Trioctylphosphine and oleylamine induced thermoelectric power of Ag nanoparticles

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Abstract. In the present study Ag nanoparticles (NPs) of average particle size of 31-51 nm were prepared by the thermal decomposition method in the presence of appropriate concentration of Trioctylphosphine (TOP) and Oleylamine (OA). The X-ray diffraction measurements indicate the occurrence of face-centered cubic metallic Ag-NPs. The compacted pellets of these nanoparticles were investigated using thermoelectric power in the temperature range from 5 to 300 K. The observed thermoelectric power for all the samples are typical of a good metal and are found to be strongly dependent on grain size and the type of cappant used. The magnitude of thermo electric power increases as the particle size decreases. These results clearly indicate dominant role of disorder at grain boundaries and quantum confinement, which influence scattering of phonons and electrons in a significant way.

1. Introduction
Nano size materials exhibit remarkable structural and physical properties different from conventional macroscopic polycrystalline materials. Atoms at grain boundaries (GB) occupy a volume fraction significantly higher than that of conventional materials. Crystal structure, transport, magnetic, optical and mechanical properties can be influenced due to nanostructure [1], which serves as a bridge between molecule and condensed phase. Nano structured transition metal nanoparticles and their compounds are the most studied materials among other elements in the periodic table. These elements show variable valance states due to their low ionization potential. Over the past decades silver and its compounds have been used extensively in many applications. As an antimicrobial agent, the silver was widely applied in wound treatment, medical devices, water purification, air treatment, cosmetics, aqueous paint etc. Along with the rapid development of nanotechnology, special attention has been focused on the Ag nanoparticles because of their exhibited stronger microbial activity and wider range of applications. Due to high electrical conductivity, the Ag nanoparticles are also applied in conductive inks, adhesives and pastes for variety of advanced electronic devices [2]. In the present investigation the synthesis of Ag NPs by chemical route is discussed, which is an easy, simple and convenient route for preparing metal particles in nanometer range. The prepared silver nano particles were characterized using X-ray diffraction (XRD) and thermopower.
2. Experimental

Silver nanoparticles were prepared by thermal decomposition method [3]. Initially 1.0 gram of silver acetate was mixed with 5 ml of Oleylamine (OA) and 100 ml of ethylene glycol (EG) in a 100 ml 3-neck round bottle flask, equipped with condenser and thermometer. The chemical mixture was heated to 180°C. When temperature reached 180°C, the refluxing arrangements were made. The color of complex changed from off-white to light grey and then finally nearly black after an interval of about 2hr which indicates the initiation of formation of silver nanoparticles. The reaction was continued for another two hour. It was cooled to room temperature and sample was separated in the beaker with the help of 20ml hexane and 50ml ethanol. Then, the obtained precipitate was washed with ultrasonic processor and 3-4 times by ethanol. After washing the precipitate the sample was dried and finally it was obtained in the form of dark grey powder. This sample was coded as Ag-1. Similarly, after keeping all the parameters constant, OA was taken 10ml and 15ml to prepare second and third samples. They were coded as Ag-2 and Ag-3. Further Silver nanoparticles were prepared by Trioctylphosphine in place of Oleylamine and rest all experimental conditions were same. This samples was coded as Ag-4. Similarly, after keeping all the parameters constant, TOP was taken 10ml and 20ml to prepare second and third samples. They were coded as Ag-5 and Ag-6.

These NPs were examined by X-ray diffraction (XRD) using Bruker D8 advanced X-ray diffractometer with Cu Kα radiation in the 2θ range from 30º to 90º. Thermopower measurement down to the liquid helium temperatures (5-300k) were carried out using compacted pellet sandwiched between two oxygen free highly conducting blocks and absolute Thermopower was measured with reference to copper block.

3. Results and discussion

XRD data of samples denoted by Ag-1, Ag-2 and Ag-3 for various silver nanoparticles are shown in Fig. 1. Diffraction peaks were observed and matched with standard JCPDS data of two reports viz (87-0720), (75-0969) and lattice parameters were calculated using the matched (hkl) values. It is clear from Fig. 1 that all peaks correspond to face centered cubic structure of Ag-metal showing that the samples prepared were of pure silver metal nanoparticles. Further, XRD data of samples denoted by
Table 1: Particle size and lattice parameter of silver nanoparticles

| Sample | Cappants (ml) | Angle (degree) | FWHM (β, degree) | Particle size (D) (nm) | Lattice parameter (nm) |
|--------|---------------|----------------|-------------------|-----------------------|-----------------------|
| Ag-1   | OA(5ml)       | 38.162         | 0.19372           | 51                    | 0.4081                |
| Ag-2   | OA(10ml)      | 38.163         | 0.17597           | 47                    | 0.4080                |
| Ag-3   | OA(15ml)      | 38.149         | 0.17469           | 44                    | 0.4082                |
| Ag-4   | TOP(5ml)      | 38.35          | 0.1798            | 51                    | 0.4098                |
| Ag-5   | TOP(10ml)     | 38.29          | 0.2389            | 37                    | 0.4061                |
| Ag-6   | TOP(20ml)     | 38.25          | 0.2561            | 31                    | 0.4058                |

Ag-4, Ag-5 and Ag-6 for various silver nanoparticles are shown in Fig. 2. The observed diffraction peaks were matched with standard JCPDS data of two reports and lattice parameters were calculated using the matched (hkl) values. Fig. 2 shows that all the peaks correspond to face centered cubic structure of Ag-metal showing that the samples prepared were of pure silver metal nanoparticles. The calculated particle size and lattice parameter were reported in Table 1.

Figure 3 and 4 show the variation of thermopower ($S$) of silver nanoparticles with different particle sizes and cappants. For a comparison, the data for bulk Ag (Ag-bulk) is also included from literature [4]. It is clear that in the bulk Ag, the sign of $S$ is positive throughout the temperature range (10-300K), indicating the holes as majority charge carriers as consequence of contribution from the necks of the Fermi surfaces [4]. In stark contrast, the $S$ of the nanocrystalline silver show almost mirror-reflection of that of bulk Ag. Such an observation indicates that the transport behavior in the samples is completely modified as compared to that of the bulk. In the range ~85 K to 205 K, $S$ exhibit positive values, indicating that the holes are majority charge carriers.

On the other hand, $S$ shows negative values in the temperature range ~10 to 85 K and 205 to 300 K, indicating that the electrons are the majority charge carriers. Such behavior indicates that the overall contributions of the majority charge carriers are highly temperature-dependent. These results clearly indicate dominant role of disorder at grain boundaries, which influence scattering of phonons and
electrons in a significant way. Size effect on contributions from electrons and phonons is, in particular, attributed to their effective mean free path being reduced when $D$ is comparable to or smaller than mean free path. In such situation, flow of phonon is restricted i.e. localized continually and transport of phonons is limited thereby decreasing phonon thermo power as $D$ decreases.

4. Conclusion
Nanocrystalline samples were prepared by thermal decomposition method. The estimated particle size is found to be in the range of 31-51nm from XRD data. As we increase the amount of cappant in sample the particle size was found to be decreasing. The magnitude of thermopower decreases as the particle size decreases. These results clearly indicate dominant role of disorder at grain boundaries which influence scattering of phonons and electrons in a significant way.

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