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Thermoelectric Properties of Perovskite-Type Mn Oxides Thin Films

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Almost thermoelectric properties have been measured only with the bulk sample or the single crystal conventionally. In this research, measurement was tried about the thin film sample. Therefore, the cryostat about measuring thermoelectric properties for evaluation was produced. The measured sample is Perovskite-type Mn oxides and it is known for various characteristics being shown with composition. Although the result better than the conventional sample was not obtained in this measurement. Production conditions will be changed from now on, or it will strive for the further improvement in a performance by superlattice etc.

[Keywords] Thermo electronics, Seebeck coefficient, Perovskite-Type Mn Oxides, PLD, Thin film

1. Introduction

The truly remarkable pictures of the rings of Saturn transmitted to Earth from the Voyagers 1 and 2 spacecraft captured the imagination of people throughout the world. No less remarkable is the source of electrical power, which enabled the information to be transmitted from the spacecraft after more than a decade into its mission and from over 1.5 billion miles in space.

The power source is not a solar cell as one might at first think. The craft is too far away from the sun to receive sufficient light energy to power the transmitters. On-board power is provided by an RTG (radioisotope thermoelectric generator), which utilizes the Seebeck effect in converting the heat from a radioactive heat source directly into electrical energy. The Seebeck effect and the reverse phenomenon, the Peltier effect, are principal components in Thermoelectric the science and technology associated with thermoelectric generation and refrigeration.

In attempting to make practical use of thermoelectric generation, the quantity which is of great interest to us is the efficiency for a given temperature difference between the source of heat and the sink. In applying thermoelectric refrigeration, we require the highest coefficient of performance for a given temperature difference. In both cases the performance, under the optimum operating conditions, can be expressed in terms of a figure of merit. It is perhaps, not surprising that it is the same figure of merit that applies both for thermoelectric generation and for refrigeration. This figure of merit *Z* for a single material may be written as

$$Z = \frac{S^2\sigma}{\kappa}$$

Where *S* is the Seebeck coefficient expressed in volts per degree, or more often in micro volts per degree μVK^{-1} , σ the electrical conductivity expressed in *S*/cm and κ is the thermal conductivity usually expressed in W/mK. The unit of *Z* is 1/K. At a given absolute temperature T, since *Z* may vary with T, a useful non-dimensional figure-of merit is *Z*T. Thus research on materials for thermoelectric applications is aimed at obtaining the highest values for *Z*.

Although the properties favorable for thermoelectric applications were well known, the important advantages offered by Seebeck s mineral semiconductors were overlooked with the attention of researchers focused on metals and metal alloys. In these materials the ratio of the thermal conductivity to electrical conductivity is a constant (Wiedemann —Franz —Lorenz law) and it is not possible to reduce one while increasing the other. Consequently, the metals best suited are those with the highest Seebeck coefficients. Most metals possess Seebeck coefficients of 10μV/K or less, giving associated generating efficiencies of a fraction of 1 %, which are not economical as a source of electrical power. Research into compound semiconductors for possible transistor applications in the 1950s resulted in new materials with substantially improved thermoelectric properties and in 1956, Ioffe and his co— workers demonstrated that the ratio could be decreased if the thermoelectric material is alloyed with an isomorphous element or compound. Spurred on by possible military applications, a tremendous survey of materials was undertaken, particularly at the RCA laboratories in the U.S., which resulted in the discovery of a few semiconductors with *Z*T approaching 1.5. Currently established thermoelectric materials conveniently fall into three categories depending upon their temperature range of operation. Bismuth telluride and it s alloys have the highest figures–of–merit, are extensively employed in refrigeration, and have a maximum operating temperature of around 450 K. Alloys based on lead telluride have the next highest figures of merit with silicon germanium alloys having the lowest. Lead telluride and silicon germanium are used in generator applications with upper operating temperatures of around 1000 K and 1300 K, respectively. The material of reference in any TE research is bismuth telluride and it s alloys. Extensive use of bismuth-antimony telluride and bismuth antimony alloys tends to confirm that Bi plays a decisive role in the enhancement of thermoelectric properties. It is important to note that its contribution is not well understood at the present time. There is great effort for developing new compounds that could surpass the properties of bismuth telluride that has led the market for the last 30 years.

Table I : Thermoelectric properties of n – type PbTe and Bi_2Te_3

Compound	T_{max} (K)	σ (S/cm)	S(μV/K)	κ(W/mK)	ZT
Bi_2Te_3	300	800-1000	± 210	1.4-1.6	0.8-1.1
PbTe	650	360	-180	1.1	0.7

*Data provided by Marlow Industries Inc.

During the last decade there has been a worldwide search for new materials with higher thermoelectric figures-of-merit and attempts to improve the thermoelectric properties of the known compounds. It is anticipated that the successful development of such materials will lead to new fields of application for thermoelectric devices and related technologies based on bulk crystals and on films. However, the improvement of thermoelectric materials requires a detailed knowledge of all the factors that determine their properties. This study investigates thermoelectric properties of materials by careful measurement of the quantities, which occur in the figure-of-merit, i.e., the electrical conductivity σ, thermoelectric power S, and thermal conductivity κ.

2. Experiment

The main objective of this work is to measure thermoelectric properties about Perovskite-Type Mn Oxides thin films, which have shown promising characteristics for thermoelectric applications. However, most thermoelectric characteristics of a thin film were not measured at low temperature until now. Since the thermal conductivity of a substrate is the maximum near 35K degrees, Thus, it is very difficult for a difference of temperature to attach, and it was not able to measure about thermoelectric properties.

The produced sample which is$Y_{0.7}Sr_{0.3}MnO_3$ (YSMO) and $La_{0.7}Ca_{0.3}MnO_3$ (LSMO) are bulk and thin film. The substrate was radioactively heated and rotated during the deposition to ensure thickness and film homogeneity about LSMO, but YSMO is not rotated during deposition. Substrate temperature was 1047K for 10minites,in a 200m Torr O_2 atmosphere, and 2.7J/cm^2 laser energy density.

3. Result

Only a Bulk sample of YSMO is settled and reported at present.YSMO are reported According to J.M.D.coey[*1] . YSMO was reported with very high resistivity is shown fig 1..That sample was YSMO(X=0.3) on MgO substrate.

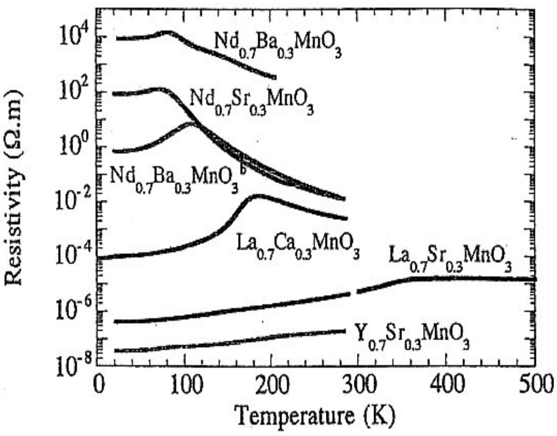

Fig1.Temperature dpendence of the resistivity of $(Mn^{3+}_{1-x} B^{2+}_x)MnO_3$ thin films.

And according to So-Jung Park[*2]reported, X-ray diffraction study indicated that the $Y_xSr_{1-x}MnO_3$ system has three different structures depending on composition, namely, 4L-hexagonal perovskite (when x is less than 0.3), pseudocubic perovskite (when x is 0.3~0.7), and hexagonal nonperovskite (when x is larger than 0.7) structures. The structural changes and electronic properties were interpreted based on two factors, i.e., the size of cations and the oxidation state of manganese ion. When the concentration of Y substitution exceeds 30%, the Mn-Mn repulsive interaction dominates over intermetallic attraction, and thus structure changes to pseudocubic perovskite. In perovskite phase the unit cell dimensions increases with increasing Mn3+ ions due to yttrium substitution. The band gap of $Y_{0.1} Sr_{0.9}MnO_3$ is greater than that of $Y_{0.5} Sr_{0.5}MnO_3$. The greater band gap of $Y_{0.1} Sr_{0.9}MnO_3$ indicates that the 4L-hexagonal structure is more stabilized than cubic perovskite due to the Mn-Mn bond. As for guessing it from now, a conductivity improved because a lattice was being pulled.Because lattice constant of YSMO(X=0.3) is about 3.8Å.And MgO is 4.6Å.

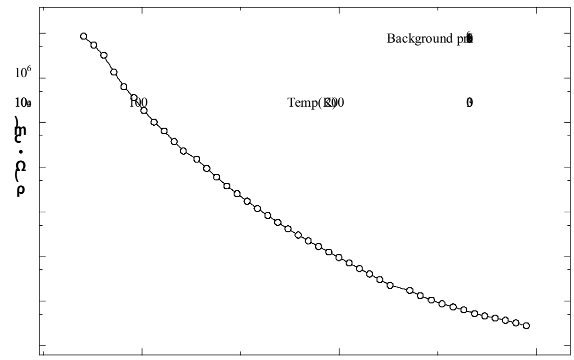

Fig2.Temperature dependence of the resistivity of YSMO(x=0.3)

A result of resistivity with a bulk sample about YSMO (x=0.3) is shown fig.2. And Seebeck coefficient is Fig.3, and Power Factor is Fig4.

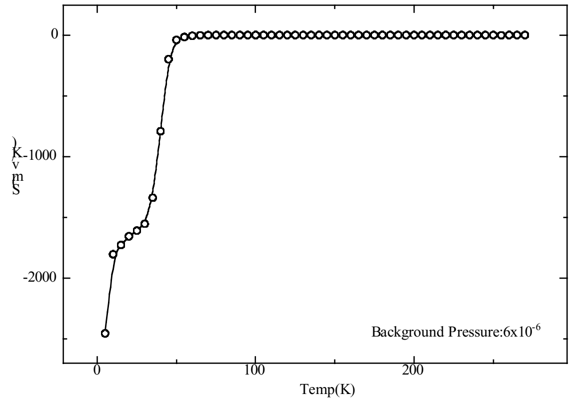

Fig3. Temperature dependence of the Seebeck coefficient of YSMO (x=0.3) bulk sample

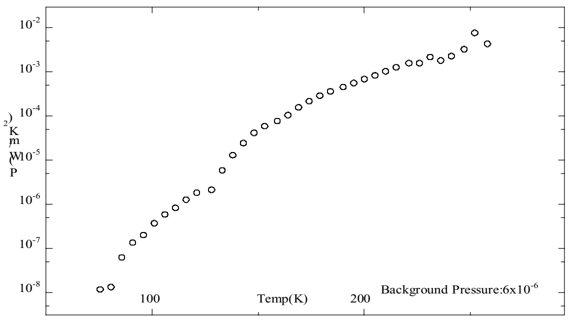

Fig4.Temperature dependence of the Power Factor of YSMO (x=0.3) bulk sample

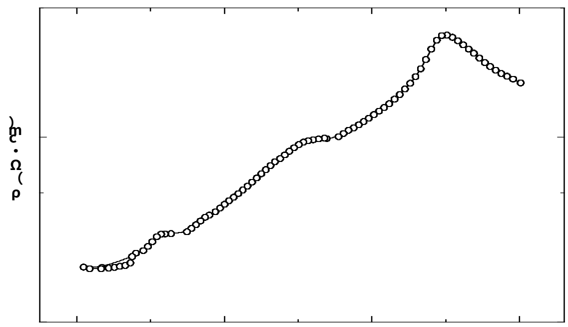

Fig5.Temperature dependence of the resistivity of LCMO(X=0.3) thin film

4.Conclusion

As for understanding from these results, it is important that resistance is lower. Usually resistively is poor, a seebeck coefficient is high. But this material is not.

The possibility of even a thin film which is bad when it is when a Seebeck coefficient with YSMO bulk sample is bad can't be denied, even if it becomes low receptivity.

An expectation can have it because the resisivity of LCMO (x=0.3) thin film is low to be in fig.5.

And, the result that it was measured with the device made this time was about the same as the result of last year [*3]

5.Acknowledgement

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6.Reference

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