity of a PL peak generally depends on various hardly controllable factors, such as a subtle difference in the mutual angles among the photon source, the sample, and the detector. This sometimes makes it difficult to compare the PL intensities among different samples. Therefore, the PL intensities around 3.0 eV, 2.85 eV and 2.65 eV are shown in Figure 5 (b) after being normalized by the highest peak around 4.0 eV. It is noted that the PL peak at 468 nm (2.65 eV) is not present in the thermally annealed samples. La2Hf2O7 crystallizes in the cubic pyrochlore structure. The structure can be viewed as an interpenetrating network of HfO6 and LaO8 polyhedra whose geometries are dependent upon the amount of oxygen in the lattice [26]. A broad emission band peaking at about 468 nm found in a spectrum of as grown LHO films can be attributed to oxygen vacancies. The additional air annealing may enable oxygen to fill in the existing vacancies. Decreasing the concentration of O vacancies with in LHO films will thus lead to a decrease or disappear in the PL intensity. These results are indicative of the formation of more oxygen vacancies during the film deposition.

The PL peaks at 412nm (3.0eV) and 435nm (2.85) are present in common with all as grown (amorphous) and annealed (amorphous or crystalline) samples. The as grown and annealed samples have crystallinity from amorphous to crystalline. However, the difference in crystallinity is not reflected in the PL properties. As mentioned above, oxygen vacancies are certainly not responsible for the present PLs. Furthermore, the thermal treatment decreases their PL intensities as shown in Figure 5 (b). It seems that some structural change induced by the thermal treatment extinguishes localized states at the band tails due to defects, although the details are unknown. Therefore, The PL peaks at

![Figure 5 (a) Photoluminescence spectra of for LHO films. (b) Changes in PL intensity around 412 nm, 435 nm and 468 nm. Note that the PL intensity was normalized by the intensity around 308 nm.](Image)
412 nm (3.0 eV) and 435 nm (2.85 eV) are luminescence inherent in LHO films, and are most likely due to radioactive recombination between localized states at the band tails.

4. Conclusion
In summary, we investigated the structure, scaling behaviour, optical and PL characteristics of LHO films. LHO films have shown high crystallization temperature ( > 900°C). Quantitative surface characterization for the films in the annealing process by 1DPSD analysis identified two types of growth front dynamic scaling behavior. For annealed LHO films, the intermediate-frequency self-affine region with $\alpha_2 = 0.1$–0.25 is characterized by balance between grain growth induced roughening and longer range diffusion processes, while the high frequency region with $\alpha_1 = 1.21$–1.39 corresponds to anomalous dynamic scaling behavior dominated by surface diffusion. Photoluminescence (PL) spectra show that for as grown LHO films a broad emission band peaking at about 468 nm can be attributed to oxygen vacancies, indicating the formation of more oxygen vacancies during the film deposition. In addition, the PL peaks at 412 nm (3.0 eV) and 435 nm (2.85 eV) are luminescence inherent in LHO films, and are most likely due to radioactive recombination between localized states at the band tails. This PL can be diminished or decreased by adjusting structural properties i.e. the amount of oxygen vacancies or some other kind of structure defects in the films by thermal annealing processing.

Acknowledgments
The work is supported by the Fundamental Research Funds for the Central Universities no. DUT19LAB14.

References
[1] Bansal N P and Zhu D M 2007 Mater. Sci. Eng. A45 192-195
[2] Zhang J, Guo X Y, Jung Y G, Knapp, J 2017 Surf.Coat.Technol.323 18-29
[3] Yin X, Li X, Gu W, Wang F, Zou Y, Sun S, Fu Z, Lu Y 2017 ACS Appl. Mater. Interfaces 9 19908-16
[4] Fennell T, Deen P P, Wildes A R, Schmalzl K, Prabhakaran D, Boothroyd A T, Aldus R J, McMorrow D F, Bramwell S T 2009 Scinece 326 415-417
[5] Mahato N, Banerjee A, Gupta A, Omar S, Balani K 2015 Prog.Mater.Sci. 72 141-337
[6] Gupta S K, Sudarshan K, Ghosh P, Srivastava A, Bevara S, Pujari P, Kadam R 2016 J.Mater.Chem.C4 4988-80
[7] Ewing R C, Weber W J, Lian J 2004 J.Appl.Phys. 95 5949-71
[8] Subramanian M, Aravamudan G, Rao C S 1983 Prog.Solid State Chem.15 55-143
[9] Burggraaf A J, van Dijk T, Verkerk M J 1981 Solid State Ionics 5 519-22
[10] Zuniga J P, Gupta S K, Pokhrel M, Mao Y B 2018 New J. Chem. 42 9381-92
[11] Karthik C, Anderson T J, Gout D, Ubic R 2012 J.Solid State Chem. 194 168-172
[12] Nakauchi D, Okada G, Kawaguchi N, Yanagida T 2018 Jpn.J.Appl.Phys .57 100307
[13] Dimoulas A, Vellianitis G, Mavrou G, Apostolopoulos G, Travlos A, Wiemer C, Fanciulli M, Rittersma Z M 2004 Appl.Phys.Lett.85 3205-07
[14] Yamamoto T, Kita K, Kyuno K, Toriumi A 2006 Appl.Phys.Lett.89 032903
[15] Wang X P, Li M F, Chin A, Zhu C X, Shao J, Lu W, Shen X C, Yu X F, Chi R, Shen C et al 2006 Solid-State Electron 50 986-991
[16] He W, Chan D S H, Kim S J, Kim Y S, Kim S T, Cho B J, 2008 J.Electrochem.Soc. 155 G189-G193
[17] Kaichev V V, Smirnova T P, Yakovkina L V, Ivanova E V, Zamoryanskay M V, Saraev A A, Pustovarov V A, Perevalov T V, Gritsenko V A 2016 Mater.Chem.Phys. 175 200-205
[18] Xiong Y H, Tu H L, Du J, Wei F, Zhang X Q, Yang M M, Zhao H B, Chen D P, Wang W W 2013 Appl.Surf.Sci. 283 554-558
[19] Triyoso D H, Hegde R I, Grant J, Fejes P, Liu R, Roan D, Ramon M, Werho D, Rai R, La L B et al 2004 J. Vac. Sci. Technol. B22 2121-27
[20] Ma J W, Lee W J, Cho M H, Lee K M, Sohn H C, Kim C S, Cho H J 2011 J. Appl. Phys. 109 124106
[21] Lita A E, Sanchez J E 1999 J. Appl. Phys. 85 876-882
[22] Li B Q, Kojima I, Zuo J M 2002 J. Appl. Phys. 91 4082-89
[23] Eisenmenger-Sittner C 2001 J. Appl. Phys. 89 6085-91
[24] Papernov S, Brunsman M D, Oliver J B, Hoffman B N, Kozlov A A, Demos S G, Shvydky A, Cavalcante F H M, Yang L, Menoni C S 2018 Opt. Express 26 17608-23
[25] Rastorguev A A, Belyi V I, Smirnova T P, Yakovkina L V, Zamoryanskaya M V, Gritsenko V A, Wong H 2007 Phys. Rev. B 76 235315
[26] Subramanian M A, Aravamudan G, Rao G V S 1983 Prop. Solid State Chem. 15 55-143.