

**SYNTHESIS OF  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$  COMPOUND FOR THERMOELECTRIC APPLICATION**

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**Abstract**

In this work,  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$  thermoelectric compound was synthesized using high energy milling and heat treatment. The starting mixture include Cu, Bi and S elemental powders at the stoichiometry ratio of the formula  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$  were ball milled in a planetary ball mill and heat treated in an electric furnace. The results shown that after 10 hours of milling, a compound identified as  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  was formed. The 16h milled powder was heat-treated at 350, 400 and 450°C for 1 hours at a heating rate of 8 °C/minute, XRD of the annealed powder reveals that the  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  obtained fully transformed into  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$  after being heat treated at 400°C. Meanwhile,  $\text{Bi}_2\text{S}_3$  was found in the powder being annealed at 350°C. The 5h milled powder was also annealed at 400°C for 1 hours at a heating rate of 2 and 8 °C/minute, XRD analysis show that  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$  was also formed in the heat-treated powder with the heating rate of 2 °C/min.

**Keywords:** bismuth chalcogenide, thermoelectric materials, clean energy material, powder metallurgy

**1 Introduction**

Energy is central to the survival and prosperity of human society. It is no surprise that sciences consider energy production, consumption and distribution as a major subject of research and development [1, 2]. Currently, the main source of energy in the world is fossil fuels. However, fossil fuel resources are increasingly exhausted along with serious environmental problems arises from their used that have led to the development of new technology to improve the efficiency of fossil fuel usage or finding new energy sources [3-8].

Thermoelectric technology based on thermoelectric materials is an advanced technology for directly converting heat into electricity. When developed to take advantage of waste heat sources, thermoelectric plants help improve energy efficiency and reduce environmental pollution. Thermoelectric equipment has many advantages such as high reliability, has no moving parts and produces no noise and emission [7, 9, 10]. There are different types of thermoelectric materials under development. Each type of thermoelectric material operates efficiently within a specified temperature range: high (>700°C), medium (~400°C) and low (<230°C) [11].

$\text{Bi}_2\text{Te}_3$  is one of the most common thermoelectric material for use near room temperatures of up to 230°C [12-14]. However, Te is considered a toxic and expensive element so research and development are focusing on non-toxic thermoelectric materials such as  $\text{Bi}_2\text{S}_3$ , PbS, CdS, TiS<sub>2</sub> and Ag<sub>2</sub>S [15]. At high temperatures, the Si-Ge material is remarkable for its ability to work at temperatures up to 1000°C and is commonly used in spacecraft. However, this material has the

disadvantage of high thermal conductivity which lowered its conversion coefficient. There have been studies to reduce the thermal conductivity of this type of thermoelectric materials [16-22]. At medium temperature (about 400 °C), CuS thermoelectric material has many advantages such as: high thermal conversion efficiency, low production cost, low toxicity and abundant supply. This is a common temperature range for the application of thermoelectric materials. As a result, more and more researches are being done to develop thermoelectric materials that operate at medium temperature ranges.

Studies on medium temperature CuS thermoelectric materials began with researches on kesterite ( $\text{Cu}_2\text{ZnSnS}_4$ ), digenite ( $\text{Cu}_{1.8}\text{S}$ ), and chalcopyrite ( $\text{CuFeS}_2$ ). Subsequent studies on  $\text{Cu}_{12-x}\text{Tr}_x\text{Sb}_4\text{S}_{13}$  (where Tr is the 3d transition metal and Zn) [23]. Some other materials such as lead telluride, clathrate, silicite, skutterudite also have good conversion efficiency at temperatures of 500-600 °C [2, 24-27].

In this work,  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$  thermoelectric compound was synthesized by powder metallurgy. The compound was synthesized from Cu, Bi and S powders, the factors that influence the synthesis process such as milling time and heat treatment condition are also studied.

## 2 Experimental procedure

In this work, copper (Cu), bismuth (Bi), and sulfur (S) powder were used as the starting materials. The Cu powder was 99.5% of purity (Strem Chemicals Inc.), Bi powder was 99% of purity (Sigma Aldrich), and S powders was 99.5% of purity (Alfa Aesar Co. Ltd). The Cu, Bi and S powder were mixed at an atomic ratio of 1.6:4.6:8 under argon atmosphere.

The powder mixture was then milled using a planetary ball mill (Fritsch Pulverisette 6) with a ball to powder ratio of 10:1 and a milling speed of 300 rpm. The milling process was carried out under argon atmosphere. The obtained milled powder was compacted at 250 MPa using a hydraulic press into a disk shape pellet of 10 mm in diameter and 3 mm in thickness. The compacted pellets were then heat treated in an electric chamber furnace (Nabertherm B150).

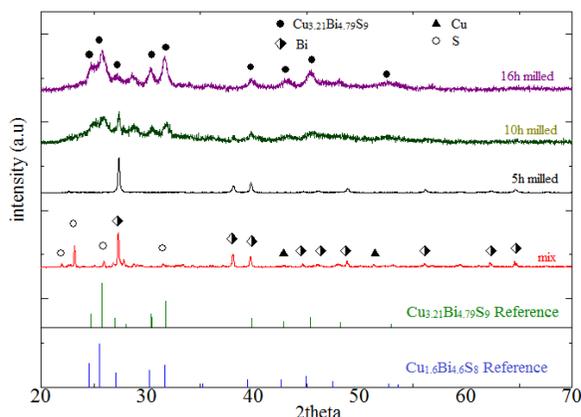
Phase analysis was carried out using XRD (Bruker D8 Advance). The surface morphologies and topologies of powder were studied by FE-SEM (Hitachi S-4800). The thermal stability of the milled powder was investigated using a differential scanning calorimeter (Setaram Labsys 18)

## 3 Results and discussion

### 3.1 CuBiS compounds prepared under different milling time

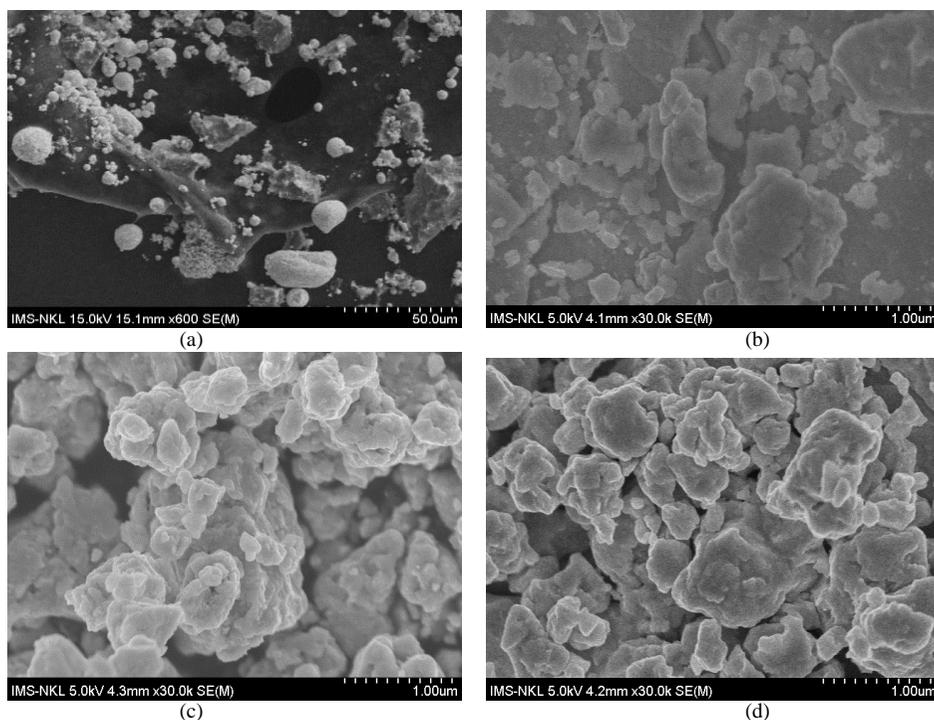
**Fig. 1** shows the XRD patterns of powders after different milling time. After being milled for 5 h, Cu and S phases were disappeared whereas the intensity of Bi showed little decreased. The results showed that in the incipient stage of milling, the milling energy was not enough to make Bi react with Cu or S, just causing the reaction of Cu and S. The increasing of milling time accumulated energy and Bi powders were gradually involved in the reaction with Cu and S. When the milling time was extended to 10 h, a compound identified as  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  (PDF# 01-073-1202) was detected and the intensity of Bi was vastly reduced. After 16 h of milling, nearly single-phased  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  compound was synthesized.

The formation of  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  was also reported, according to Barma [28], the  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  compound was found after only 5 h of milling whilst the presence of secondary phases such as  $\text{Bi}_2\text{S}_3$  and  $\text{Cu}_2\text{S}$  were also detected. These secondary phases were disappeared after 15h milling. This work revealed that the ternary compound  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$  cannot be directly synthesized by milling. The final stable compound obtained after the milling process was  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$ .



**Fig. 1** XRD patterns of the powders after different milling duration

**Fig. 2** shows the SEM images of powder obtained at various milling times. After 5 h of milling, the powders were blended together, and the boundary of particles was blurred. The increasing of milling time resulted in finer particles and a homogeneous mixture was obtained after 16 h.

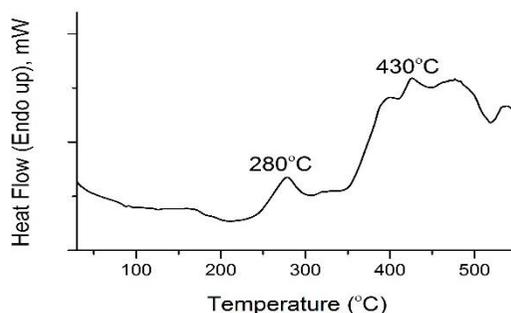


**Fig. 2** SEM images of powders after a) 0h, b) 5h, c) 10h and d) 16h of milling

### 3.2 Thermal analysis

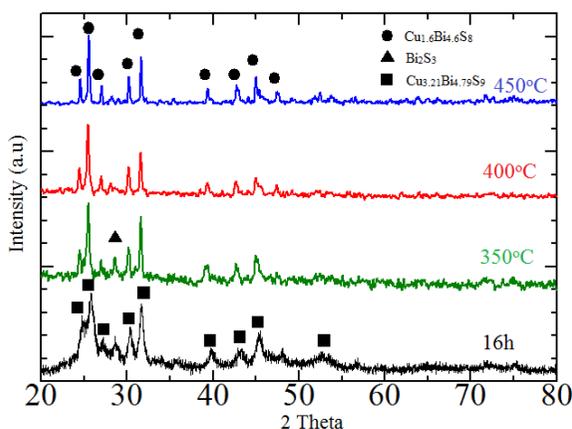
The  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  compound obtained after 16 hours of milling was subjected to thermal analysis using a differential scanning calorimeter (DSC) with a heating rate of  $8\text{ }^\circ\text{C}/\text{min}$ , the DSC curve obtained is shown in **Fig. 3**.

The DSC curve suggested that there were phases change when the  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  was heated up to 500 °C. The first phase transformation may have occurred at approx. 280 °C and might be a second change at approx. 430 °C. The endothermic peak at 280 °C might have indicated the decomposition of  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  upon heating. Thus, the  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  compound, which also can be used as a thermoelectric material, should not be used for higher than 250 °C application. In another study [28], the decomposition of  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  was suggested at 260 °C.



**Fig. 3** DSC curve obtained from 16h milled powder

The  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  powder were heat treated at 350, 400 and 450 °C, phase transformation of the compound was investigated using XRD to interpretation of the DSC results. **Fig. 4** shows the XRD patterns of powders at different heat-treated temperature and the XRD patterns of powders before heat treated. **Fig. 4** has depicted that after being heat treated at 350 °C, the  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  compound was disappeared in the powder and the present of another compounds, the  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$  was detected. It can be concluded that the  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  was transformed into  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$ , this result confirmed that there was phase changed at 280 °C as suggested in the DSC curve.



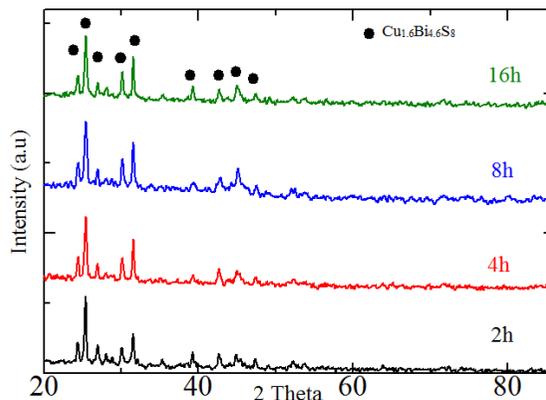
**Fig. 4** XRD patterns of powders at different heat-treated temperature

There was also another phase identified in the powder heat treated at 350 °C, the  $\text{Bi}_2\text{S}_3$  which was not found in the milled powders. The presence of  $\text{Bi}_2\text{S}_3$  suggested that to some extent, the  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  was not directly transformed to  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$ . The heat treatment temperature was not able to convert the  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  powder into  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$  powder. At higher heat-treated temperature, the

$\text{Bi}_2\text{S}_3$  peak was no longer appear in the XRD pattern, the obtained powders were solely  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$ .

### 3.3 Synthesis of $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$ using heat treatment

In order to investigate the effectiveness of the milling process, powder with different milling duration are subjected to similar annealing condition. The compacted powders were heated at the heating rate of  $2\text{ }^\circ\text{C}/\text{min}$ , the XRD analysis results are shown in **Fig. 5**.



**Fig. 5** XRD patterns of powders with different milling duration, heat-treated at  $400\text{ }^\circ\text{C}$

After being heat treated at  $400\text{ }^\circ\text{C}$ ,  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$  was successfully synthesized in all the sample regardless the milling duration. The only phase detected in all cases was  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$ . The milling process has helped to create a homogeneous powder mixture. It is also provider part of the energy need for the reaction of elemental powders. In this case, it helped in the formation of intermediate phase, the  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$ , which stabilizer the powder before heat-treating.

The results suggest that it is possible to directly synthesis  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$  by heat treatment only. However, the process might require special apparatus and carefully control of the heat-treated conditions such as heating rate and temperature.

## 4 Conclusion

$\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$  thermoelectric compound was successfully synthesis using high energy ball milling and heat treatment. The milling process has helped to create a homogeneous powder mixture, provided part of the energy need for the reaction of elemental powders and assist the formation of intermediate phase, the  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$ , which stabilizer the powder before heat-treating. After 10 hours of milling,  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  was formed and remains the major phase in milled powders. The  $\text{Cu}_{3.21}\text{Bi}_{4.79}\text{S}_9$  obtained fully transformed into  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$  after being annealed at  $400\text{ }^\circ\text{C}$  and above.  $\text{Cu}_{1.6}\text{Bi}_{4.6}\text{S}_8$  could also be synthesized form powder with less than 10h of milling. The short-milled powder required carefully control of the heat-treating process.

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