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Microstructure analysis and thermoelectric properties of iron doped $CuGaTe_2$

Fahim Ahmed [a, b], Naohito Tsujii [a, *], Takao Mori [a, b, **]

[a] International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba 305-0044, Japan
[b] Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8577, Japan

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ABSTRACT

Chalcopyrite related compounds have attracted much attention in recent years due to their promising thermoelectric properties. In this research we report Fe doping in chalcopyrite-type $CuGaTe_2$ and its influence on structural and thermal transport properties. We synthesized polycrystalline samples with composition $CuGa_{1-x}Fe_xTe_2$ with $x = 0.0$ to 0.05 by spark plasma sintering method. For structural analysis powder X-ray diffraction and electron probe micro analysis were employed. Solubility of Fe in $CuGaTe_2$ was found to be very small, and other phases like $FeTe_2$ and CuTe were identified. Thermal conductivity showed a significant decrease with the addition of Fe up to $x = 0.02$, which started to increase for $x \geq 0.03$. On the other hand, the addition of Fe caused slight increase in the power factor from 1.3 mW/K^{2}m for $x = 0.0$ to 1.6 mW/K^{2}m for $x = 0.02$ at $T = 770$ K. As a result, ZT peak value of 0.92 is recorded for $x = 0.02$ at 870 K, which corresponds to an enhancement of 60% from that of non-doped $CuGaTe_2$. This work demonstrates that thermoelectric properties of composite materials can be greatly improved by controlling its microstructure.

1. Introduction

Energy statistics shows that a large portion of fossil fuel consumed is wasted in the form of heat. This enormous energy loss is not only a waste but also considered as a source for global warming. Growing demand for energy and continuously shrinking fossil fuel reserves call for alternative energy sources. Possible solutions have been proposed in the form of renewable energy techniques like solar cells, fuel cells, and wind turbines etc. Waste heat recovery, which can be possible by thermoelectric (TE) generators, is also considered to be a promising source for renewable energy. Thermoelectric generators have many advantages over other renewable energy techniques; long operating life time, no moving parts, and being environmental friendly. As a result, thermoelectrics are a hot research topic in the energy field [1–3]. Generally TE materials are evaluated by the dimensionless figure of merit, $ZT = S^2T/\rho\kappa$ where S is Seebeck coefficient, ρ is electrical resistivity, κ and T are used for thermal conductivity and absolute temperature, respectively. Higher ZT represents better heat converting efficiency. To overcome the interdependence of parameters described above is the main challenge in achieving high ZT. Materials with high electrical conductivity are apt to have low Seebeck coefficients, and high thermal conductivity [4,5]. Optimization of charge carriers by doping and phonon scattering by introducing defects and nanostructures inside the materials has resulted in higher ZT values [6–12]. Nevertheless, TE generators are not yet widely used for practical applications, which shows higher ZT is required to make this technology economically viable [13].

Chalcopyrite-type compounds are extensively being studied and considered as a good TE family due to its remarkable TE properties [14–22]. $CuGaTe_2$ is a p-type compound with an energy gap of 1.2 eV. In terms of TE performance, $CuGaTe_2$ has attained a leading position in ternary chalcopyrite compounds. Therefore, it has attracted much attention recently and many reports show high ZT values, including $Cu_{1-x}Ag_xGaTe_2$ [23], $CuGa_{1-x}Zn_xTe_2$ [24], $CuGa_{1-y}In_yTe_2$ [25], $CuAg_xGa_{1-x}Te_2$ [26], $Cu_{1-x}GaSb_xTe_2$ [27], and so on. Until now the highest ZT value of 1.4 was reported at 950 K for $CuGaTe_2$ [28], which has not been achieved afterwards. In our previous work we observed a high power factor of 1.5 mW/K^{2}m in Mn-doped $CuGaTe_2$, which was able to be explained by the influence of magnetic moments and charge carriers interactions [29]. In this research we synthesized

* Corresponding author.
** Corresponding author. International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba 305-0044, Japan.
E-mail addresses: TSUJII.Naohito@nims.go.jp (N. Tsujii), MORI.Takao@nims.go.jp (T. Mori).
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dense sintered samples of $CuGa_{1-x}Fe_xTe_2$ where $x = 0.0$, 0.01, 0.02, 0.03, 0.04, 0.05. Solubility limit of Fe inside $CuGaTe_2$ was analyzed through electron probe micro analysis (EPMA) and X-ray diffraction. Proportion of secondary phases are found to increase upon Fe-doping, and Fe has poor solubility in $CuGaTe_2$. It is found that the morphology and the grain size of the secondary phase changes sharply at $x = 0.02$, which plays essential part in altering TE properties, especially through reducing thermal conductivity while almost maintaining electrical properties. As a result, *ZT* peak value of 0.92 was recorded at 870 K for $x = 0.02$, which is substantial enhancement compared to $ZT = 0.50$ for non-doped $CuGaTe_2$, observed in the present study. Our results show that this material is promising for TE applications at high and intermediate temperature range. This work also describes the role of secondary phases to enhance TE properties from the viewpoint of the relation between microstructure and thermal conductivity.

2. Method and materials

2.1. Sample preparation

We synthesized polycrystalline samples with compositions $CuGa_{1-x}Fe_xTe_2$ where $x = 0.0$, 0.01, 0.02, 0.03, 0.04, and 0.05 by melt and anneal method. High purity specimens, Cu (99.99%), Fe (99.99%) Ga (99.9999%), Te (99.9999%) were used in synthesis. After weighing in stoichiometric amounts and dry mixing, starting materials were sealed in evacuated quartz tube. These tubes were then heated gradually to 1173 K, and were held at this temperature for 12 h followed by annealing at 873 K for same period of time. After annealing, samples were slowly cooled down to ambient temperature. Obtained ingots were then crushed into fine powders with mortars. Pellets of obtained powders were prepared by Spark plasma sintering at 823 K under 50 MPa in an inert atmosphere. These high dense pellets were used for further characterizations.

2.2. Sample characterization

Structural analysis was done by powder X-ray diffraction Technique using Cu Kα radiation using a RINT TTR-3 diffractometer (Rigaku Co., Akishima, Tokyo, Japan). Thermal stability of samples were analyzed by thermogravimetric analysis (TG) and differential thermal analysis (DTA) using Thermo-Plus EVO (Rigaku Co.) under argon flow. Minute weight loss was observed in the temperature range of 800–900 K. Hence, all physical-property measurements were done up to 870 K. To avoid any ambiguity we recorded cooling data as well, which agreed with those of the heating process.

Microstructure and elemental mapping analysis were performed by means of electron probe micro analysis (EPMS) using JEOL JXA-8900F. Chemical composition of the samples was analyzed by the wavelength dispersive spectroscopy (WDS). Standard materials for chemical composition analysis were Cu, Fe, Te, and GaP.

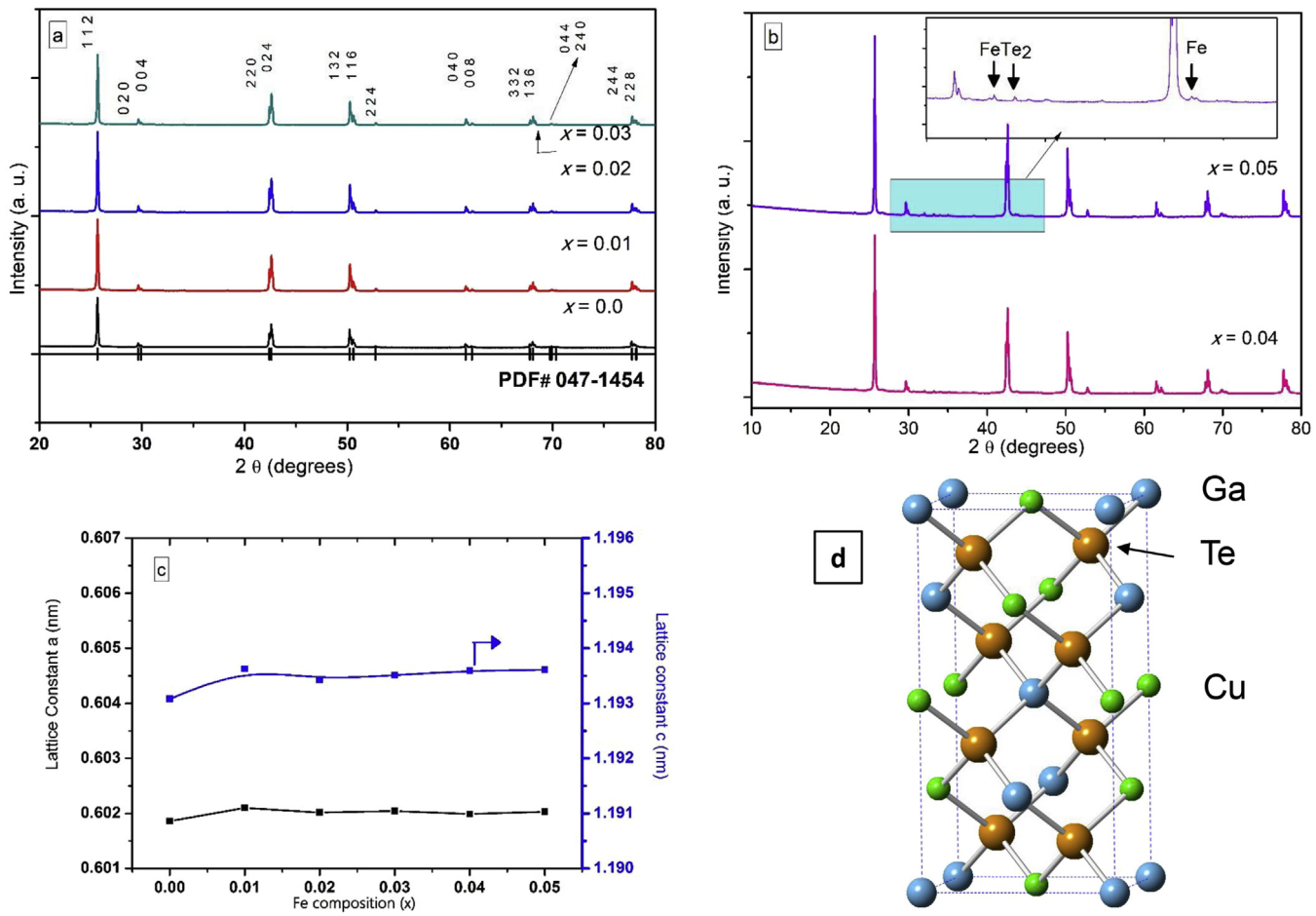

Fig. 1. Powder XRD patterns of polycrystalline samples of $CuGa_{1-x}Fe_xTe_2$ ($x = 0$, 0.01, 0.02, 0.03). Reference card data for standard chalcopyrite structure is shown below the PXRD patterns. (b) XRD patterns of $CuGa_{1-x}Fe_xTe_2$ ($x = 0.04$, 0.05) clearly showing secondary phase peaks in the inset. (c) Plot of Lattice constants with respect to Fe composition.(d) Schematic of chalcopyrite type structure of $CuGaTe_2$.

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