

Dielectric properties of Pr₆O₁₁ nanorods grown chemically at low temperature and atmospheric pressure

Lalit Sharma¹, Partheepan Ganesan², Ranjit Kumar¹, T.D. Senguttuvan¹, Vidya N. Singh^{1*}

¹CSIR- National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi 110012, India

²Department of Civil Engineering, MVGR College of Engineering, Vizianagaram, Andhra Pradesh 535005, India

*Corresponding author. Tel: (+91) 11-45608562; E-mail: singhvn@nplindia.org

Received: 12 February 2015, Revised: 26 May 2015 and Accepted: 30 June 2015

ABSTRACT

Due to high dielectric constant, Pr₆O₁₁ is viewed as a prospective gate dielectric material in decanano metal-oxide-semiconductor devices. In this study, structural, optical and dielectric properties of Pr₆O₁₁ nanorods have been investigated for its possible application as gate dielectric materials for the future generation optoelectronic devices. Pr(OH)₃ nanorod structure was synthesized in an alkaline medium (KOH and NaOH) at a moderate temperature (~188°C) and atmospheric pressure. The Pr(OH)₃ nanorods were converted to Pr₆O₁₁ nanorods by annealing them at 400°C. XRD studies showed that both Pr(OH)₃ as well as Pr₆O₁₁ were highly crystalline. TEM studied showed that the diameter and length of nanorods were ~30 nm and 100 nm, respectively. Optical studies showed that the band gap of these nanorods is 5.31 eV. Dielectric studies showed that dielectric constant at 1 kHz is ~4000. Copyright © 2015 VBRI Press.

Keywords: Pr(OH)₃; Pr₆O₁₁; nanorods; dielectric properties; gate dielectric.

Introduction

Due to their unique physical, chemical, mechanical properties and various potential applications, one-dimensional (1-D) nanostructures have attracted great attention in the recent past [1]. Rare earth compounds have been widely used because they possess outstanding optical, electrical, magnetic and catalytic properties [2]. The rare earth compounds in 1-D nanostructures are poised to exhibit extraordinary physical properties as a result of specific size and shape associated with quantum-confinement effects [3, 4]. Nanowires, nanorods, and nanotubes nanostructures of rare earth compounds; such as, Pr(OH)₃, Tb(OH)₃, Y(OH)₃, Ce(OH)₃, Pr₆O₁₁, Y₂O₃, CeO₂ have been synthesized by hydrothermal technique [5-15]. Praseodymium oxides have been used as promoters, catalysts and stabilizers in combustion, and materials for higher electrical conductivity [16, 17]. It has been reported that there is only a small mismatch between PrO₂ (Pr₆O₁₁ is close to the structure) and Si [18]. Due to high dielectric constant and good epitaxy on Si, Pr₆O₁₁ is viewed as a prospective material to substitute SiO₂ for gate dielectric in decanano metal-oxide-semiconductor devices of the next generation of optoelectronic materials [19]. A few studies on the synthesis of 1-D praseodymium oxide nanostructures have been summarized here. Wang et al. [20] synthesized single crystalline Pr₆O₁₁ nanotubes employing molten salt method in which bulk Pr₆O₁₁ is taken as the Pr source and NaCl/KCl as the salt. Huang et al. [21] also synthesized

Pr(OH)₃ nanorods hydrothermally and obtained Pr₆O₁₁ nanorods by further calcinations. Ma et al. [22, 23] reported microwave-assisted hydrothermal route to prepare Pr(OH)₃ nanorods and obtained Pr₆O₁₁ nanorods by annealing the Pr(OH)₃ nanorods.

One of the major difficulties encountered in these studies is poor crystallinity. In order to utilize the anisotropic properties which are useful for low dimensional applications, it is highly desirable that these materials should be in the form of crystalline 1-D nanostructures [24]

The synthesis of Pr(OH)₃ nanorods has been carried out in a teflon beaker at an atmospheric pressure. Pure and highly crystalline hydroxide and oxide nanorods have been obtained. The products were characterized using X-ray powder diffraction (XRD), UV-Vis spectrophotometer and high-resolution transmission electron microscopy (HRTEM). The dielectric properties of Pr₆O₁₁ nanorods have also been studied.

Experimental

Material synthesis

Highly Crystalline Pr(OH)₃ and Pr₆O₁₁ nanorods were synthesized by an alkaline assisted growth method at atmospheric pressure. In a typical reaction, 0.5g Pr(NO₃)₃.6H₂O, 34g KOH and 25g NaOH were placed in a 250 mL teflon beaker. The beaker was covered and placed in a furnace preheated to 188°C. After the reactants melted,

the beaker was mixed uniformly by shaking it. After 120 h of reaction, the beaker was taken out of the furnace and cooled down to room temperature. The color of the solid product changed to bluish. The solid product obtained was dispersed in deionized water and filtered. It was washed with ethanol and warm deionized water several times in order to remove the alkaline hydroxide present on the surface of the product. To obtain the Pr_6O_{11} nanorods, $\text{Pr}(\text{OH})_3$ nanorods were annealed at 400°C for 40 h.

Characterizations, device fabrications, response measurements

Phase identification of the synthesized powders were carried out using X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation using Philips X'pert PRO-PW 3040) system. The scan speed was $5^\circ/\text{min}$ and the step size was 0.05° . High resolution transmission electron microscopy (HRTEM, Tecnai G20 S-twin) was used to characterize the microstructure of the samples. EDAX attached with it was used for chemical analysis. A drop of the dispersion was put on the TEM grid for the HRTEM measurements. UV-vis spectrum was recorded using a UV-vis spectrophotometer (Perkin Elmer Lambda 900). For the UV-vis spectrum measurements the powders were dispersed in deionized water. The dielectric properties at different frequencies were measured using the LCR bridge circuit. For the dielectric measurement, pellet was made from the annealed powder. The diameter of the pellet was 8.26 mm and its thickness was 1.6 mm. Silver paste was used for making contacts on the pellet.

Results and discussion

X-ray diffraction pattern of as-synthesized as well as annealed powder are shown in **Fig. 1**. The X-ray diffractogram shows sharp diffraction peaks. In **Fig. 1(a)**, peaks having d-values 3.228 \AA , 3.120 \AA , 2.830 \AA , 2.247 \AA , 2.140 \AA , 1.871 \AA , 1.847 \AA , 1.626 \AA , 1.563 \AA , 1.439 \AA , 1.406 \AA , 1.326 \AA and 1.224 \AA correspond to (110), (101), (200), (201), (210), (300), (211), (112), (202), (131), (400), (302) and (401) planes of cubic $\text{Pr}(\text{OH})_3$. In **Fig. 1(b)** peaks having d-values 3.160 \AA , 2.737 \AA , 1.935 \AA , 1.650 \AA , 1.581 \AA , 1.369 \AA , 1.256 \AA , and 1.224 \AA correspond to (111), (200), (220), (311), (220), (400), (331) and (420) planes of Pr_6O_{11} . Thus, crystalline Pr_6O_{11} nanorods can be obtained by sintering the as-prepared hydroxide nanorods (without altering the morphology). For better clarity the XRD patterns have been plotted on the ln scale. In the plot two very insignificant peaks at 30.8 and 45.1° have been observed which may be due to the impurity phases.

Fig. 2(a) shows the TEM and HRTEM image of $\text{Pr}(\text{OH})_3$ nanorods. The diameters of rods are $\sim 30 \text{ nm}$ and length was upto hundreds of nanometers. The EDAX analysis in **Fig. 2(b)** confirms the presence of elements Pr and O of $\text{Pr}(\text{OH})_3$. EDAX analysis shows that as synthesized nanostructure have Pr/O ratio of 26/74, which corresponds to the $\text{Pr}(\text{OH})_3$ phase. **Fig. 2(c)** shows the TEM, HRTEM micrographs and EDAX spectrum of Pr_6O_{11} nanorod which were obtained by annealing $\text{Pr}(\text{OH})_3$ nanorods at 400°C for 40 h. From the TEM micrograph (**Fig. 2(a)**) it is obvious that the diameter of Pr_6O_{11}

nanorods is same as that of $\text{Pr}(\text{OH})_3$ nanorods, i.e. it is nearly 30 nm thick and hundreds of nanometers in length. It is clear from the micrograph that there is no change in the morphology and the dimension of the nanorods due to the phase change from $\text{Pr}(\text{OH})_3$ to Pr_6O_{11} nanorods. The presence of Pr and O was confirmed by EDAX analysis (**Fig. 2d**).

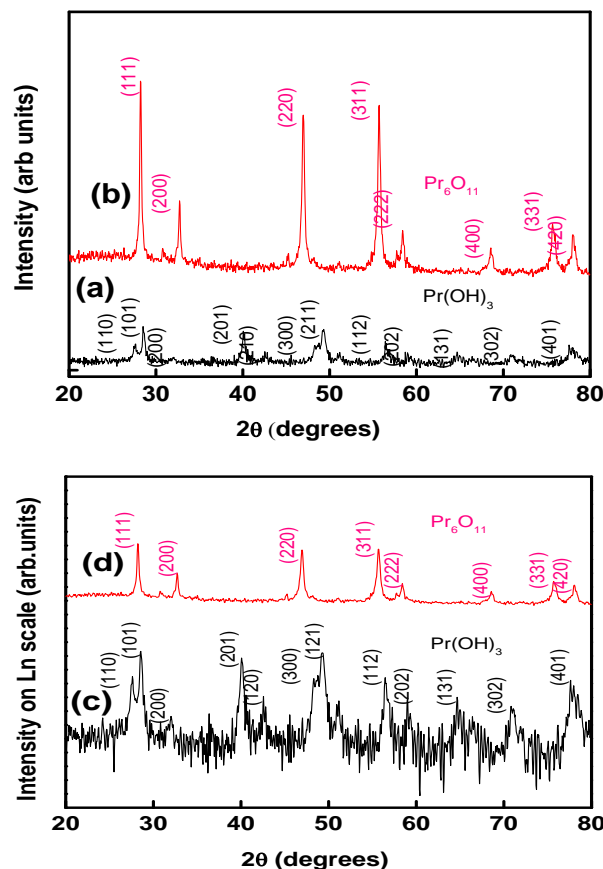


Fig. 1. XRD pattern of (a and c) $\text{Pr}(\text{OH})_3$, and (b and d) Pr_6O_{11} . Figure b and d have been plotted on the ln scale for better clarity.

Fig. 3 shows the optical absorbance spectra of $\text{Pr}(\text{OH})_3$ and Pr_6O_{11} nanorod structures. The band edge is at 233 nm which corresponds to the band gap value of 5.31 eV . A band gap value of this order indicates the insulating nature of Pr_6O_{11} . Thus, this material can be used as a gate dielectric material and therefore its dielectric properties have been studied.

Variation of capacitance and dielectric loss as a function of frequency is shown in **Fig. 4(a)** and variation of dielectric constant (ϵ_r) as a function of frequency ($1 \text{ kHz} - 1 \text{ MHz}$) is shown in **Fig. 4(b)**. The graphs indicate a dispersive behavior at lower frequencies which reflects blocking effects. A dispersive behavior of the dielectric constant may be due to: (i) polarized structure (or space charge polarization) of material and (ii) mobile charge carriers. The room temperature dielectric constant at 1 kHz is measured to be ~ 4000 . The high value of ϵ_r at lower frequency is due to ionic polarization. Further, ϵ_r decreases with increase in frequency. The above behaviors prove dielectric nature of the material. Similar variation in loss tangent ($\tan \delta$) is also observed. Temperature dependent dielectric constant as a function of frequency is shown in

Fig. 4 (c). Result shows that at all frequencies the dielectric constant is increasing with increase in temperature. This is due to the thermally excited space charge polarization as well as dipole orientations which are compatible with applied frequencies.

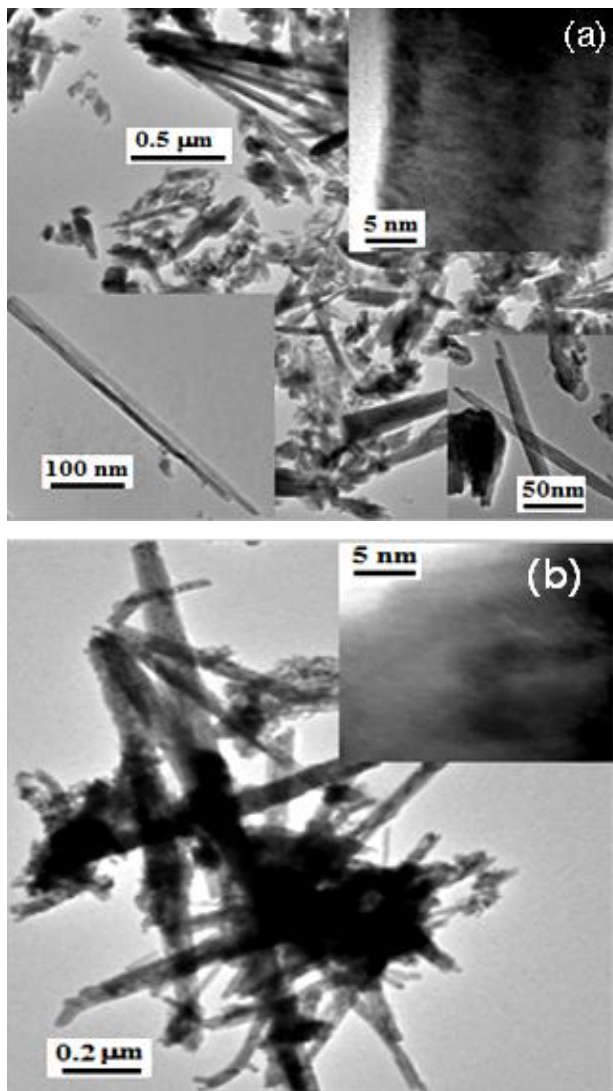


Fig. 2. (a) TEM images of Pr(OH)₃ nanorods having thickness of 30 nm and length upto 150 nm. The HRTEM images shows the lattice spacing of 0.315 nm which corresponds to the (101) plane of Pr(OH)₃ and (b) TEM images of the Pr(OH)₃ nanorods annealed at 400°C for 40 h. It is clear from the micrograph that there is no change in the morphology and the dimension of the nanorods upon annealing due to the phase change.

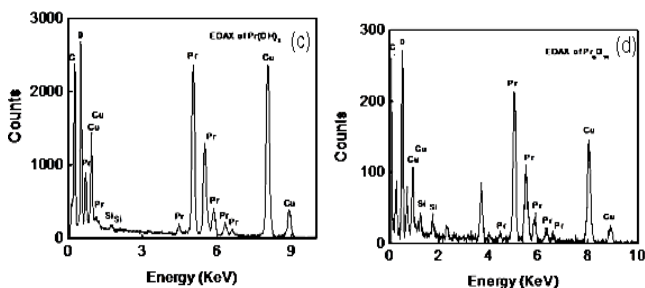


Fig. 2(c). shows EDAX analysis for Pr(OH)₃ sample. The ratio of Pr/O is 26/74, which corresponds to the Pr(OH)₃ phase. The EDAX analysis of Pr₆O₁₁ nanorods is shown in Fig. 2(d). Si in the EDAX spectrum is from the detector used for EDAX studies.

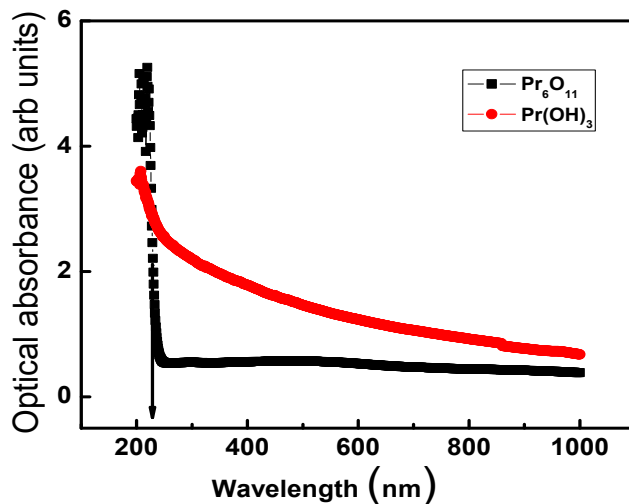


Fig. 3. Optical absorbance spectra of Pr(OH)₃ and Pr₆O₁₁ nanorods dispersed in DI water. Optical band gap of 5.31 eV has been estimated for Pr₆O₁₁ nanorods.

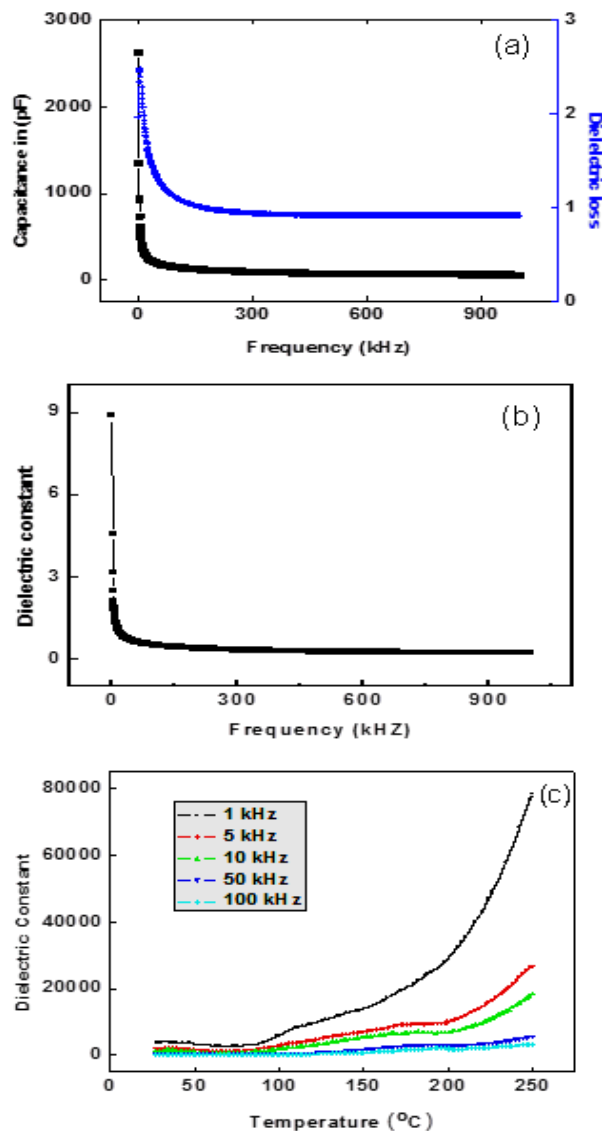


Fig. 4. Variation of (a) capacitance and dielectric loss as a function of frequency, (b) dielectric constant as a function of frequency and (c) dielectric constant with temperature.

It should be noted that the growth of Pr(OH)₃ nanorods at lower temperature in the present study is based on the eutectic temperatures of the hydroxides. The eutectic point of NaOH:KOH (51.5:48.5) is about 165°C; though the melting points of KOH and NaOH are 323 and 360°C, respectively. When the mixed hydroxides melt, the liquid consists of only two kinds of cations, Na⁺ and K⁺, and anion, OH⁻. Thus, the solvent is a kind of ionic liquid at this temperature. Pr(NO₃)₃·6H₂O dissolves in the ionic liquid, and form Pr³⁺ ions. Because of the presence of OH⁻ adjacent to the cation Pr³⁺ in the solution, Pr³⁺ links with hydroxyl ions and forms Pr(OH)₃. They link together by condensation reaction among them and form one, two or three dimensional structures under different conditions. This is evident from the TEM/HRTEM results, where Pr₆O₁₁ rods are polycrystalline and appear to be made of single crystalline particles.

Conclusion

In this work, synthesis of Pr(OH)₃ nanorods by alkaline route (using eutectic temperature of KOH and NaOH) carried out at lower temperature (~188°C) and atmospheric pressure is reported. The as-synthesized powder of Pr(OH)₃ was converted to Pr₆O₁₁ nanorods upon annealing. Various techniques have been used to characterize the products. Hydroxide and oxide nanorods both showed uniform morphology and good crystallinity. The lower cost of reactants and simplicity of the synthesis procure make it a promising method for scaling-up the production of Pr₆O₁₁ and similar other oxide nanorods. The results show that Pr₆O₁₁ shall be useful as a gate dielectric for future generation optoelectronic devices.

Author contributions

Conceived the plan: GP, VNS; Performed the experiments: VNS; Data analysis: LS, RK, TDS; Wrote the paper: VNS, GP, LS. Authors have no competing financial interests.

Reference

- Zhou, W.; Liu, H.; Boughton, R.I.; Du, G.; Lin, J.; Wang J.; Liu, D.; *J. Mater. Chem.* **2010**, *20*, 5993.
DOI: [10.1039/B927224K](https://doi.org/10.1039/B927224K)
- Wang, X.; Li, Y.; *Chem. Euro. J.* **2003**, *9*, 5627.
DOI: [10.1002/chem.200304785](https://doi.org/10.1002/chem.200304785)
- Ozawa, M.; Onoe, R.; Kato, H.; *J. Alloys Compounds.* **2006**, *408*, 556.
DOI: [10.1016/j.jallcom.2004.12.073](https://doi.org/10.1016/j.jallcom.2004.12.073)
- Yan, C.-H.; Yan, Z.-G.; Du, Y.-P.; Shen, J.; Zhang, C.; Feng, W.; Chapter 251 Controlled synthesis and properties of rare earth nanomaterials; in Handbook of Physics and Chemistry of Rare earths; **2011**, *41*, 275.
DOI: [10.1016/B978-0-444-53590-0.00004-2](https://doi.org/10.1016/B978-0-444-53590-0.00004-2)
- Borchert, Y.; Sonstrom, P.; Wilhelm, M.; Borchert, H.; Baumer, M.; *J. Phys. Chem. C.* **2008**, *112*, 3054.
DOI: [10.1021/jp0768524](https://doi.org/10.1021/jp0768524)
- Yan, L.; Yu, R.; Liu, G.; Xing, X.; *Scripta Materiali.* **2008**, *58*, 707.
DOI: [10.1016/j.scriptamat.2007.12.007](https://doi.org/10.1016/j.scriptamat.2007.12.007)
- Wang, X.; Yang, C.; Wang, T.; Liu, P.; *Electrochimica Acta.* **2011**, *58*, 193.
DOI: [10.1016/j.electacta.2011.09.060](https://doi.org/10.1016/j.electacta.2011.09.060)
- Zhao, J.; Chen, W.; Yu, G.; Li, X.; Zheng, Y.; Xu, Z.; *Chem. Lett.* **2005**, *34*, 738.
DOI: [10.1246/cl.2005.738](https://doi.org/10.1246/cl.2005.738)
- Ozawa, M.; Onoe, R.; Kato H.; *J. Alloys and Compounds.* **2006**, *408* 556.
DOI: [10.1016/j.jallcom.2004.12.073](https://doi.org/10.1016/j.jallcom.2004.12.073)
- Tao, F.; Wang, Z.; Yao, L.; Cai, W.; Li X.; *Nanotechno.* **2006**, *17*, 1079.
DOI: [10.1088/0957-4484/17/4/039](https://doi.org/10.1088/0957-4484/17/4/039)
- Hassan, M.S.; Kang, Y. Sic.; Kim, B. Suhk.; Kim, I.-Soo.; Kim, H.-Yong.; Khil, M. Seob; *Superlattices Microstructures.* **2011**, *50*, 139.
DOI: [10.1016/j.spmi.2011.05.010](https://doi.org/10.1016/j.spmi.2011.05.010)
- Sonström, P.; Birkenstock, J.; Borchert, Y.; Schilinsky, L.; Behrend, P.; Gries, K.; Müller, K.; Rosenauer, A.; Bäumer, M.; *Chem. Cat. Chem.* **2010**, *2*, 694.
DOI: [10.1002/cctc.200900311](https://doi.org/10.1002/cctc.200900311)
- Hassan, M.S.; Akhtar, M.S.; Shim, K.-Bo; Yang, O-Bong; *Nanoscale Res. Lett.* **2010**, *5*, 735.
DOI: [10.1007/s11671-010-9547-8](https://doi.org/10.1007/s11671-010-9547-8)
- Matović, B.; Pantić, J.; Prekajski, M.; Stanković, N.; Bučević, D.; Minović, T.; Čebela, M.; *Ceramics International.* **2013**, *39*, 3151.
DOI: [10.1016/j.ceramint.2012.09.098](https://doi.org/10.1016/j.ceramint.2012.09.098)
- Mehrotra, S.; and Bandyopadhyay, A.K.; *J. Alloys Compounds.* **2007**, *436*, 56.
DOI: [10.1016/j.jallcom.2006.11.040](https://doi.org/10.1016/j.jallcom.2006.11.040)
- Liu, J.P.; Zaumseil, P.; Bugiel, E.; Osten, H.J.; *Appl. Phys. Lett.* **2001**, *79*, 671.
DOI: [10.1063/1.1389509](https://doi.org/10.1063/1.1389509)
- Gevers, S.; Weisemoeller, T.; Zimmermann, B.; Bertram, F.; Deiter, C.; Wollschl'ager, J.; *J. Phys.: Condens. Matter.* **2009**, *21*, 175408.
DOI: [10.1088/0953-8984/21/17/175408](https://doi.org/10.1088/0953-8984/21/17/175408)
- Mekki, A.; Ziq, Kh.A.; Holland, D.; McConville, C.F.; *J. Magn. Magn. Mater.* **2003**, *260*, 60.
DOI: [10.1016/S0304-8853\(02\)00568-1](https://doi.org/10.1016/S0304-8853(02)00568-1)
- Wang, X.; Zhuang, J.; Li, Y.; *Eur. J. Inorg. Chem.* **2004**, *2004*, 946.
DOI: [10.1002/ejic.200300652](https://doi.org/10.1002/ejic.200300652)
- Huang, P.X.; Wu, F.; Zhu, B.L.; Li, G.R.; Wang, Y. L.; Gao, X.P.; Zhu, H.Y.; Yan, T.Y.; Huang, W.P.; Zhang, S.M.; Song, D.Y.; *J. Phys. Chem. B.* **2006**, *110*, 1614.
DOI: [10.1021/jp055622r](https://doi.org/10.1021/jp055622r)
- Ma, L.; Chen, W.-X.; Zhao, J.; Zheng, Y.-F.; Li, X.; Zhude, X.; *Mater. Lett.* **2007**, *61*, 1711.
DOI: [10.1016/j.matlet.2006.07.116](https://doi.org/10.1016/j.matlet.2006.07.116)
- L. Ma; W.-X. Chen; J. Zhao; J. -F. Zheng; Synthesis of Pr(OH)₃ and Pr₆O₁₁ nanorods by microwave-assisted method: Effects of concentration of alkali and microwave heating time, *J. Cryst. Growth.* **2007**, *303*, 590.
DOI: [10.1016/j.jcrysgro.2006.12.035](https://doi.org/10.1016/j.jcrysgro.2006.12.035)
- Hussein, G.A.M.; Balboul, B.A.A.; A-Warith, M.A.; Othman, A.G.M.; *Thermochimica Acta.* **2001**, *369*, 59.
DOI: [10.1016/S0040-6031\(00\)00727-9](https://doi.org/10.1016/S0040-6031(00)00727-9)
- Wakiya, N.; Chun, S.-Y.; Saiki, A.; Sakurai, O.; Shinozaki, K.; Mizutani, N.; *Thermochimica Acta.* **1998**, *313*, 55.
DOI: [10.1016/S0040-6031\(98\)00242-1](https://doi.org/10.1016/S0040-6031(98)00242-1)

Advanced Materials Letters

Copyright © VBRI Press AB, Sweden
www.vbripress.com

Publish your article in this journal

Advanced Materials Letters is an official international journal of International Association of Advanced Materials (IAAM, www.iaamonline.org) published by VBRI Press AB, Sweden monthly. The journal is intended to provide top-quality peer-review articles in the fascinating field of materials science and technology particularly in the area of structure, synthesis and processing, characterisation, advanced-state properties, and application of materials. All published articles are indexed in various databases and are available download for free. The manuscript management system is completely electronic and has fast and fair peer-review process. The journal includes review article, research article, notes, letter to editor and short communications.

