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Influence of high energy β-radiation on thermoelectric performance of filled skutterudites compounds

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ABSTRACT

The influence of MeV β-rays irradiation on the thermoelectric performance of n-type filled skutterudite material has been investigated using an electron accelerator. Using a Monte-Carlo simulation base on Fluka code, the deposited energy in the sample material from the irradiation is estimated, which shows a large power deposited around 50 W/mm. Nevertheless, the thermoelectric performances of the filled skutterudite samples are compared before and after irradiations. It indicates that the thermoelectric material will not be easily jeopardized by 'light' irradiations with energy lower than MeV range.

1. Introduction

Thermoelectric (TE) technique has received considerable attention since the middle of last century, due to its possibility to achieve the conversion between thermal and electric energies in solid state through Seebeck or Peltier effects [1]. For both electric power generation from temperature difference and cooling from electric power, the conversion efficiency is determined by the figure of merit ZT, $ZT = S^2\sigma T/\kappa$, where S, σ and κ represent the Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively [1–3]. The past twenty or so years have witnessed a fast improving in the ZT value of thermoelectric compounds, especially for filled skutterudite system [4]. Currently, the maximum ZTs, 1.3–1.4 for dual-filled skutterudites [5,6] and 1.7–1.9 for multiple-filled skutterudites, [7,8] have been achieved in this system. Due to such excellent thermoelectric performances, filled skutterudites have emerged as prospective candidates for many applications, such as Radioisotope Thermoelectric Generators (RTGs) as the power source for spacecraft or deep space satellite [9,10].

Apart from the progresses in improving the thermoelectric performances of filled skutterudites, the stability of this system in practical applications is of equal importance. This is critical, in particular, when applying filled skutterudites in RTGs, which are required to carry out the space missions lasted for multi-year or even several decades. In this case the thermoelectric materials are exposed under high-energy irradiations from X-rays, electrons, and ion beams [11–13]. High energy radiation are commonly found in space environment, and well known powered by high energy cosmic rays. Primary Cosmic rays are originated outside the earth's atmosphere, and primarily high-energy protons, atomic nuclei and β-rays (electrons). Significant fraction of cosmic rays arises from the explosion or supernova of massive stars, and active galactic nuclei, which is powered by supermassive black holes, probably also emit significant amount of cosmic rays into space [11–13]. These irradiations are considered to generate defects [14,15] in the materials that may jeopardize the thermoelectric performances for long-term usage. For example, a decrease in both the carrier concentration and mobility of the SiGe has been observed after radiation by neutron beam [16]. In contrast to the numerous investigations reports on how to improve the performances of skutterudite, limited investigation has been performed to address the influence of various high-energy irradiations on different types of thermoelectric materials. Important questions are, e.g. what kind of irradiation affects the thermoelectric performance of filled

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skutterudites and why? These are vital information to the future application of filled skutterudites for the RTGs purpose.

Depending on the properties of the irradiations, such as mass, electrical charge or kinetic energy, it may result in the following three consequences: (1) improving the *TE* performances, (2) reducing the *TE* performance and (3) not varying the *TE* performances. In this work, an electron accelerator is used to investigate how the light irradiations of β-rays (6 MeV) influences the thermoelectric performance of n-type filled skutterudite $Yb_{0.3}Co_4Sb_{12}$. The β-ray consists of electrons, which possesses a much smaller mass (1/2000) as compared to protons or neutrons. The β-ray at this energy scale is expected to completely penetrate the $Yb_{0.3}Co_4Sb_{12}$, which possesses a thickness around millimeter scale. On the one hand, the electrical and thermal transport properties of the filled skutterudite samples are compared before and after the irradiation. On the other hand, a Monte-Carlo simulation base on Fluka [17] code is used to calculate the deposited energy into the material from the β-ray irradiation. The main purpose of the present investigation is to address this open question and give a clear answer about what will happen if the skutterudite compound is irradiated by the high energy β-ray, which is one of the most important radiations in the universe.

2. Experimental

2.1. Fabrication of the skutterudite samples

n-type filled skutterudite with the composition of $Yb_{0.3}Co_4Sb_{12}$ were prepared by traditional melting-quenching-annealing method. Highly pure raw elements, Yb (ingot, 99.99%), Co (bulk, 99.985%), and Sb (shot, 99.9999%), were weighed in the designed atomic ratio and sealed in evacuated quartz ampoules with coated carbon. The sealed ampoules were heated slowly up to 1350 K for 10 h, then quenched into water bath, and annealed for 7 days at 1073 K. The ingots were ground into powders and sintered by Spark Plasma Sintering (SPS) for 10–15 min at 873 K. High-density samples (>95% of the theoretical density) were obtained. The purity of the products was confirmed by X-ray diffraction (XRD, Rigaku, Rint2000) and electron probe micro-analysis system (EPMA, JEOL, JXA-8100) with an energy dispersive spectroscopy (EDS). All samples were identified as single phase belonging to cubic Co_4As_{12} skutterudite structure.

2.2. Radiation experiment through electron accelerator

Fig. 1 shows the schematic illustration of the experimental setup for the irradiation. The accelerator used in this experiment is an S-band standing-wave 6 MeV industrial electron accelerator, which is made by NUCTECH in 2008 [17]. It can provide 100 mA peak current and the duty rate is normally 0.1%. In this experiment we set the duty rate 0.03% in order to have 30 μA average electron beam. There is no X-ray target at the terminal of accelerating structure. Instead, a Ti window with 50 μm thickness is mounted to isolate the ultra-high vacuum environment in accelerator from outside atmosphere. This window will have very little effect on the electron beam. The distance between accelerator and sample material is 20 cm. Thus the beam spot can be enlarged to 8 mm [18], which is closed to the diameter of the sample material. The accelerator together with the sample material was placed at the high power tested stand in accelerator laboratory of Tsinghua University [19,20]. A Clamping aluminum disks are built to hold the sample material and the alignment is ensured. Electrical fan is used to cool down the sample material as the beam power is still very high and may cause a lot of heat.

Before the experiment, accelerator was tested in order to find out the appropriate parameters. A dosimeter was placed 1 m away in front of the accelerator, and a tungsten X-ray target with 2.5 mm thickness was attached on the Ti window. When the accelerator work at 0.1% duty rate, the dosimeter detected approximate 900 rad/min dose. The simulated dose using 6 MeV and 100 μA electron beam by the FLUKA code is 1000 rad/min, which is close to measured one. This tested dose show the accelerator able to work at its design value [17]. However, during the experiment the energy of the beam is mainly absorbed by the sample material so the dose measured by the dosimeter could not reflect the status of accelerator. However, by observing the current of cathode and radio-frequency power reflection from the accelerating structure, we can deduce that the accelerator was working at normal status.

2.3. Characterization of the thermoelectric performance

For electrical transport property measurement, a ZEM-3 (ULVAC-RLKO) was applied to measure the electrical conductivity as well as Seebeck coefficient in the temperature range of 30–600 °C. For thermal transport measurement, the thermal diffusivity (λ) was measured using the laser flash method in a flowing Ar atmosphere (Netzsch LFA 427). Thermal conductivity (κ) was calculated from the relationship: $\kappa = \rho\lambda C_p$, where λ is the thermal diffusivity coefficient, C_p is the heat capacity and ρ is the density of the material.

3. Results and discussions

3.1. Simulation on the radiation process

When the high energy-electrons beam passes though the sample material, the total energy of the incident beam will gradually decrease along the beam penetrating route inside the sample during the reactions. For example, the electron beam with particular 6 MeV energy, the energy loss is mainly due to the ionization and bremsstrahlung [21]. The ionization effect can remove the orbit electron of one atom and meanwhile creates the vacancy, resulting in the formation of electron–hole pairs in the lattice of the irradiated material. In addition, the ionization process may also affect the chemical bond of the material, or produce Auger effect. In comparison, the bremsstrahlung is a process to describe the interaction with nucleus. For instance, under the irradiation of β-ray, the incident electrons are decelerated and deflected by the atomic nucleus, the resulting energy loss turns into so called secondary particles, including photons, photoelectrons, auger electrons, knock-on electrons or electron–positron pairs [21]. The as-generated secondary particles will further interact with the lattice of the target materials.

From both processes, the energy from the incident ion beam deposed at the material in the form of thermal, chemical or even nuclear energy. In particular, the high energy beam interactions may cut the chemical bond or cause the realignment of the atoms in the lattice, and therefore, causes changes of the structural characters, mechanical or transport properties of the material. The deposed energy is impossible to be directly measured in the present investigation. Instead, a Monte-Carlo simulation using Fluka code [22] is employed to simulate the deposited energy vs. the thickness of the material.

The Monte-Carlo simulation mimics the real transport and interaction of particles in the matter by numeric method. It starts with an incident particle with initial state including position, energy and momentum. The motion of this particle in the defined geometry is tracked and the reactions between the particle and matter are taken place during the transportation. In the simulation, dices (generating pseudo random number) are used to determine the details of this reaction including position, type, particle's state changing and secondary particles producing. Numeric technical on the random number are employed to make the dices follow the probability distributions (or cross sections) of real reactions which are defined in the nuclear reaction data-base. The tracking of one particle will finish when reaching the termination state, e.g. absorbed, out of geometry, etc. Then the trace of this particle and secondary particles are record as one sample. A number of samples can be collected by repeating the particle tracking. Each sample shows different to others due to the random behavior of particles. However, by averaging all samples the results could be estimated.

There were several Monte-Carlo codes for tracking high-energy particles in the matter: Geant4, EGS, MCNP, Fluka, etc. Fluka is an open source code capable of simulating electrons, photons, ions and neutrons interacted with matter in the wide energy range from keV to TeV [14]. Shown in Fig. 2, a Fluka model is built for simulating this experiment. It is know that the electron accelerator used in the experiment can provide 30 μA beam with average kinetic energy 6 MeV. The transverse distribution is Gaussian-like and the spot size is about 5 mm. In Fluka, a radial Gaussian-distribution planar source is applied to model the circumstance. Cylinder geometry is used to define the sample using. In Fluka the matter