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Study of Oxidation and Evaporation Behavior of PbTe Compounds by Using Thermal Analysis

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Thermal analysis was carried out in order to study the apparent oxidation and evaporation behavior of PbTe compounds (p-type: $Pb_{0.5}Sn_{0.5}Te$; n-type: PbTe + 0.5mass% PbI_2). A fine powder (particle diameter below 25 μm) of each of the PbTe compounds was investigated at temperatures ranging from room temperature to 773 K by using a DSC (differential scanning calorimeter) and TG-DTA (thermogravimetry/differential thermal analyzer). From the results of the heat capacity measurement, an exothermic reaction and an endothermic reaction were observed to occur at 593 K and 673 K, respectively, in $Pb_{0.5}Sn_{0.5}Te$. Exothermic and endothermic reactions were not evident in PbTe + 0.5mass% PbI_2. From the results of the thermogravimetry, it was found that the weight of $Pb_{0.5}Sn_{0.5}Te$ increased above 593 K and decreased above 673 K; on the other hand, the weight of PbTe + 0.5mass% PbI_2 increased above 573 K and did not decrease. From these thermal analysis results, the oxidation and evaporation behavior of PbTe compounds was apparent.
Key words: thermoelectrics, thermal properties, TG-DTA, DSC, PbTe, PbSnTe, oxidation, evaporation

1. INTRODUCTION

It has been reported that the electrical properties of PbTe thermoelectric materials are altered when the materials are heated [1,2,3]. Oxidation and evaporation of structure material of PbTe is expected, and the mechanisms of the oxidation and evaporation of PbTe system compounds are just now emerging [4,5]. However, any explicit evidence has not been obtained since the variations in the physical properties of these materials due to their oxidation and evaporation are slight.

It is expected that the oxidation and evaporation effects of structure material increase in proportion to their surface areas. Therefore, we conceived investigation of oxidation and evaporation behavior to increase surface areas by using fine powders.

In this research, thermal properties of fine powders of PbTe thermoelectric material were investigated in order to prove the oxidation and evaporation behavior of PbTe compounds.

2. EXPERIMENTAL

2.1 Preparation of thermoelectric materials

Pb (6N), Te (6N), Sn (5N) and PbI_2 (5N) were weighed out at the composition ratios of $Pb_{0.5}Sn_{0.5}Te$ and PbTe + 0.5mass%PbI_2 in a globe box filled with Ar gas. They were encapsulated in quartz tubes 10 mm in diameter and 220 mm in length in a vacuum of 3×10^{-3} Pa, and sealed by using a burner. The contents of the capsules were placed in a rocking furnace, and melted and mixed for an hour at 1373 K. The capsules were then cooled down at a sweep rate of 150 K/h and a rocking cycle of 0.3 Hz. The temperature gradient applied to the capsules was 0.5 K/mm. X-ray diffraction analysis was performed, and it was confirmed that the p- and n-type ingots possessed a single phase. The starting materials for sintering were prepared from these ingots. They were ground and classified into fine powders (particle diameter below 25 μm) in an aluminous mortar. The powders used were sufficiently fine to pass through a 25 μm sieve. The powder grain sizes were measured by using a SEM-4000 (Hitachi, Ltd.).

2.2 Measurement of Thermal Analysis

(1) TG-DTA (thermogravimetry / differential thermal analyzer)

The schematic diagram of the TG-DTA system is shown in Fig. 1. The TG system comprises a balance section to measure the weight of sample weight and a temperature control section to measure and control the sample's temperature. In the DTA system, a criteria material is arranged in symmetrical sample position from a heating furnace in order to measure the temperature difference between the sample and the criteria material. Al_2O_3 was used as the criteria material in this experiment. The sample's temperature and the weight difference between the sample and the criteria material are concurrently measured as a function of time in order to obtain a TG-DTA curve.

The TG-DTA measurements of $Pb_{0.5}Sn_{0.5}Te$, PbTe doped with 0.5mass%PbI_2 were obtained by using SDT2960 (TA Instruments) in an Ar atmosphere.

The samples were heated at a rate of 5 K/min from room temperature up to 773 K and held at 773 K for 10 min. They were then cooled down to 343 K at a rate of 5 K/min.

(2) DSC (differential scanning calorimeter)

The schematic diagram of the method of detection by DSC system is shown in Fig. 2. In the measurement of DSC, a difference of heat flow rate between a sample and a criteria material is detected with changing the temperature.

The heat of reaction for $Pb_{0.5}Sn_{0.5}Te$ and, PbTe doped with 0.5mass%PbI_2 was measured by using DSC-60 (Shimadzu Corporation) in a N_2 atmosphere.

The samples were heated at a rate of 5 K/min from room temperature up to 723 K. They were then cooled down to 373 K at a rate of 5 K/min.

(3)XRD (X-ray diffraction analysis)

In an Ar atmosphere, the XRD analysis for $Pb_{0.5}Sn_{0.5}Te$ and PbTe + 0.5mass% PbI_2 was performed by using RINT2500 (Rigaku) at room temperature, before and after heating up to 773K. A Pt sample folder was used for the XRD measurement.

3. RESULTS and DISCUSSION

3.1 *p*-type $Pb_{0.5}Sn_{0.5}Te$

The TG, DTA, and temperature characteristics of TG-DTA measurements are shown in Fig. 3, 4, and 5, respectively.

The sample's weight decreased in the temperature range from 373 to 593 K during the heating. It is considered that the weight reduction was caused by evaporating moisture that was adsorbed onto the powder surface. The sample's weight increased in the temperature range from 593 to 673 K. Moreover, an exothermic peak was observed at 593 K in the DTA curve, and the thermal behavior of oxidation was shown at 593 K in these results. The sample's weight decreases in the temperature range form 673 to 773 K at 593 K in these results. The sample's weight decreases in the temperature range form 673 to 773 K during the heating and down to 683 K during the cooling. Moreover, an endothermic peak was observed at 677 K in the DTA curve. It was found that the thermal behavior of evaporation was shown around 673 K in these results. The sample's weight increased in the temperature range from 683 to 573 K during the cooling. An exothermic peak was observed at 654 K in the DTA curve. It was found that the thermal behavior of oxidation was shown around 653 K in these results.

The DSC result is shown in Fig. 6. The exothermic reaction of 2.59 J/g and the endothermic reaction of 0.53 J/g were observed at 586 and 675 K, respectively, during the heating, as well as in the TG-DTA result. Moreover, the exothermic reaction of 59 J/g was observed at 543 K during the cooling.

The XRD result is shown in Fig. 7. SnO_2 was identified in the XRD profile at room temperature for the sample after heating up to 773K. It was found that oxide was generated by heating in $Pb_{0.5}Sn_{0.5}Te$.

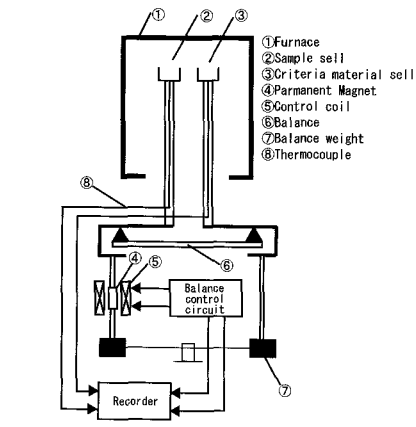

Fig.1, TG-DTA system

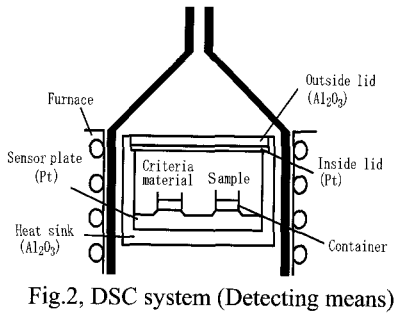

Fig.2, DSC system (Detecting means)

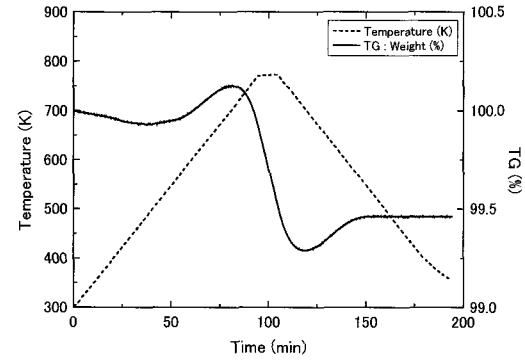

Fig.3, TG ($Pb_{0.5}Sn_{0.5}Te$)

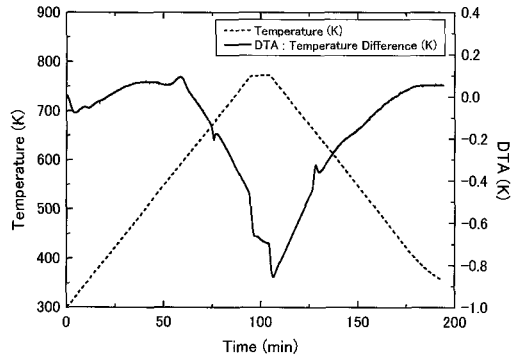

Fig.4, DTA ($Pb_{0.5}Sn_{0.5}Te$)

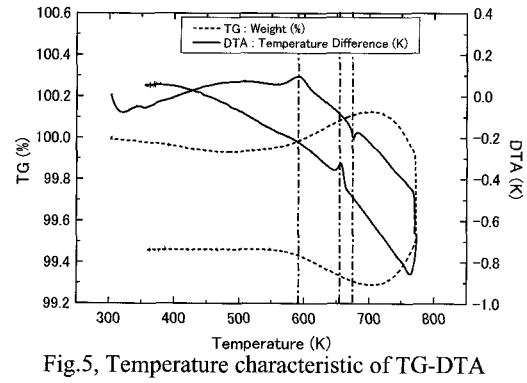

Fig.5, Temperature characteristic of TG-DTA ($Pb_{0.5}Sn_{0.5}Te$)

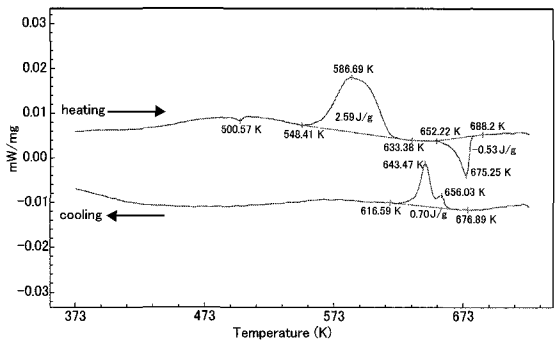

Fig.6, DSC ($Pb_{0.5}Sn_{0.5}Te$)

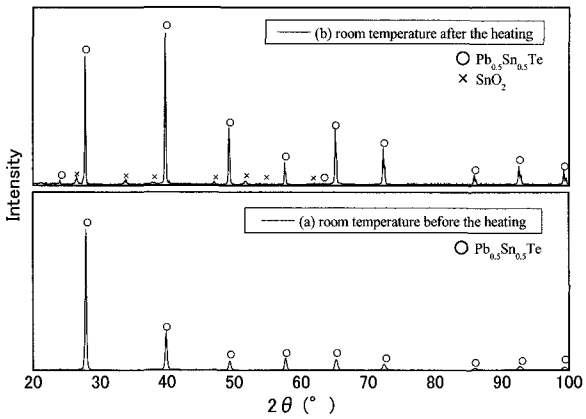

Fig.7, XRD patterns ($Pb_{0.5}Sn_{0.5}Te$)
(a) at room temperature before heating up to773K
(b) at room temperature after heating up to773K

3.2 *n*-type PbTe + 0.5mass% PbI_2

The TG, DTA and temperature characteristics of TG-DTA measurements are shown in Fig. 8, 9, and 10, respectively.

The sample's weight decreased in the temperature range from 373 to 573 K during the heating as well as $Pb_{0.5}Sn_{0.5}Te$. It is considered that the weight reduction was caused by evaporating moisture that was adsorbed onto the powder surface. The sample's weight continued to increase in the temperature range from 573 to 773 K during the heating and down to 343 K during the cooling. The thermal behavior of evaporation was not observed around 637 K.

The DSC result is shown in Fig. 11. The exothermic reaction of 0.18 J/g was observed at 623 K during the heating. In the TG and DSC results, the thermal behavior of oxidization was shown around 623 K.

The XRD result is shown in Fig. 12. $PbTeO_3$ was identified in the XRD profile at room temperature for the sample after being heated up to 773K. It was found that oxide was generated by heating in PbTe + 0.5mass% PbI_2.

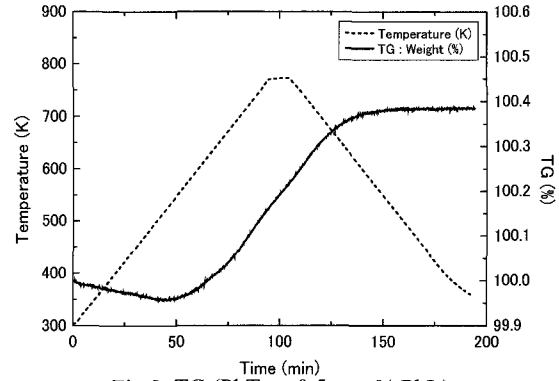

Fig.8, TG (PbTe + 0.5mass% PbI_2)

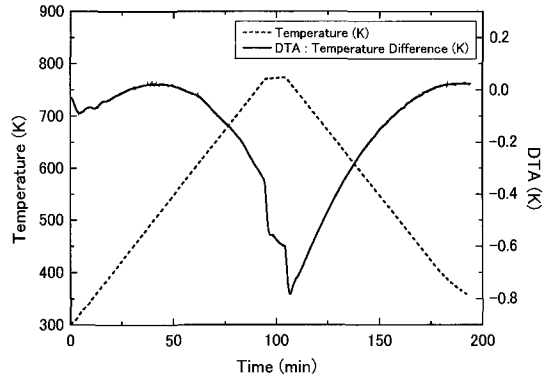

Fig.9, DTA (PbTe + 0.5mass% PbI_2)

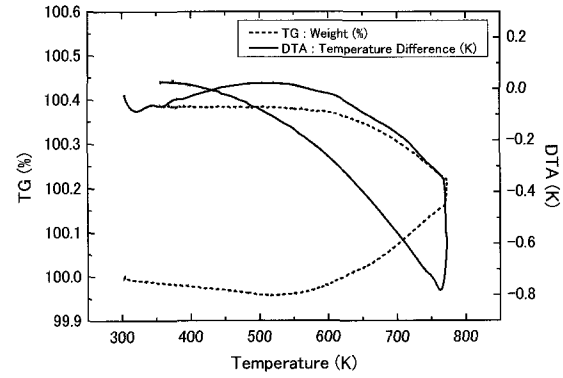

Fig.10, Temperature characteristic of TG-DTA (PbTe + 0.5mass% PbI_2)

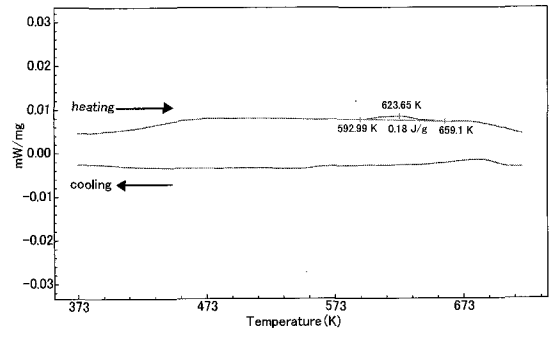

Fig.11, DSC (PbTe + 0.5mass% PbI_2)

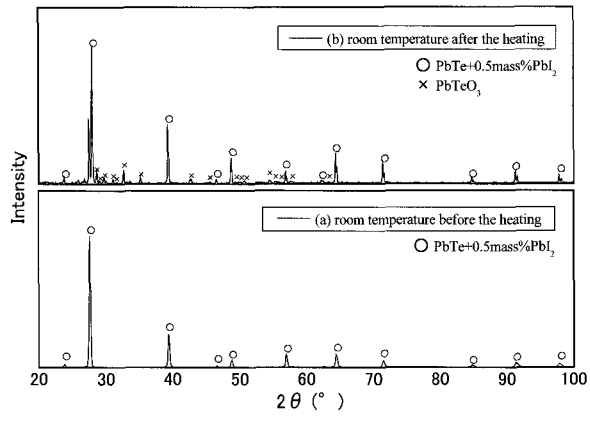

Fig.12, XRD patterns (PbTe + 0.5mass% PbI_2)
(a) at room temperature before heating up to773K
(b) at room temperature after heating up to773K

4. CONCLUSIONS

The thermal behaviors of fine powders (particle diameter below 25 μm) of $Pb_{0.5}Sn_{0.5}Te$, and PbTe + 0.5mass% PbI_2 were investigated. The following conclusions were obtained.

In $Pb_{0.5}Sn_{0.5}Te$, an exothermic reaction and an endothermic reaction were observed at 586 and 675 K, respectively, from the results of the DSC. It was found that the sample's weight increased in the temperature range from 593 to 673 K and decreased above 673 K in the results of the TG. From these thermal analyses, the oxidation and evaporation behavior was obvious in $Pb_{0.5}Sn_{0.5}Te$.

In PbTe + 0.5mass% PbI_2, an exothermic and an endothermic reaction were not evident from the results of the DSC. It was found that the sample's weight increased above 573 K and there was no reduction of it from the results of the TG. From these thermal analyses, although the oxidation behavior was obvious, the evaporation behavior was not apparent in PbTe + 0.5mass% PbI_2.

5. REFERENCES

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