PHOTOLUMINESCENCE STUDIES OF MICROWAVE ASSISTED SYNTHESIZED ZnO MICRO STRUCTURES

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ZnO micro particles in the range 0.4-0.6 μm were synthesized by microwave irradiation method. The XRD analysis reveals that the sample is in the wurtzite phase with orientation along the (101) plane. SAED pattern of the sample reveals the single crystalline nature of the micro grains. TEM images show the formation of cylindrical shaped ZnO micro structures with hexagonal faces. The optical phonon modes were slightly shifted in the Raman spectrum,attributed to the presence of various crystalline defects and laser induced local heating at the grain boundaries. A broad transmission profile was observed in the FTIR spectrum from 1550-3400 cm^{-1} which falls in the atmospheric transparency window region. PL spectrum centered at 500 nm with a broad band in the region 420-570 nm comprised of different emission peaks attributed to transition between defect levels. Various emission levels in the sample were expliained with a band diagram.

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1. Introduction

ZnO is a wide bandgap (3.37 eV) semiconductor having large exciton binding energy (60 meV) at room temperature, has attracted considerable attention due to its unique piezoelectric, pyroelectric, catalytic and photocatalytic properties [1-2]. The morphology and the size of inorganic materials are detrimental in determining their physicochemical properties [3]. Thus the synthesise of ZnO with uniform size and various morphologies has been attained considerable focus in recent years. Among these synthesis of ZnO having micrometer range such as cylindrical cavities hollow microspheres, micro boxes have been reported in the literature [1,4-5]. Further, ZnO based micro cavities are potential one for development new laser sources in the visible region [3]. In this context, microwave assisted synthesis is a simple and relatively new method for the preparation of micro sized crystalline materials very rapidly. Microwave heating in a closed reaction chamber has some advantages over other methods of conventional heating. The reaction rate can be accelerated, yield can be improved and the reaction path way can be selectively activated or suppressed. Recently microwave assisted synthesis attain much attention among researchers due to the ultra purity of the sample synthesized and the simplicity of the basic requirements of the experimental set up etc [6-7]. In the present work, microwave assisted synthesized ZnO micro structures are characterized with XRD, TEM and with vibrational spectroscopic techniques. Photoluminescence studies of these ZnO micro structures are investigated in detail in order to understand light emitting nature and to understand its suitability as laser micro cavity.

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2. Experimental

Analytical reagent grade Zinc acetate (0.1M), sodium hydroxide (0.1M) were dissolved in hydro ethanolic solution in the ratio 1:1 and mixed well using magnetic stirrer. The as prepared precursor was irradiated with microwave radiation by placing inside of a domestic microwave oven (Electrolex-2000). The power level of the microwave oven was adjusted to 80 W. The precursor was treated with microwave radiation for about one minute and repeated intermittently three times. The white colloidal suspension obtained was filtered and washed with ethanol and distilled water number of times.

Structural characterization of the sample was carried out using X-ray diffraction spectrometer with CuK_{α} radiation having wavelength of 1.54 A^0. TEM of the sample were done with Tecnai G30 instrument. Optical absorption spectrum of the sample was obtained by using JASCO-V-570-Spectrophotometer. FTIR spectrum of the sample in the region 400-4000 cm^{-1} was recorded by KBr pellet method by using Perkin Elmer FTIR spectrophotometer. FT Raman spectrum of the sample in the region 50-4000 cm^{-1} was obtained from Bruker RFS 100 spectrometer with a resolution better than 4 cm^{-1} using Ge detector. The PL spectrum of the sample was recorded using Spectroflurometer (Jovin Yvon, Fluoro Log-3) with 325 nm from Xe lamp as excitation source.

3. Results and discussion

XRD pattern (Fig 1) shows well defined peaks which can be indexed to wurtzite phase of ZnO (JCPDS 03-0888) with a= 3.258 A^0 and c = 5.2059 A^0. The (101) peak in the XRD pattern corresponding to 2θ value 36.8^0 is the most intense peak and is found to be 32% more intense than the next intense peak at 2θ value 31.08^0 (100). The micro grains are oriented along the (101) plane and are of good crystalline quality [8].

The TEM image of the sample (Fig.2 a, b and c) shows cylindrical structures with hexagonal faces with size ranging from 0.4-0.6 μm. SAED (Fig. 2.d) pattern of the sample shows periodic distribution of lattice points indicating single crystalline nature of the material [9]. In the present synthesis process, microwave irradiation played a crucial role in the rapid formation of ZnO micro structures. Water is one of the base materials in the synthesis process which posses high dipole moment will act as a medium for microwave assisted reactions. Microwave radiation falling on the precursor reactants contributes both thermal and non thermal effects for the formation of micro crystallites [10].

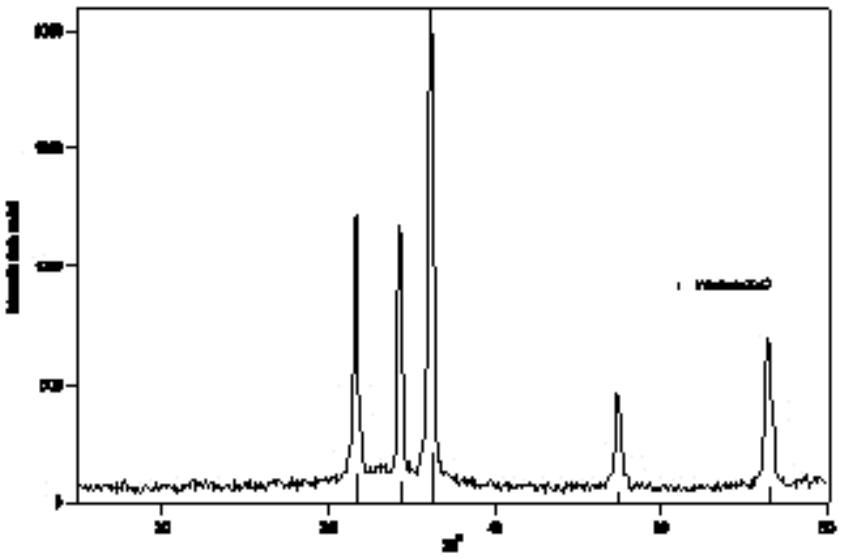

Fig .1. XRD of the ZnO micro grains synthesied by microwave assisted synthesis.

The polarization and rapidly changing electromagnetic field of microwave radiation will create anisotropic micro domains of materials.

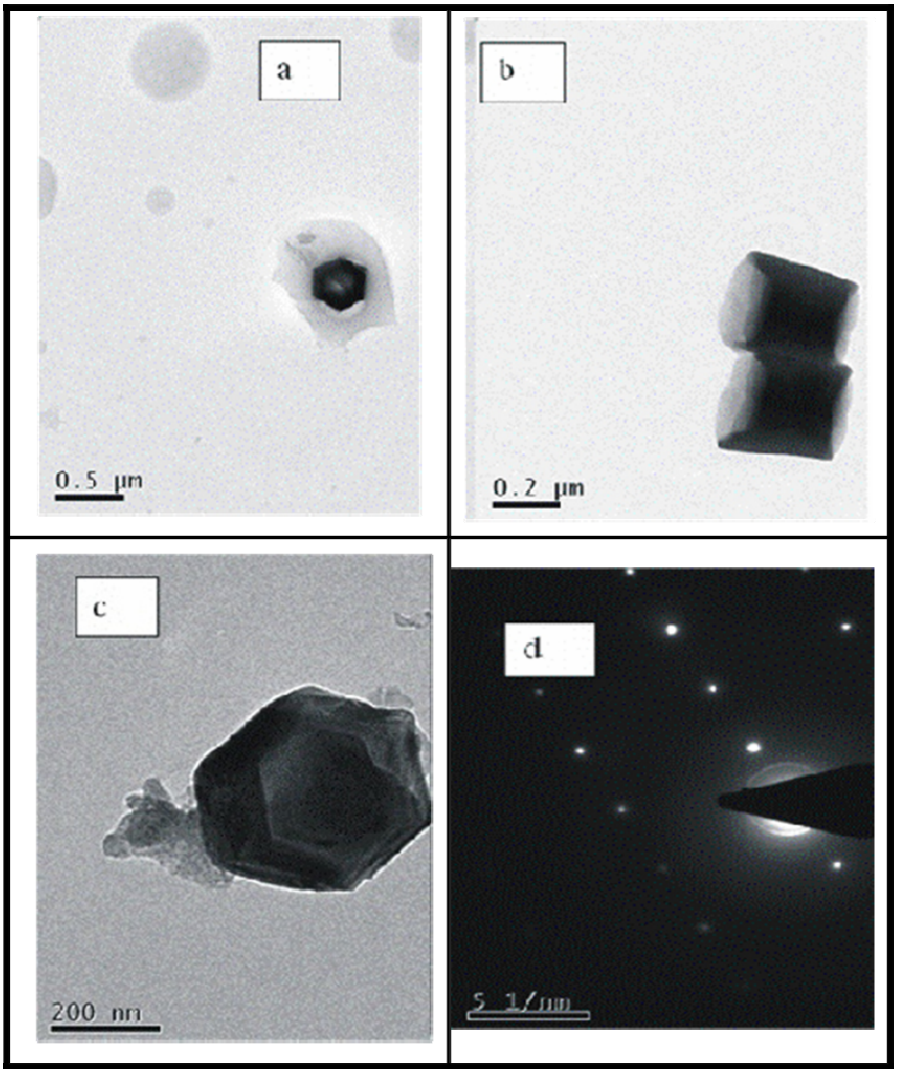

Fig .2 .TEM images of (a), (b) & (c) ZnO microcrystals synthesized by microwave assisted method with different magnification (d) SAED pattern of ZnO

Significant rise in diffusion rate in microwave field causes localized intense temperature region within the reaction assembly which will facilitate anisotropic growth of ZnO. As the temperature increases due to the rise in the diffusion rate of microwave field, the oxidation rate will increase. Nucleation phase of solid ZnO abruptly increases with respect to oxidation rate and hence crystalline size [11-12].

Raman spectrum of the sample (Fig. 3.) shows, the peak attributed to E_1 (TO) which is shifted by 15 cm^{-1} as compared with the bulk and is obtained at 395 cm^{-1} (Table .1). Similarly a weak shoulder observed at 432 cm^{-1} in the Raman spectrum corresponds to E_2 high mode which is red shifted of the order of 7 cm^{-1} as compared with bulk ZnO reported in the literature [13-14].

Table. 1. Raman shift (cm^{-1}) observed in ZnO micro crystals synthesied by microwave assisted synthesis.

Sample	E_2(low)	A_1(TO)	E_1(TO)	E_2(high)	A_1(LO)	E_1(LO)
Bulk ZnO[13]	591	102	379	410	439	574
Presant Sample.			333,350,395	395	432	560

Further the A_1 (LO) phonon frequency is shifted by 14 cm^{-1} and is observed at 560 cm^{-1} in the present sample. The weak band obtained at 350 cm^{-1} is probably the energy corresponds to the difference of E_2 (high) – E_2 (low) [15]. The presence of A_1 (LO) at 560 cm^{-1} is the indication that the crystalline defects such as Oxygen vacancy, Zinc interstitial and their clusters are present in the crystal [13]. The shift in most of the peaks observed in the Raman spectrum as compared to that of bulk ZnO is attributed to the presence of crystalline defects in the sample [16]. On the other hand, laser source used for the excitation of the sample will cause strong local heating of ZnO micro crystallites which leads to shift in the Raman spectrum [17]. The presence of E_1 (TO) in the Raman spectrum of the present sample confirms that the sample is not well oriented along the c-axis which is in agreement with the XRD observations [18]. The peak at 333 cm^{-1} is related to phonon resonance at the edge of Brillion zone shows the good crystalline quality of the sample [19]. In nano crystalline materials, the breaking of symmetry of crystal structure may activate overtones of fundamental modes. But the absence of such overtones in the Raman spectrum of the sample reveals that the grains are having size in the micrometer range which is more than that calculated from the XRD.

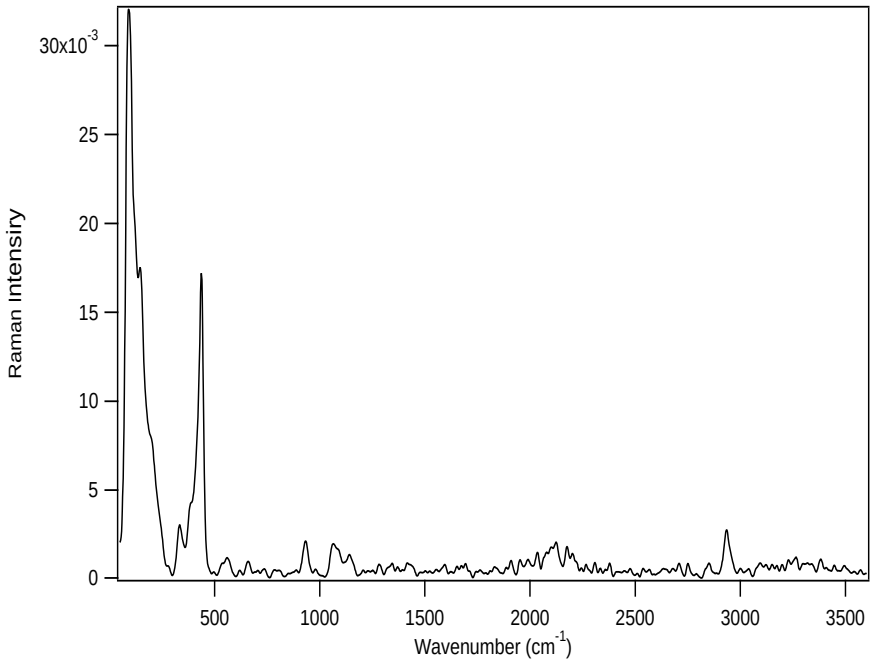

Fig. 3. Raman spectrum of ZnO micro grains synthesied by microwave assisted synthesis.

A broad transmission profile is observed in the FTIR spectrum which extends from 1550 - 3400 cm^{-1} which falls in the atmospheric transparency window region. The absence of well defind peaks in the organic fingerprint region indicates organic free formation of microcrystalline ZnO. The optical band gap (E_g) of the sample is calculated by using the relation $(\alpha h\nu)^2 = A(h\nu - E_g)$, since ZnO is a direct band gap semiconductor. Here α is the absorption coefficient, $h\nu$ is the

photon energy and A is a constant [20]. The linear extrapolation of the representation to the hυ axis directly gives the band gap and is found to be 3.3 eV

The photoluminescence emission nature of oxide semiconductor like depends on the surface morphology, grain size and the nature of different types of defects. The defects involved in the defect level emission are localized at the surfaces which are attributed to various intrinsic defects in crystalline structure. These defects are zinc vacancy $V_{Zn,}$ Oxygen vacancy V_o ,interstitial zinc Z_{in}, interstitial Oxygen $O_{i,}$ and antisite Oxygen O_{Zn} etc [21-22]. The PL spectrum has a strong peak at 420 nm (2.95 eV) with shoulders at 437 nm (2.83 eV) and 452 nm (2.74 eV) (Fig 4.). Another moderately intense peak is observed at 469 nm (2.64 eV) with shoulder peaks at 484 (2.56 eV) and 491 nm (2.52 eV).

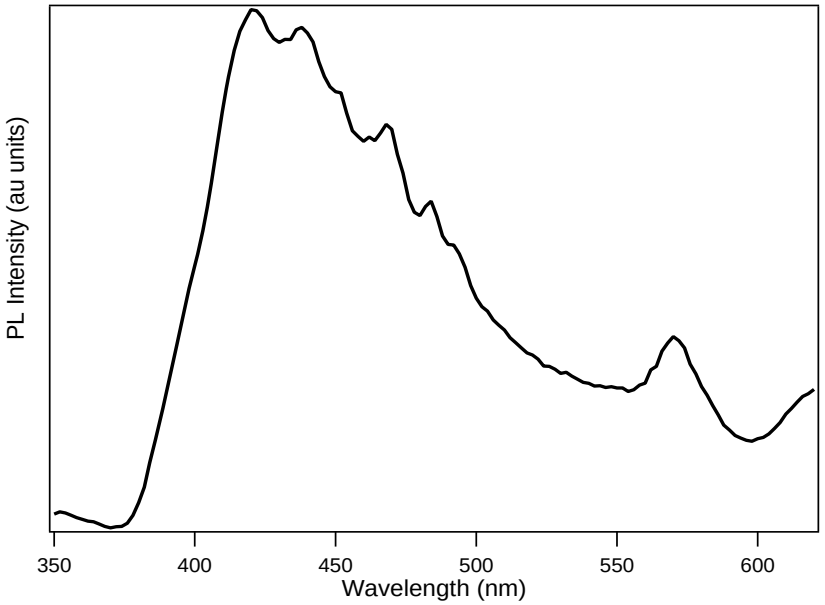

Fig. 4. PL Spectrum of ZnO micro grains synthesied by microwave assisted synthesis.

All these peaks were part of a broad band centered at 500 nm which extends from 420-570 nm (Fig.4). The centre energy of the broad band is at 2.48 eV (500 nm) which is less than the band gap energy of ZnO, so the observed emission is probably related to local levels in the band gap [23]. The position of various intrinsic defect levels such as interstitial zinc is located 0.5 eV below the bottom of conduction band (CB) (Fig 5). Similarly interstitial oxygen is located at 0.4 eV from the top of valence band (VB). Zinc vacancy V_{Zn} and oxygen vacancy V_o were located at 0.36 eV from VB and 1-1.2 eV from CB (Fig.5). More over complex intrinsic defect such as V_oZ_{in} is located at 2.16 eV from the CB [24-25]. In our case the intense peak obtained at 420 nm (2.9 eV) is due to the transition from CB to O_i. The oxygen vacancies on the surface of the agglomerated particles are comparatively less which reduces the intensity of greenish yellow peak. The shoulder peak at 438 nm (2.8 eV) is due to the radiative transition from Zn_i to valence band. The intensity variation corresponds to different peaks observed in the PL spectrum may be resulted from the variation in the concentration of the above mentioned intrinsic defects in ZnO.

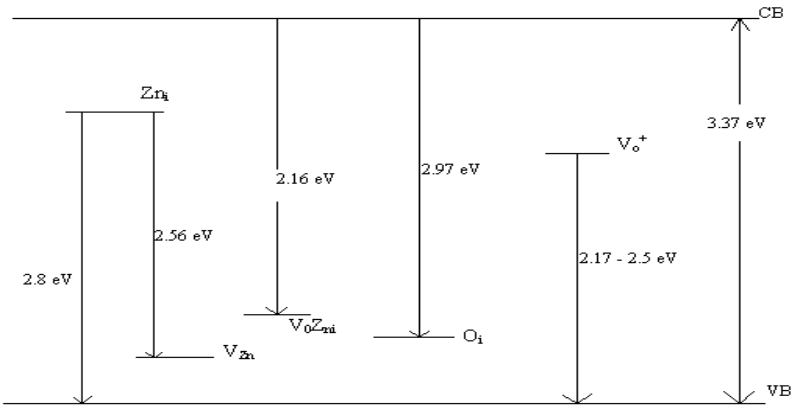

Fig. 5. Energy level diagram of ZnO micro grains.

A semiconductor shaped like a parallelepiped, cylinder, or sphere with size on the order of the wavelength of light that is placed into a transparent medium with a smaller refractive index has several coupled states, i.e., emitted light modes. The mode lifetime controls the quality factor of the micro cavity and optical pump threshold for stimulated emission. As per TEM observation (Fig.2) present sample is in the micrometer range (0.4-0.6 μm) hexagonopod which may be used as micro cavity in the visible region possibly have several coupled states, i.e., emitted light modes [6].

4. Conclusions

The XRD analysis reveals that the microwave assisted grown ZnO is in the wurtzite phase with orientation along the (101) plane. SAED pattern of the sample reveals the single crystalline nature of the micro grains. Optical phonon modes of ZnO in the Raman spectrum of the sample is slightly shifted which is attributed to the presence of various crystalline defects and laser induced local heating at the grain boundaries. A broad transmission profile in the FTIR spectrum extends from 1550-3400 cm^{-1} which falls in the atmospheric transparency window region, helps to use as an IR transmission window material. PL spectrum centered at 500 nm with broad profile in the region 420-570 nm comprised of different emission peaks attributed to transition between defect levels. TEM images show the formation of cylindrical shaped ZnO micro structures in the range 0.4-0.6 μm, which may be able to use as microcavity in the visible region to amplify several optical modes.

References

[1] A. N Gruzintsev, V. T Volkov, S. V Dubonos, M. A Knyazev, E. E.Yakimov, Phy.of Semicon. Devices , **38**,1426-1429(2004).
[2] K .Krunks, O .Bijakina, V .Mikli, T. Varema, E. Mellikov, Physica Scripta, **T79**, 209-212 (1999).
[3] R.Yi, Z .Ning, Z.H.Rongrong , Q. Guanzhou, L. Xiaohe, Materi. Sci. and Engg. B, **153,** 25-30 (2008).
[4] G.R Li, X.H .Lu, D.L .Qu, C.Z .Yao, F.L. Zheng, Q. Bu, C.R .Dawa, Y.X Tong, J. Phys.Chem. ***C*** **111**, 6678 -6683 (2007).
[5] M .Mo, J.C .Yu, L.Z. Zhang, K.A .Li , Adv. Mater. **17**, 756 -760 (2005).
[6] G .Atul, Sunil Kumar, H.S Bhatti, J.Mater.Sci.Mater.Electron, **21**, 765-771(2010)
[7] S. Komarneri, M. Bruno, E. Mariani, Mater.Res.Bull., **35**, 1843-1847 (2000).
[8] C.X .Xu, X.W .Sun, X.H .Zhang, L .Ke, S.J .Chua, Nanotechnology, **15**, 856-861 (2004).
[9] S.Brahma, K.J.Rao,and S.R.Shivsankar , Bull.Mater.Sci., **33** , 89-95 (2010).

[10] A.S.Shaporev, V.K.Ivanov A.E.Baranchikov, Tretyakov, D.Yu, Inorganic Mater, **43**, 35-39 (2007).
[11] Xian-Luo Hu, Ying-Jie Zhu, Shi-Wei Wang, Mater. Chem. Phys.,**88,** 421-426 (2004).
[12] K.J .Rao., Krishnamurthy Mahesh and K .Sundeep, *Bull.Mater.Sci.*, **28**, 19-24 (2005).
[13] K.A. Alim, V.A. Fonoberov, M. Shamsa and A. Baladin, J.Appl.Phys, **97**, 124313-124318 (2005).
[14] N.Ashkenov, B.N Mbenkum, C. Bundesmann, V .Riede, M.Lorenz, D. Spemann, E.M. Kaidashev, A.Kasic, M.Schubert, M.Grundmann, G.Wagner, H.Neumann, V.Darakchieva, H.Arwin, Monemar, J.Appl.Phys. **93**, 126-134 (2003).
[15] Diaz-Reyes, J. Martinez-juarez, R .Galeazzi, G .Juarez-Diaz, M .Galvan-Arellano, P. Rodriguez-Fragoso, Lopez-Cruz , Adv.in Sen, Sig and Mater., 105-110(2010).
[16] D,Krishnan, T. Pradeep , J.Crys Growth, **311**, 3889-3897(2009).
[17] M.H Huang, S.Mao, H Feik, H.Yan, Y.Wu, H.Kind, E.Weber, R.Russo, P.Yang, Scienc*e,* **292** , 1897-1899(2001).
[18] K. Sreenivas, S.Kumar , J.Choudhary and V.Gupta, Pramana**, 65**, 809-814 (2005) .
[19] T .Monterio, A. J .Neves, M. C. Carmo, M. J .Soares, M .Peres, J .Wang, E.Alves , E. Rita, U.Wahl, J.Appl.Phys**. 98**, 013502(1-4) (2005).
[20] S .Senthilkumaar, K. Rajendran , S.Banerjee, T.K. Chini, V. Sengodan , Mater. Sci in Semicon.Proc. **11**, 6-12 (2008).
[21] A.B Djurisic , Y.H Leung, K.H .Tam, Y.F. Hsu, L. Ding, W.K. Ge, Y.C. Zhong, K.S .Wong, W.K .Chan, H.L .Tam, K.W. Cheah, W.M. Kwok, D.L. Phillips, Nanotechonology, **18**, 095702 (1-8)(2007).
[22] G .Yinyan, A .Tamar, F .Gertrude, Neumark,Stephen O Brien, I. L. Kuskovsky ,Nanoscale Res.Lett. , Nanoscale Res. Lett .**2**:297–302(2007).
[23] Yonghong N, C .Xiaofeng, W.Guogen,H .Guangzhi, Y. Zhousheng, W.Xianwen, Nanotechnology, **18**, 155603(1-6)(2007) .
[24] H .Qinyu, C .Jian, Z. Wenxia, L .Zhi, R. Hao, L. Xiaoling, J. Phys and Chem.of Solids, **66,** 31-35 (2005).
[25] Fushan Wen , Wenlian Li , Jong-Ha Moon,Jin Hyeok Kim, Solid State Comm. **135**, 34-37(2005).