International Journal of Multidisciplinary Research and Development
www.allsubjectjournal.com
ISSN Online: 2349-4182 ISSN Print: 2349-5979
Received: 15-01-2023, Accepted: 31-01-2023, Published: 17-02-2023
Volume 10, Issue 2, 2023, Page No. 18-21

One-pot chemical synthesis and characterization of intermetallic iron antimonide ($FeSb_2$)

Sunidhi[1], Manish Srivastava[2], Deepak Gujjar[3*]
[1] Department of Chemistry, Banasthali Vidyapith, Tonk, Rajasthan, India
[2] Department of Chemistry, Allahabad University, Prayagraj, Uttar Pradesh, India
[3] Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand, India

Abstract
Intermetallic nanocrystals show promising magnetic, thermoelectric and electronic properties. Nonetheless, nonorange synthesis methods are scarce, which restrict their exploration in applications. Here, we report a powerful and economical one-pot polyol approach for the synthesis of low-temperature thermoelectric $FeSb_2$ nanoparticles. The structure of $FeSb_2$ was confirmed by X-ray diffraction (XRD). The formation of spherical particles in the range of 10-20 nm was confirmed by scanning electron microscope (SEM) and transmission electron microscope (TEM). Furthermore, the thermal stability and magnetic nature of particles were analyzed by thermogravimetric analysis (TGA) and superconducting quantum interference device (SQUID) magnetometer, respectively.

Keywords: intermetallics, $FeSb_2$, polyol approach, thermoelectrics, magnetization

Introduction

Intermetallics, consisting of transition-metal and main group elements, gain tremendous attraction in the research community, due to their multifunctionality in various fields such as hydrogen storage, thermoelectrics, spintronics, shape memory effect, superconductivity, etc. [1, 2] The unique character of adopting of specific crystal and electronic structure compared to its constituent elements, makes them structurally and mechanically stable [3].

Intermetallic $FeSb_2$ has been well explored in the field of thermoelectrics for cryogenic applications as it exhibits a huge Seeback coefficient of 45000 $\mu V\ K^{-1}$ at temperatures around 10 K. [4-5] But, the very high value of its thermal conductivity limits the overall thermoelectric performance and hence, restricts its use for practical applications [6]. Several studies revealed an improvement in the thermoelectric performance of materials by introducing more scattering points in the system, i.e., nanostructuring of the materials [7].

Synthesis of intermetallic compounds generally requires a high reaction temperature, which is possible in physical techniques such as arc-melter, sputtering, flux growth, chemical vapour transport, etc [1]. But, the main disadvantage of these routes is bulk sampling as it again requires top-down approaches such as ball-milling for the nanostructuring of the material. Therefore, the direct synthesis of nanosized materials using a bottom-up approach is the need of the hour. wet-chemical synthesis of $FeSb_2$ has previously been reported in literature via solvothermal, [8-10] low-temperature molten-salt, [11] and modified polyol approaches [1, 12].

In this contribution, we report the successful synthesis of $FeSb_2$ nanoparticles via a simple and economical one-pot polyol (high-boiling solvent) approach without adding any external surfactant or reducing agent. It is worth highlighting the main advantage of this method to solvent (polyol) reusability, which makes it a green synthesis method.

Material and methods

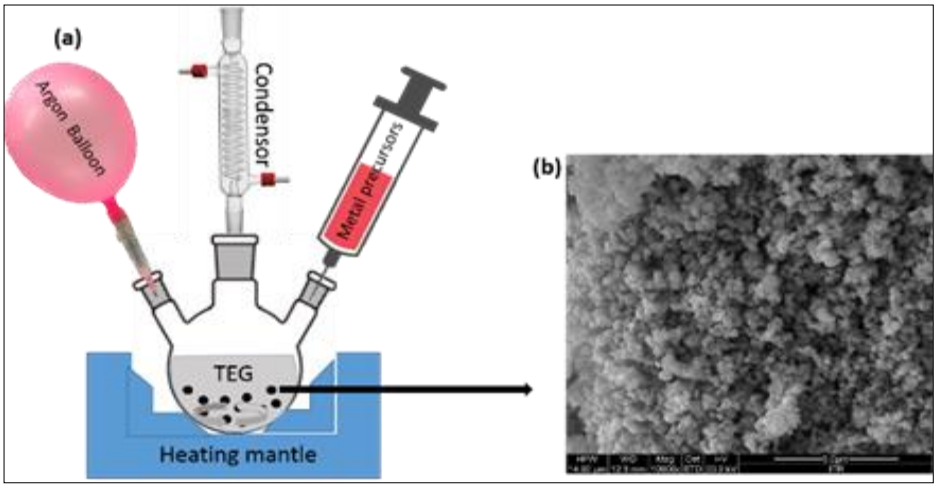

Fig 1: Synthesis protocol of FeSb2 (a) and SEM micrograph of FeSb2 revealing agglomeration of spherical particles (b).

Chemicals

Anhydrous $FeCl_3$ (Loba Chemie, 99%) and $SbCl_3$ (Alfa Aesar, 99+ %) were used as metal precursors. Triethylene Glycol (Sisco Research Laboratory Pvt. Ltd, 99%) was used as solvent, which itself plays the role of reducing agent and capping agent as well. Ethanol, acetone and deionized water were used for washing of particles. All the chemicals were utilized without any further purification.

$FeSb_2$ Synthesis

The nanoparticles were synthesized using a simple polyol method without adding any external reducing agent. Firstly, 1 mmol of $FeCl_3$ and 2 mmol of $SbCl_3$ were added and sonicated in 30 ml triethylene glycol (TEG) and transferred to three-necked round-bottommed flask under argon atmosphere. The mixture was refluxed at 270 °C for 3h with constant stirring. The formed black precipitate was centrifuged at ~10000 rpm and washed with ethanol, acetone and deionized water to remove any residual impurities. The powder was dried at 80 °C for 8 h to remove any residual moisture and used for further characterization. The synthesis process is schematically illustrated in fig. 1.

Characterization

The structural phase investigation of as-synthesized $FeSb_2$ sample was carried out using X-ray diffraction (Bruker D8 Advance,) equipped with LINEYE XE detector and CuKα (λ=0.154056 nm) as X-ray source with a step size of 0.02°/s in the continuous scan mode. Microstructural and morphological characteristics were studied using Carl Ziess ultra plus scanning electron microscope (SEM). Transmission electron microscope (TEM) images, energy dispersive X-ray analysis (EDXA) and selected area diffraction (SAED) patterns were obtained using FEI Tecnai G2 20 S-Twin microscope equipped with LaB_6 as electron source. Thermogravimetric analysis (TGA) and differntial thermal analysis (DTA) were performed in argon atmosphere at flow rate of 200 mL/min using a SII 6300 EXSTAR with a heatng rate of 10 °C/min. Quantum design MPMS3 superconducting quantum interference device (SQUID) magnetometer was used for magnetic moment measurements.

Result and discussion

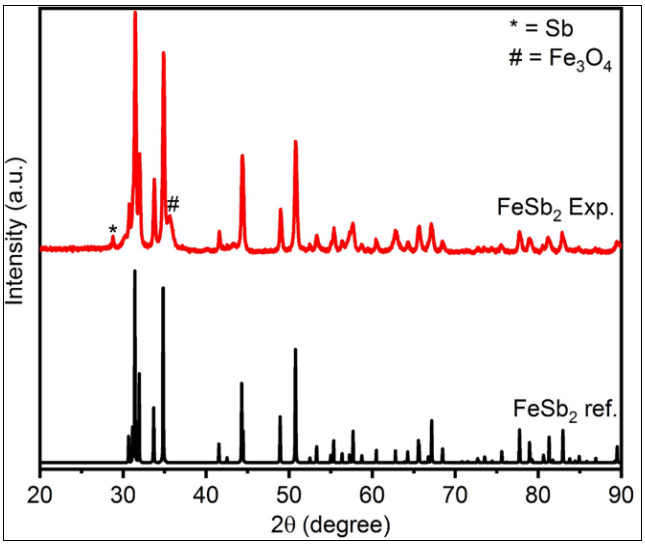

Fig 2: XRD pattern of as-synthesized $FeSb_2$ Sample along with reference data.

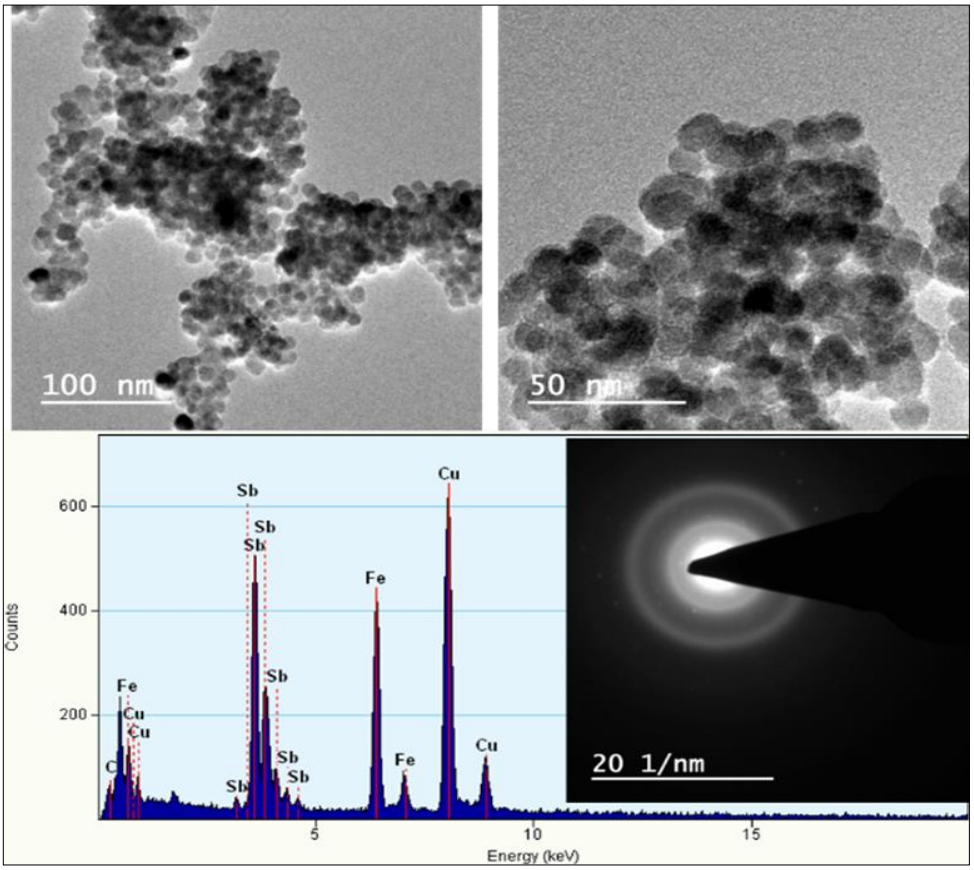

Fig 3: TEM images of $FeSb_2$ smaple with EDXA analysis and SAED pattern.

The XRD pattern of as-synthesized $FeSb_2$ particles was recorded in the 2θ range of 20°–90° at room temperature. The pattern shown in Fig. 2 indicates the crystallization of $FeSb_2$ in orthorhombic phase (marcasite-type) with space group Pnnm. The relative peak intensities and peak positions of generated pattern are consistent with the referenced XRD pattern (ICCD No: 04-010-4959). The strong reflection peaks correspond to (011), (101), (120), (210), (111), (130), (211) and (031) planes. The sharp peaks without any significant broadening showed the highly crystalline nature of the sample. The presence of two small additional peaks at around 30° and 36° correspond to the Sb and Fe_3O_4 phase, respectively, suggesting minor impurity in the sample.

The transmission electron microscopy (TEM) images of as-synthesized $FeSb_2$ were captured by drop-casting the ethanol dispered particles on a copper-grid and are shown in images is in good agreement with that observed from SEM images (though agglomerated). The size of the nanoparticles was found to be in the range of 10-20 nm. The presence of bright rings in the selected area electrons diffraction (SAED) pattern, indicates that the synthesized particles are well crystalized and are polycrystalline in nature. The elemental composition of Fe and Sb, based on Energy dispersive X-ray analysis (EDXA) was found to be in the ratio of 1:1.23, confirming the formation of additional Fe_3O_4 phase as indicated by the XRD pattern.

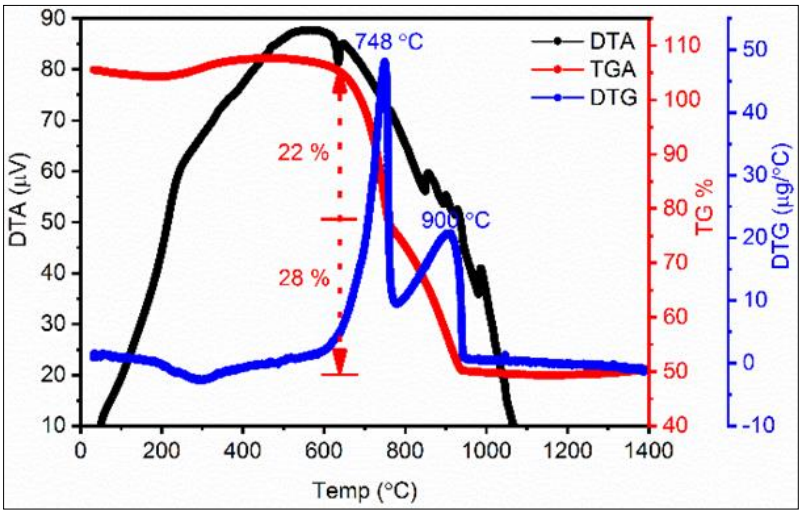

Fig 4: Thermal analysis of $FeSb_2$ sample: TGA(red), DTG(blue) & DTA(black) recorded under argon atmosphere.

Thermal analysis of $FeSb_2$ was investigated with a 10 mg sample with same amount of reference alumina powder in argon atmosphere in the temperature range 35 -1400 °C and the recorded data are shown in Fig. 4. The TGA (red) and corresponding first derivative DTG (blue) curve clearly indicate that about 22 % weight loss occurs at 748 °C which corresponds to the melting temperature of $FeSb_2$. The approximately 28 % reduction in weight at 900 °C is probably due to decompostion of $FeSb_2$ into FeSb at this temperautre. Both conclusions are supported by endothermic peaks in DTA (black) curve at the respective temperatures. No weight loss before the melting point of $FeSb_2$ suggests its anhydrous nature. The small amount of weight gain after 200 °C is probably due to oxidation or buoyancy effects.

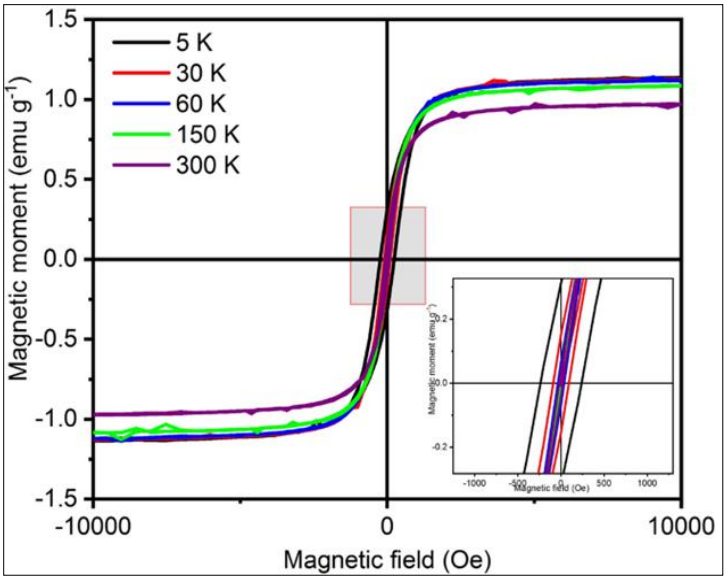

Fig 5: Magnetization of as-synthesized $FeSb_2$ samplele as a function of applied magnetic field at five different temperatures (5-300 K). Insets: enlarged area around the origin.

Fig. 5 shows the field dependence of the magnetization at five different temperatures in the range of 5-300 K. The magnetic moment increases with the applied magnetic field and magnetization saturation occurs at the magnetic field of ~3KOe. The generation of hysteresis loop and greater opening at low temperature reflect the ferromagnetic nature of the particles. The coercivities values of 240, 90, 40, 10 and 20 Oe, were observed at 5, 30, 60, 150 and 300 K, respectively. Since, the pure $FeSb_2$ is diamagnetic at low temperatures and paramagnetic at 300 K,[13] it is evident that this weak ferromagnetism is due to the small Fe_3O_4 impurity in the sample.

Conclusion

We have presented a one-pot wet-chemical synthesis of $FeSb_2$ nanoparticles via simple polyol approach using metal chlorides as precursors. The particle size has been controlled under 20 nm without the addition of any external capping and reducing agent. Sample characteristics has been analysed using XRD, SEM, TEM, TGA, DTA and SQUID. The result revealed a slight magnetic impurity of Fe_3O_4 in the sample. The synthesis method estabilished here should guide the researchers to develop other binary intermetallics using transition-metal and main group elements.

Acknowledgement

Authors are thankful to institute instrumentation center (IIC), IIT Roorkee for providing sample characterization facilities.

References

1. Birkel CS, Kieslich G, Bessas D, Claudio T, Branscheid R, Kolb U *et al*. Wet chemical synthesis and a combined X-ray and mossbauer study of the formation of $FeSb_2$ nanoparticles. Inorg. Chem,2011:50:11807-11812.
2. McGrath AJ, Thompson JD, Ronning F, Ivanov SA. One-pot size-controlled synthesis of tin- and antimony-based intermetallic nanoparticles. Chem. Mater.2023:35(2):457-467.
3. Furukawa S, Komatsu T. Intermetallic compounds: promising inorganic materials for well-structured and electronically modified reaction environments for efficient catalysis. ACS Catal,2017:7(1):735-765.
4. Homes CC, Du Q, Petrovic C, Brito WH, Choi S, Kotliar G. Unusual electronic and vibrational properties in the colossal thermopower material $FeSb_2$. Sci. Rep,2018:8:11692-11701.
5. Sun P, Oeschler N, Johnson S, Iversen BB, Steglich F. $FeSb_2$: prototype of huge electron-diffusion thermoelectricity. Phys. Rev. B,2009:79(15):153308-153312.
6. Sun P, Oeschler N, Johnsen S, Iversen BB, Steglich F. Narrow band gap and enhanced thermoelectricity in $FeSb_2$. Dalton Trans,2012:39:1012-1019.
7. Zhao H, Pokharel M, Zhu G, Chen S, Lukas K, Jie Q, *et al.* Dramatic thermal conductivity reduction by nanostructures for large increase in thermoelectric figure-of-merit of $FeSb_2$. Appl. Phys. Lett,2011:99:163101-163104.
8. Kumari L, Li W, Huang JY, Provencio PP. Nanosize transition metal antimonides, NiSb and $FeSb_2$: solvothermal synthesis and characterization. J. Phys. Chem. C,2010:114:9573-9579.
9. Datta A, Nolas GS. Synthesis and characterization of nanocrystalline $FeSb_2$ for thermoelectric applications. Eur. J. Inorg. Chem,2012:1:55-58.
10. Wei K, Martin J, Nolas GS. Synthesis, SPS processing and low temperature transport properties of polycrystalline $FeSb_2$ with nano-scale grains. Mater. Lett,2014:122:289-291.
11. Saleemi M, Tafti MY, Jacquot A, Jägle M, Johnsson M, Toprak MS. Chemical synthesis of iron antimonide ($FeSb_2$) and its thermoelectric properties. Inorg. Chem,2016:55:1831-1836.
12. Kieslich G, Birkel CS, Veremchuk I, Grin Y, Tremel W. Thermoelectric properties of spark-plasma sintered nanoparticular $FeSb_2$ prepared via a solution chemistry approach. Dalton Trans,2014:43:558-562.
13. Pokharel M, Zhao H, Modic KA, Ren Z, Opeil C. Magnetic properites of hot-pressed $FeSb_2$. IEEE Trans. Mag,2014:50(5):2400304.