Kinetics of processes in the thermoelectric material of the Sn-Pb-Te system during heat treatment

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Introduction

Thermoelectric generators are actively developed now. Their advantages are following:

- high reliability;
- compactness;
- low inertia;
- -no moving parts;
- quite operation;
- ease of use.

Motivation

• The relatively low efficiency of TEG constrains their widespread application.

• The efficiency of the TEG is determined mainly by the quality of materials used for fabrication of the legs.

• Materials of the Sn-Pb-Te system are perspective as middle temperature material for TEG applications.

• Nanostructuring of thermoelectric materials may lead to a significant progress in their performance.

• Thermoelectric materials must be stable under the heat treatment.

• Investigation of thermal processes in the materials (in particular, kinetics) are quite important for TEG technology optimization.

Aim: investigate kinetics of processes occurring in the thermoelectric material of the Sn-Pb-Te system during heat treatment.

The method of differential scanning calorimetry is well suited for solving this task.

Experimental

Synthesis

- Direct alloying of Sn, Pb,Te.
- Temperature 950 °C.
- Quartz ampoules.

Processing

- Jaw crusher.
- Knife mill.
- Planetary mill.

} Size of the particles: 80-120 nm

- Hot pressing of the powders.

Thermal characteristic measurements

• Differential Scanning Calorimeter DSC-50 (Shimadzu).
• 5 heating rates (from 5 to 20 deg/min).
• Masses of the samples were about 10 mg.
• Al pans.
• Nitrogen atmosphere (20 ml/min).
• Temperature range - from room temperature to ~600°C.

Determination of kinetic triplet

Pre-exponential factor

Activation energy

Reaction model

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\left(\frac{1}{\beta}\right) = \frac{A}{\beta}\, exp\left(\frac{-E}{RT}\right) f(\alpha)$$

α – conversion,
T – temperature,
t – time,
R – Gas constant,
β - heating rate

Model-free method
- does not require knowledge of the reaction model;
- allows to determine E as a function of conversion (α);
- does not allow to determine the reaction model f(α).

Model-fitting method
- allows to determine all kinetic parameters;
- determines only average values of E.

• Simultaneous use of model-free and model-fitting methods was proposed.

• This approach allows to estimate activation energy and pre-exponential factor at progressive conversion, and determine reaction model.

• Model-free Ozawa-Flynn-Wall and model-fitting Coats-Redfern methods were used.

Results and discussion

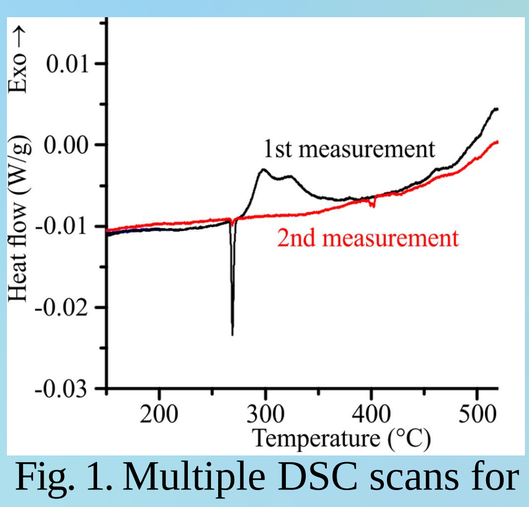

Fig. 1. Multiple DSC scans for $Sn_{0.9}Pb_{0.1}Te$

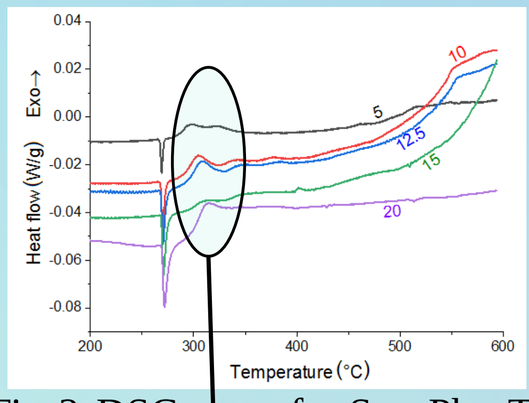

Fig. 2. DSC scans for $Sn_{0.9}Pb_{0.1}Te$ with different heating rates

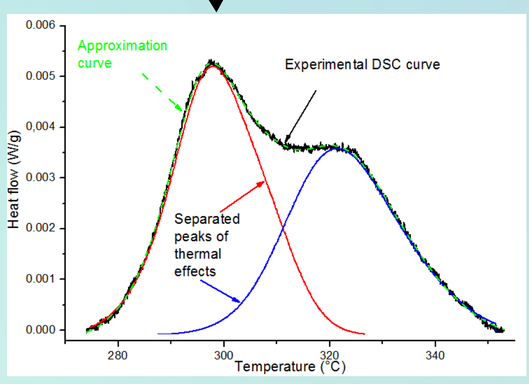

Fig. 3. Peak separation from overlapping effects by Gaussian distribution

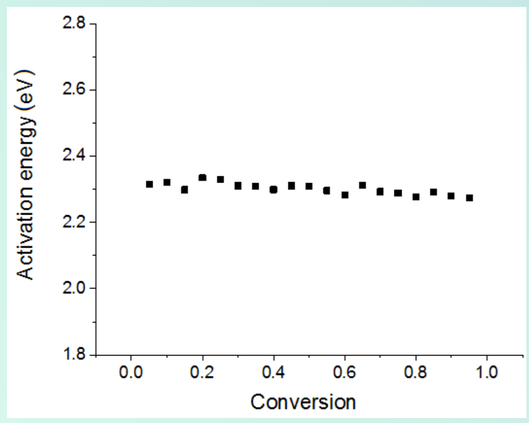

Fig. 4. Dependences of E_a of crystallization on conversion

• Endothermal effect in the temperature range of 267-272 °C and several exothermal effects with overlapping peaks in the temperature range of 281-346 °C can be seen at the first measurement (Fig. 1).

• This peaks are associated with structural relaxation, which is confirmed by the absence of these peaks after the multiple measurements (Fig. 1).

• Kinetics of exothermal peak with initial temperature about 280 °C was investigated.

• Peak separation of overlapping effects with using of Gaussian distributions was performed (Fig. 3).

• E at the initial stage of the reaction is 2.3 eV (Fig. 4).

• E changes only slightly during the reaction (Fig. 4).

• Nineteen various possible models, which describe different solid-state reactions were checked.

• The investigated reaction is most likely described by the reaction model of second order.

Conclusion

1. The kinetic parameters of the exothermic effect, which appear at onset temperature of about 280 °C were calculated.

2. One stage dominates during that process.

3. The investigated process is most likely described by the reaction model of second order.

4. Investigated thermal effect associated with structural transformation.

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