Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2014, 6(1):7-13
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Role of nanostructured materials in recent developments of thermoelectric nanocomposites

C. Sarala Rubi[a*], S. Gowthaman[b], and N. G. Renganathan[c]

[a]*Department of Physics, Vel Tech Dr. RR & Dr. SR Technical University, Tamil Nadu, India*
[b]*Department of Mechanical Engineering, Vel Tech Dr. RR & Dr. SR Technical University, Tamil Nadu, India*
[c]*Department of Chemistry, Vel Tech Dr. RR & Dr. SR Technical University, Tamil Nadu, India*

ABSTRACT

Alternative renewable energy source is immensely necessary in view of increase in worldwide energy needs. Since Thermo Electric (TE) power generation is renewable and clean energy source, it is quiet useful to meet the energy demands globally. It leads to overall efficiency of energy generation. Materials which exhibit TE effect have the ability to convert waste heat into electricity. But the efficiency of TE power is lower than possible generation because of the interconnecting linkage between electrical conductivity, thermal conductivity and Seebeck co-efficient in bulk materials. The challenge behind this bulk TE material can be broken by introducing nanostructures. Nanostructures are able to disconnect the link between physical parameters such as electrical and thermal conductivity at the interfaces. The main goal of the present report is to report how the reduction in thermal conductivity is achieved without affecting electrical conductivity. In nanostructures, thermal conductivity is eased by increasing phonon scattering without much variation in electrical conductivity. Also, increase in electronic density of states provide increases in carrier concentration and thereby enhances the electrical conductivity. Thus in this report an attempt has been made to indicate the ways to enhance the figure of merit in nanostructures.

Key words: Thermoelectric, Bulk, Nanostructured, Figure of merit.

INTRODUCTION

Ozone depletion, global warming, atmospheric pollution and worldwide energy shortage are the serious environmental problems which occurred because of the increase in use of fossil fuels recently [1]. In order to overcome these energy problems, it is important to implement certain low cost and eco friendly energy system to cope up with modern society. Harvesting low grade heat (LGH) from environmental sources such as waste heat from power plants, automobile engines, and solar panel substrates, has shown a superior way to meet the need of energy [2]. The amount of energy emitted from the Sun is, around 3×10^{24} J/year, which is some hundred fold times greater than what we use at present. So conversion of 0.1 % of solar energy into useful energy with 10 % efficiency is more than enough to meet our current energy needs. Thus solar energy can be the substitute for nuclear energy. But the real challenge lies in designing a low cost and reliable system in the conversion of solar energy into useful energy [3]. It was reported that thermoelectricity, considered to be a kind of green and flexible source of electricity, and had attracted great attention. Since the 1950s when the semiconductor materials with small band gap were found, more and more researchers have been engaged in these materials. This may be due to the better performance of these semiconducting materials than metals. The important factor in this direction is towards the development of nanocomposites which will have safe, clean and sustainable energy for the future mankind. In this direction thermoelectric is going to provide an alternative route to convert the solar energy into electrical power. In USA, 191 million vehicles dissipated 66% of energy from gasoline as waste heat. Industrial waste heat takes a major part of the waste energy in the whole society. Hendricks et al. reported that 33% of the manufacturing industrial energy was released directly to the atmosphere or cooling systems as waste heat, because many industries were not able to recycle the excessive energy. They also pointed out that a range of 0.9 TWh to 2.8 TWh of electricity might be produced by waste heat each year if thermoelectric materials with average ZT (Z: figure-of-merit of thermoelectric materials, T: absolute operating temperature of thermoelectric materials) values ranging from 1 to 2 were available. In addition, extremely large amounts of waste heat energy are generated from inefficient transportation vehicles. One way to improve the sustainability of our electricity base is through the harvesting of waste heat with thermoelectric generators i.e., thermoelectric materials. Home heating, automotive exhaust, and industrial processes all generate waste heat that could be converted to electricity by using thermoelectrics. Thermoelectrics have long been too inefficient to be cost-effective in most applications. However, in 1990s theoretical predictions suggested that thermoelectric efficiency could be greatly enhanced through nanoscale engineering [4]. The available waste heat sources include recoverable industrial heat-generating process, the exhausted waste heat of transportation vehicles, solar energy and combustion of solid waste and geothermal energy and so on.

Thermoelectric technology and solid-state devices based on the TE effect have a number of advantages. The technology has therefore cause worldwide interest in many fields, including waste heat recovery and solar heat utilization (power generation mode), and temperature-controlled seats, portable picnic coolers and thermal management in microprocessors. Over the past ten years, the exploration of high-performance thermoelectric materials has attracted great attention from both an academic research perspective and with a view to industrial applications.

The challenge to develop thermoelectric materials with superior performance is to tailor the interconnected thermoelectric physical parameters electrical conductivity, Seebeck coefficient and thermal conductivity for a crystalline system. Nanostructures provide a chance to disconnect the linkage between thermal and electrical transport by introducing some new scattering mechanisms. Recent improvements in thermoelectric efficiency appear to be dominated by efforts to reduce the lattice thermal conductivity through nanostructural design. The efficiency of TE devices is strongly associated with the dimensionless figure of merit (*ZT*) of TE materials, defined as ZT = $(\alpha^2\sigma/\kappa)\ T$, where σ, κ and T are the electrical resistivity, thermal conductivity and absolute temperature. High electrical conductivity, a large Seebeck coefficient and low thermal conductivity are therefore necessary in order to realize high-performance TE materials. In general, good TE materials have a *ZT* value of close to unity. However, *ZT* values of up to three are considered to be essential for TE energy converters [5]. Thermoelectric refrigeration is an environmentally ‘‘green’’ method of small-scale localized cooling in computers, infrared detectors, electronics, and optoelectronics as well as many other applications. Power generation applications are being investigated by the automotive industry as a means to develop electrical power from waste engine heat for use in the ‘‘next generation vehicle.’’ These uses range from power generation utilizing waste engine heat from the exhaust and radiator cooling system to seat coolers for comfort or electronic component cooling [6]. Recently, thermoelectric generator (TEG) has been applied to the recovery of heat energy of combustible exhaust gas or waste water, because TEG system has a good flexibility to the heat source capacity and the change of temperature range [7]. Although the solar cells are used in spacecraft, they are useful only for the short distance up to the Mars and beyond where the solar radiant flux is not adequate, thermoelectric takes over to generate the power. Micro-thermoelectric generators are used in many low power devices such as hearing aids and wrist watches. Recently Seiko and Citizen introduced commercialized thermoelectrically driven low power wrist watches [8]. This report summarizes the role of nanostuctured materials in developing thermoelectric materials with a high dimensionless figure of merits (*ZT*).

NANO STRUCTURAL APPROACHES FOR ENHANCING THERMOELECTRIC PERFORMANCE

In the past years, the ZT value of the bulk materials is found to be around one due to the simultaneous increase in electrical and thermal conductivity. The *ZT* value of greater than one is desirable for competitive energy harvesting. This can be achieved through nanotechnology because of the highest mean free path of the phonon rather than electron. The transport of phonons and electrons will become easier control in the nanostructures than in bulk materials.

The efficiency of TE materials can be calculated by the dimensionless figure of merit,

$$ZT = \frac{S^2 \sigma T}{K}$$

Where, S is the Seebeck coefficient, σ is the electrical conductivity, T is the temperature and K is the thermal conductivity. These parameters are interdependent in bulk materials. Hence it will be very difficult to get optimised for enhancing ZT in the bulk as well as in nanostructures. Nano structures and Nanocomposites are going to help thermal conductivity. By this power factor is going to be increased and thus ZT value will be increased. Also, nanocomposites are more attractive because of its simple synthesis method to produce bulk in amount. The narrow band gap semiconductors and its alloys are most commonly used TE materials [13]. The introduction of nanostructures helps to break the link between thermal and electrical properties through scattering mechanism and will enhance ZT. The Seebeck coefficient and electrical conductivity cannot be increased at the same time because both depend on the mobile charge carrier density of the material. But thermal conductivity alone can be changed and it has two parts— thermal conductivity due to phonons and thermal conductivity due to electrons. The thermal conductivity due to phonons can be suppressed in nanostructures in order to get better electrical conductivity and figure of merit. However figure of merit can be increased by density of states. Since density of states depends on the band structure, it is very difficult to perform in certain materials [14]. Decreasing the dimensionality of the material causes dramatic differences in the density of electronic states i.e., from 3D bulk material to 2D (quantum wells) to 1D (quantum wires) to 0D (quantum dots) which provide a chance to tune the physical parameters independently. Introduction of many interfaces helps to scatter phonons than electrons and the interfacial energy barriers helps to develop the nanostructure materials with improved ZT which is useful for thermoelectric applications. The low dimensional thermoelectric system was developed with the help of these two concepts, ZT can be increased either by reducing the thermal conductivity or by increasing the interfaces. However, it is necessary to increase the power factor also for the commercialization of low dimensional thermoelectric materials.

2.1. Energy band in nanostructured materials

We have to make clear two important things, one is the mean free path of electrons and phonons and the other one is the number of periods necessary to form a new energy band for both electrons and phonons. Since the time span may vary depending on the type of materials but it can be rectified by testing the quarter wavelength stack. When the GaAs/AlAs quarter wavelength stack are compared, even though the reflectivity of a Ga & As and Al & As individual interface is small, a reflectivity close to unity can be created with a small number of periodic quarter wavelength layers. In the case of bulk solids, 10 unit cells are similar to around 50 Å, which is smaller than that of the mean free path of electrons and phonons. Here it is clear that all the scattering processes deteriorate the phonon coherence. For superlattices, however, the minimum domain length required for the band formation is much larger than the bulk materials. Interface scattering causes shortening of mean free path in superlattices. In superlatices, the phonon scattering happens because of diffusive interface scattering (MFPd)

2.2. Incoherent electron and phonon transport

When the mean free paths of electrons and phonons are too short, it contains the same energy as in their bulk materials. These electrons and phonons can be treated as classical particles in the Boltzmann equation. The Boltzmann equation helps to solve the electron and phonon distribution functions and the thermoelectric transport properties of nanostructures. Boundaries and interfaces in nanostructures act as an additional scattering mechanism. Boundary scattering is an age old process. There are two different steps to deal with the boundary scattering:

1. One is to .based on Mathiessen's rule; it was decided to add an extra boundary scattering
2. Other is to make interfaces and boundaries according to Boltzmann equation.

2.3. Coherent electron and phonon transport

If the electron and phonon mean free paths are long enough to form new energy bands in nanostructures, their electrons and phonons are subject to new dispersion relations different from those in the bulk materials. This is the coherent regime, and quantum size effects on electrons and phonons must be considered to analyze thermoelectric transport in these nanostructures.

INVESTIGATING NOVEL TE MATERIALS

Thermoelectric materials consist of many material systems like semimetal, semiconductor, ceramic etc and it covers all crystalline forms such as single crystal, poly crystal and nanocomposites. It also contains various dimensions from three dimensional bulk materials to zero dimensional quantum dots Bulusu and Walker reported that the first thermoelectric materials were metals. In 1957, semiconductors were identified as thermoelectric materials by Ioffe because of its high seebeck coeffecient. Nowadays, semiconductors are considered as modern thermoelectric materials and the semiconducting materials are differentiated according to their electrical resistivity at room temperature .The resistivity values depend on temperature and are in the range of 10^{-2} to 10^{9} ohm-cm. Highly purified semiconductors are the source of intrinsic conductivity. The band gap is the minimum energy level of the conduction band and the maximum energy level of the valence band. When the temperature increases the electrons are transferred from valence band to the conduction band. Electrons in the conduction band and the holes that have been formed in the valence band lead to electrical conductivity. Normally, the semiconductors which have higher atomic weight respond lower thermal conductivity. Increase in density leads to decrease in thermal conductivity because increase in density will decrease the sound velocity in crystal Bismuth telluride has the highest figure of merit (ZT~1) at room temperature which would be sufficient for use in energy generating applications. The semiconducting materials such as n-type PbTe and p-type GeTe are used for higher operating temperatures but these materials are having higher cost of production. Since tellurium cost is more, it is advisable to find alternative materials for thermoelectric applications.

3.1. Complex chalcogenides

Various studies reveal that the lanthanum telluride and other rare-earth chalcogenides are the good high temperature thermoelectric materials and it was examined in wood's paper [15]. The lead chalcogenides present most attracting photoelectric, photo conducting, thermoelectric, optical and semi conductig properties [16].

3.2. Thermoelectric oxide materials (NaxCo2O4)

Chalcogenides may not be suitable for high temperature applications because of its poor physical and chemical stability under high temperature and high toxicity whereas oxide materials are able to withstand even at high temperatures. In general, oxide materials are considered as insulators but possess high Seebeck coefficient. Some of the oxide materials have the ability to give ZT values which is similar to semiconducting chalcogenides. At present oxide materials give low ZT~0.3. However, it is believed to increase the figure of merit in future. Oxide materials are categorized into three groups: layered complex oxides, doped zinc oxide derivatives, and perovskite-type oxides [17]. Poor mechanical strength and high contact resistance at interfaces are some of the drawbacks associated with oxide thermoelectric materials.

3.3. Zinc antimonides (b-Zn4Sb3)

Antimonides has been researched as a candidate of thermoelectric materials for years. Zinc antimony system is a good candidate for thermoelectric materials due to its high figure-of-merit. The thermal conductivity can be decreased by reducing lattice conductivity and this may be due to the disordered crystal structure.

3.4. Half-Heusler alloys

Half-Heusler alloys with the general formula ABX refer to a wide family of compounds, which crystallize in the cubic structure. Half-Heuslers (HHs) have great potential to convert waste heat into electricity through thermoelectric effect in the medium (200–500˚C) and high (500–700˚C) temperature range. Since the performance of the thermoelectric materials directly depends on the dimensionless figure-of- merit (ZT), HHs could be a good thermoelectric material due to their higher power factor (S2σ). However, the ZT of the HHs are much lower to compete with the state-of-the-art thermoelectric materials due to their relatively higher thermal conductivity. The thermal conductivity due to lattice k_{lat} , of half Heuslers is greatly suppressed by reducing average grain size from several micrometers to100–200 nm and introducing some nano-inclusions through a simple ball milling and hot pressing route. However, thermal conductivity of half-Heuslers is still much higher than that of conventional thermoelectric materials, such as Bi_2Te_3-based or PbTe-based nanocomposites. Another way to further depress the k_{lat} of half-Heuslers is through enhancing the alloy scattering. In principle, larger differences in atomic mass and size would generate substantial local stress and hence strong phonon scattering, leading to lower lattice thermal conductivity. In the recent years, different approaches have been used to improve the ZT of HH compounds such as optimization of the composition and introduction of nanostructures by a nano structuring approach [18].

3.5. Skutterudites

Skutterudites (ReTm4M12) are complex materials containing rare earth elements (Re), transition metals (Tm) and metalloids (M). Binary skutterudites have chemical formula of ReTm4M12, where Re is rare earth element, Tm is transition metal and M is metalloid. However, binary skutterudites have high thermal conductivity, but the seebeck coefficient is also large. Binary skutterudites has two large empty spaces in each unit cell. When this empty space is filled by heavy element, the thermal conductivity is reduced. The figure of merit (*ZT*) has been found to be higher than unity at 700 K. In TE materials heat is conducted through phonons, and these phonons have a wide frequency distribution. It is said that the phonons with particular range of frequency can be scattered. Various kinds of vibrational modes were introduced to scatter phonons. These phonons were forced to adopt longer wavelengths. Since the mean free paths of electrons and phonons are different, the concept of scattering low frequency phonons rather than electrons by nanoscale inclusions was advanced. Generally speaking, the radius (R) and dispersion of nano inclusions are important for the scattering effects. In order to develop the standard of filled skutterudites, various interfaces and microstructures must be designed. There are many commercial TE materials, such as Bi2Te3, PbTe, CoSb3, FeSi2 and SiGe. However, Bi2Te3 material is not suitable for industrial application when the temperature is higher than 250˚C and the conversion efficiency of $FeSi_2$ or SiGe is too low at the temperature range of 200–700˚C. PbTe material is harmful to human body and maybe causes for environmental pollution.

3.6. Clathrates

Other Phonon-Glass, Electron-Crystal (PGEC) materials include inorganic clathrates (A8B46) where B represents either gallium or germanium or their combination. Gallium and germanium atoms form an open crystal acting as an electron crystal. Clathrate ("lattice") is a material which is a weak composite, with molecules of suitable size captured in spaces which are left by the other compounds. Guest atoms are selectively incorporated into nano cavities in the crystal and vibrate independently thereby scattering phonons. The group of materials shows promise for thermoelectric applications above 600 ºC. Alloy of Pb-Sn-Sb-Ag-Te (LAST) with nano-sized inclusions was developed as n-type thermoelectric material having *ZT* values around 1.7.

APPLICATIONS OF THERMOELECTRICS

The thermoelectric is a promising technique to convert the waste thermal energies into useful power without using harmful chemicals like CFC and moving parts. Local energy supplies are becoming increasingly important for applications such as environmental monitoring with wireless sensor networks, implantable medical devices and traffic control systems. Ideally, these networks should be powered by local sources of electricity (based on energy extracted from the environment) rather than batteries, which are expensive to replace. Especially, mobile solutions and different stand alone systems can benefit local energy harvesting methods. Hybrid vehicles are optimized for low fuel consumption. This is done by means of separating the engine from direct power train by using electrical power transmission. This requires efficient energy recovery and storage, in which thermoelectric materials may be useful. The problems arise in winter time when sun does not provide enough energy. This could be overcome by developing efficient thermal power systems to support photovoltaics.

It has been suggested that the first applications for new thermoelectric materials could be a device for siphoning off electrical power from the heat in automobile exhaust. Eventually such a device could be used to supplement power from electric and fuel cell engines or provide a conventional vehicle with most of its electricity needs, running everything from its radio to its air conditioner. Other sources for thermal energy in hybrid vehicles are breaking action during deceleration. As the price of fossil fuels increases, the electric and hybrid vehicles become more attractive, and thermoelectric systems may provide additional energy capacity. As a very promising application for novel thermoelectric materials appear to be measurement and monitoring of irradiation embrittlement, as well as recovery during annealing of components. Irradiation embrittlement is a phenomenon causing metallurgical changes and takes place in nuclear reactor pressure vessels due to neutron irradiation. It is reported that utilization of Seebeck-Thomson effect (a method called STEAM – Seebeck and Thomson effects on aged materials) that takes place in thermoelectric materials gives better results than resistivity measurement. Combination of the two would give even better results. They conclude that there exists a relationship between the change of the Seebeck coefficient and the hardness changes due to embrittlement. Resistivity measurements data are less correlated, which can mean that the technique is promising but needs improvements to the experimental set-up. They also report that the use of standard specimens which are more sensitive instrumentation and better electric contacts would even improve the situation. GaSb based binary and ternary alloys have turned out to be important candidates for applications in long wavelength lasers and photo detectors for fiber optic communications. InSb has been interested in high speed applications for transistors and other devices, which is associated directly with the very low electron effective mass and high mobility [19]. Among group II to group IV compounds, the lead chalcogenides with narrow band gap have been studied because of their device applications in IR detectors, photoconductors, thin film transistor etc [20].

Challenges

ZT=1 has been a benchmark for any materials over 30 years since 1960s. The challenge behind the benchmark ZT value is the strong interconnections between (1) S and n, (2) mn and m, (3) m and klat, (4)Wiedemann–Franz law, and (5) bipolar effect. The decoupling of relationships among these physical items would give us a chance to push the ZT value beyond the benchmark. The best thermoelectric materials were defined as ‘‘phonon-glass electron-crystal’’ (or PGEC in short), which means that the materials should have a low lattice thermal conductivity as in a glass, and a high electrical conductivity as in a crystal. The interdependency of the TE parameters makes the enhancement efforts of ZT very challenging. The normal ways of optimizing TE materials are to increase the power factor by optimizing the carrier concentration n, and/or to reduce the lattice thermal conductivity K^{th} by introducing the scattering centers. These parameters are the function of scattering factor r, carrier effective mass m n and carrier mobility m and their interconnectivity limit ZT to about 1 in large bulk materials. According to the kinetic definition S is the energy difference between the average energy of mobile carrier and the Fermi energy. If the carrier concentration n is increased, the Fermi energy as well as the average energy increases. However, the Fermi energy increases more rapidly than the average energy when n is increased. As a result S decreases, dragging the power factor (S^2n) down rapidly. Thus in attempting to increase ZT for most of the homogeneous materials, the carrier concentration (n) increases electrical conductivity(s) but reduces the Seebeck coefficient(S).

Most materials having high mn have generally low m which limits the power factor by a weighted mobility with the relationship of power factor proportional to (mn) 3/2m. It should also be noted that the defects scatter not only the phonons but also the electrons. Hence there are some trade- offs carried out in carrier mobility when designing for reducing lattice thermal conductivity. The ratio of m/K^{th} determines the improvement of ZT. Wiedemann–Frenz

Law states that the electronic contribution to the thermal conductivity is proportional to the electrical conductivity of the materials and the relationship is

$$\frac{K_e}{\sigma} = LT$$

Where, L is Lorenz factor for free electrons and this can vary particularly with carrier concentration. The electrical resistivity(r) is related to the carrier concentration 'n', electron charge 'e' and chemical potential 'm' as

$$\sigma = \mu ne$$

The electronic thermal conductivity can thus be expressed as

$$K_e = \sigma LT = \mu neLT$$

This relationship shows that the low carrier concentration will result into the lower electrical conductivity decreasing ZT. High mobility carriers are most important for high value of electrical conductivity. Again, it is shown that increasing the effective mass of the carrier increases S but reduces the carrier mobility and hence the electric conductivity.

In short, any attempt to increase S, will increase K_e which contributes to thermal conductivity (K). In order to counter the increment of K_e, K_{th} can be decreased by various approaches. These are the major conflicts in the bulk materials properties which were addressed in the researches for more than a half century.

CONCLUSION

Low-dimensional materials such as super lattices offer new ways to manipulate the electron and phonon properties of a given material. The reduction in thermal conductivity is the dominant reason leading to a large increase in the thermoelectric figure of merit in several super lattice systems, which can be used to develop efficient solid-state devices that convert waste heat into electricity. Super lattices grown by thin-film deposition techniques, however, are not suitable for large scale applications. Nano composites can realize similar thermal conductivity reduction and thus represent a cheap approach that can lead to high thermoelectric figure merit. Properly choosing the mismatch in electronic properties between the constituent materials is still a challenge. Modelling the electron transport in nano composites can facilitate finding a solution. Although to date, the current TE materials cannot be in used in very broad applications due to their low conversion efficiency. However, if the combination of combined mechanisms to enhance ZT in HH alloys, such as nano structuring and band structure engineering, are able to achieve values of the *ZT* to 2 or even higher, improve the mechanical properties and maintain their good thermal stability with the nano structuring processes, then the broad range of potential applications for waste heat recovery using TE devices based on this next generation of HH alloys will be very promising .

REFERENCES

[1] Dan Dai, Yixin Zhou, Jing Liu, *Renewable Energy*, **2011**, 36, 3530-3536.
[2] Baoxing Xu, Ling Liu, Hyuck Lim, Yu Qiao, Xi Chen, *Nano Energy*, **2012**, 1, 805–811.
[3] Weishu Liu, Xiao Yan, Gang Chen, Zhifeng Ren, *Nano Energy*, **2012**, 1, 42–56.
[4] Jyrki Tervo, Antti Manninen, Risto Ilola & Hannu Hänninen, *ISBN* 978-951-38-7184-0 (URL: http://www.vtt.fi/publications/index.jsp)
[5] Jing-Feng Li1, Wei-Shu Liu1, Li-Dong Zhao and Min Zhou, *NPG Asia Mater.* **2010**, 2(4), 152–158.
[6] Thermoelectric Materials: Principles, Structure, Properties, and Applications, *Encyclopedia of Materials: Science and Technology* ISBN: 0-08-043152-6 pp. 1–11.
[7] Degang Zhao, Changwen Tian, Shouqiu Tang, Yunteng Liu, Lidong Chen, *Journal of Alloys and Compounds* **2010,** 504, 552–558.
[8] Alam Hilaal, Ramakrishna Seeram, *Nano Energy,* **2012**, http://dx.doi.org/10.1016/j.nanoen.2012.10.005
[9] Adolf Cortel, **2007** Phys. Educ. 42 88
[10] Chunlei Wan, YifengWang, Ning Wang,Wataru Norimatsu, Michiko Kusunoki and Kunihito Koumoto, *Sci. Technol. Adv. Mater.* **2010**, 11, 044306 (7pp)
[11] T.C. HARMAN, M.P. WALSH, B.E. LAFORGE, and G.W. TURNER, *Journal of Electronic Materials,* **2005**, 34, 5.
[12] Matthew Thorum, *Literature Seminar*, November 16, **2006.**
[13] Li PingTana, Ting Suna, Shufen Fana, LayYong Nga, Ady Suwardia, Qingyu Yana,

Huey Hoon Hnga, *Nano Energy* **2012**, http://dx.doi.org/10.1016/j.nanoen.2012.07.004
[14] Mikhail I. Fedorov,* Vladimir K. Zaitsev, *Material Matters,* **2011,** vol.6, No.4, 12-14.
[15] H L Gao, T J Zhu, H Wang, Z F Ren and X B Zhao, *J. Phys. D: Appl. Phys.* **2012**, 45, 185303 (6pp).
[16] K. S. Chaudhari, Y. R. Toda, D. N. Gujarathi, *Arch. Appl. Sci. Res.:* **2011**, 3 (4)21-25
[17] Lassi Karvonen, Petr Tomeš, Anke Weidenkaff, *Material Matters*, **2011**, vol.6, No.4, 4-8
[18] Giri Joshi, Tulashi Dahal, Shuo Chen, Hengzhi Wang, Junichiro Shiomi, Gang Chen, Zhifeng Ren, *Nano Energy* **2012**, http://dx.doi.org/10.1016/j.nanoen.2012.07.020
[19] Tawat Suriwong, Ken Kurosaki, Somchai Thongtem, Adul Harnwunggmoung, Tohru Sugahara,Theerayuth Plirdpring, Yuji Ohishi, Hiroaki Muta, Shinsuke Yamanaka, *Journal of Alloys and Compounds*, **2011**, 509, 4014–**4017**
[20] U. P. Khairnar, S. S. Behere, P. H. Pawar, *Arch. Phy. Res.*, **2011**, 2 (2):157-163