High-throughput screening of thermoelectric oxides

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Abstract

In order to discover a new *n*-type oxide possessing good thermoelectric properties, high throughput screening of (La, M^1)NiO_3 and La(Ni, M^2)O_3 systems has been carried out. Aqueous solutions of metal nitrates were used as starting materials in this screening. One precursor library with 100 samples composed of different compositions was prepared on a 100 x 100 mm alumina plate within an hour. After heating the libraries at various temperatures higher than 973 K, evaluation of Seebeck coefficient (S) of the samples was performed using a high-speed two terminal method ('Seebeck tester'). It is found from this screening that Bi-, Nd-, and K-substitution and Cr-, Mn-, Fe-, and Cu-substitution for La and Ni are effective to improve S in the (La, M^1)NiO_3 and La(Ni, M^2)O_3 systems, respectively.

Introduction

Humanity urgently requires solutions to energy and environmental problems which are now reaching crisis levels. As one such solution, thermoelectric power generated from the vast amounts of waste heat emitted by automobiles, factories, and similar sources is expected to develop in the near future as a resource-conserving form of energy. Waste heat offers a high-quality energy source equal to about 70% of total primary energy, but is difficult to reclaim due to its source amounts being small and widely dispersed. Thermoelectric generation systems provide the only viable method of overcoming these problems by converting heat energy directly into electric energy irrespective of source size and without using turbines or producing CO_2 or radioactive substances. The requirements made of the materials needed for the task, however, are not easily satisfied. Not only they must possess high conversion efficiency, but they must also be composed of non-toxic and abundantly available elements, in addition to having high chemical stability even at high temperatures of 800-1000 K in air. It has been reported that CoO_2-based oxides with layered structures show good *p*-type thermoelectric properties at high temperatures in air [1-3]. In order to realize thermoelectric power generation, *n*-type oxides possessing thermoelectric properties as good as CoO_2-based oxides are indispensable. Unfortunately, although the exploration of the *n*-type oxides has been performing eagerly, no *n*-type oxides with sufficient properties for power application have been discovered. In this paper, results of the high throughput screening of substituted (La, M^1)NiO_3 and La(Ni, M^2)O_3 systems showing *n*-type property are described.

Experimental

As starting materials, aqueous solutions of metal nitrates were used. The concentration of the solutions was 1.0 metal mol/*l*. The solutions were distributed using a high-speed library preparation machine. This was designed by the authors and produced by Bio Tech Co., Ltd. in Japan. At most 5 kinds of metals can be mixed. Using this machine, 100 kinds of mixed solutions with different compositions are available within 15 min. Only a few 100 μg of the metals is included in each solution, which is about 10^{-5} times smaller than the conventional solid state method. After distribution, the mixed solutions were applied (drawn) on an alumina plate (100 mm x 100 mm) using the same machine. Each sample has a line-shape with length of 10 mm and includes only several μg of metals. The 100 line-shape samples can be applied on the alumina plate within 45 min. Namely, after 1h from the beginning of distributing the solutions, one precursor library has been prepared (Fig. 1). After application, the precursor libraries were heated at 973-1373 K for 10 h in air. The 1000 kinds of samples (10 libraries) are synthesized using the above method within one day.

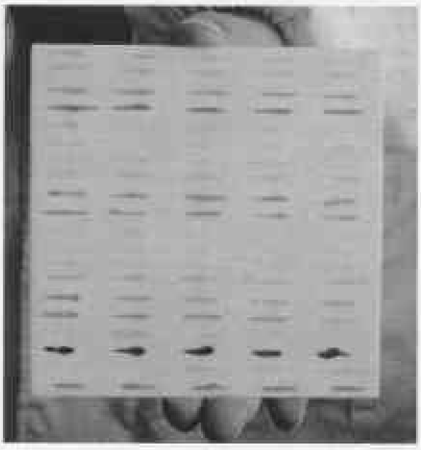

Figure 1 A precursor library including 100 samples on a palm-sized alumina plate.

In the high throughput screening technique, evaluating properties of the samples must be as fast as synthesizing them. For this purpose, a high-speed evaluation method for Seebeck coefficient (S) was developed. The measurement is carried out at room temperature using two terminals composed of thermocouples (Fig. 2). One of the terminals equips a heater (hot side). The two terminals are touched to both ends of the line-shape samples. Temperature difference and thermoelectric voltage between both ends are taken in a personal computer via digital volt-meters. The evaluation of S of the one library including 100 samples can be finished about for 15 min using this system.

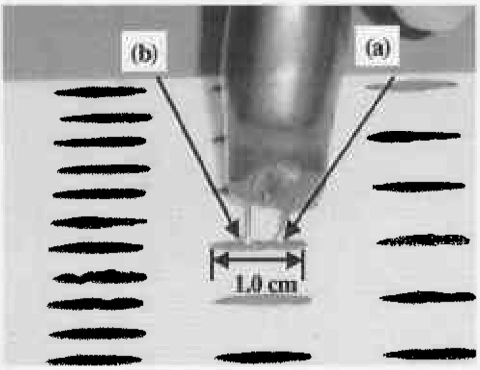

Figure 2 High-speed thermoelectric evaluation using 'Seebeck tester'. (a) cold side and (b) hot side thermocouples.

Results

Seebeck tester

Figure 3 shows time dependence of temperature for both hot and cold sides and S values for a $Ca_3Co_4O_9$ (Co-349) bulk material possessing good thermoelectric properties. Even for materials possessing quite different properties, it was found that all values, particularly S, were stable within several seconds after attachment of the two terminals of the Seebeck tester. The S values of metallic and oxide materials evaluated using this method largely agree with those measured using a conventional method (Table I).

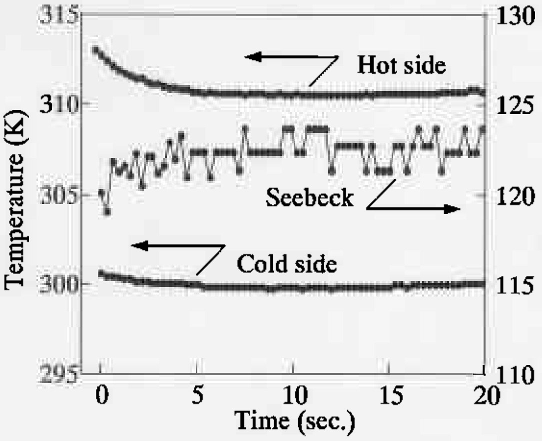

Figure 3 Temperature dependence of temperatures for cold and hot sides and S values of a Co-349 bulk.

Table I. S values of metallic and oxide materials measured using a conventional method and the Seebeck tester.

(μV/K)

Samples	Conventional method	Seebeck tester
Constantan	-42.46	-43.02
Platinum	-2.3	-3.58
$Bi_2Sr_2Co_2O_9$	68.42	73.94

Screening of M-Co-O systems

Figure 4 shows the qualitative screening of ternary systems containing Co. The greater the number of stars in the table, the larger the S value. A large, positive S is observed in the Na–Co–O and Ca–Co–O systems. The cationic compositions possessing large S are around M:Co = 1:1. This result indicates that good p-type thermoelectric oxides have been discovered. However, we already know $NaCo_2O_4$ and $Ca_3Co_4O_9$ have good thermoelectric properties. From X-ray diffraction (XRD) patterns, samples showing the large S consist of mainly $NaCo_2O_4$ and $Ca_3Co_4O_9$ phases. Although no n-type oxides are discovered in the Co-based ternary systems, the validity of the high-throughput synthesis and evaluation is proved.

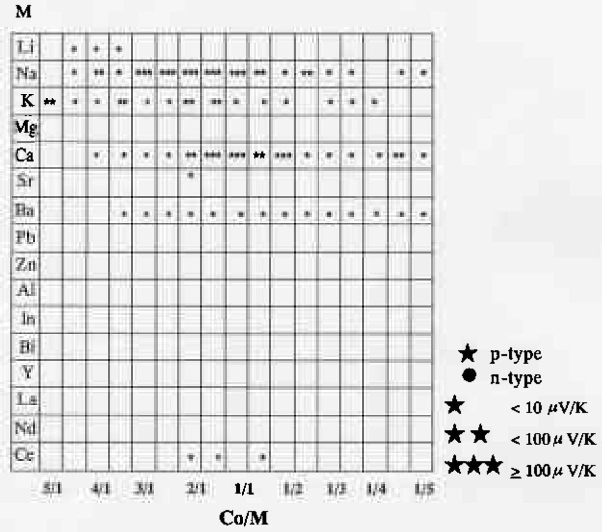

Figure 4 Screening M-Co-O ternary systems.

Screening of M-Ni-O systems

Only La–Ni–O systems exhibited n-type behaviour (Fig. 5). Although only about –10 μV/K at room temperature, the largest S in this system appears at an approximate molar ratio of La:Ni = 1:1. From XRD patterns of these samples, it was found that perovskite $LaNiO_3$ is formed as a main phase. To allow a more detailed examination, $LaNiO_3$ bulk samples were prepared using the sol-gel method and their thermoelectric properties measured. Both S and ρ increase with increasing temperature, i.e. a metal-like behaviour is observed. Although this oxide shows n-type character at temperatures higher than room temperature, both S and ρ are insufficient for practical power applications. Therefore, partial substitution of La or Ni was tried to enhance S values in the $LaNiO_3$ phase.

Screening of (La, M^1)NiO_3 and La(M^2, Ni)O_3 systems

Figure 6 (a) shows the S of the (La, M^1)NiO_3 libraries heated at 1073 K for 10h. It is found from screening that substitution of K, Bi, and Nd for La is effective to enhance S, no clear effect, however, is observed by Na-, Ca-, and Sr-substitution. On the other hand, the substitution of 3d transition metals for Ni is effective to enhance S.

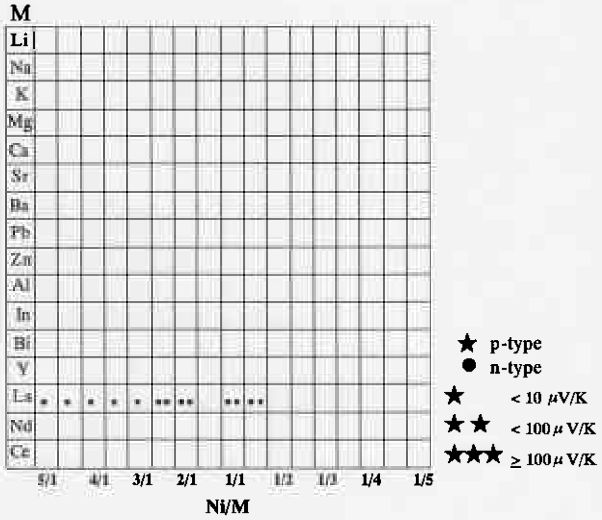

Figure 5 Screening M-Co-O ternary systems.

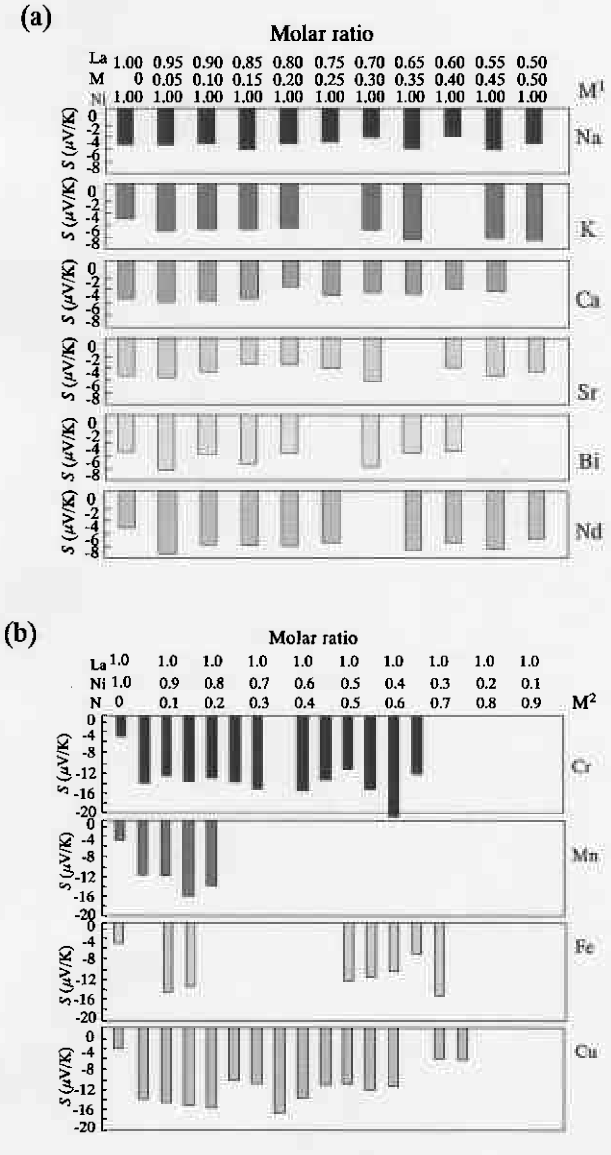

Figure 6 *S* values for (a) (La, M^1)NiO_3 and (b) La(Ni, M^2)O_3 systems.

Bulk samples of (La, M^1)NiO_3 and La(Ni, M^2)O_3 systems

Bulk samples of $La_{0.9}M^1_{0.1}NiO_3$ (M^1; Na, K, Ca, Sr, Bi, and Nd) and $LaNi_{0.9}M^2_{0.1}O_3$ (M^2; Cr, Mn, Fe, Cu) were prepared using aqueous solutions of metal nitrates by a sol-gel method. XRD patterns of these samples are shown in Fig. 7. In all samples except for Ca and Sr substituted sample, almost peaks are attributed to perovskite ABO_3 structure (indicated by ○), although some weak peaks due to secondary phases appear in the no- and Bi substituted samples. In the Ca and Sr substituted samples, perovskite related $(La, Sr)_2NiO_4$ (A_2BO_4) phase (indicated by □) is formed as a main phase. On the other hand, no secondary phases were detected by XRD measurement in any of the substituted bulk samples with compositions of $LaNi_{0.9}M^2_{0.1}O_3$.

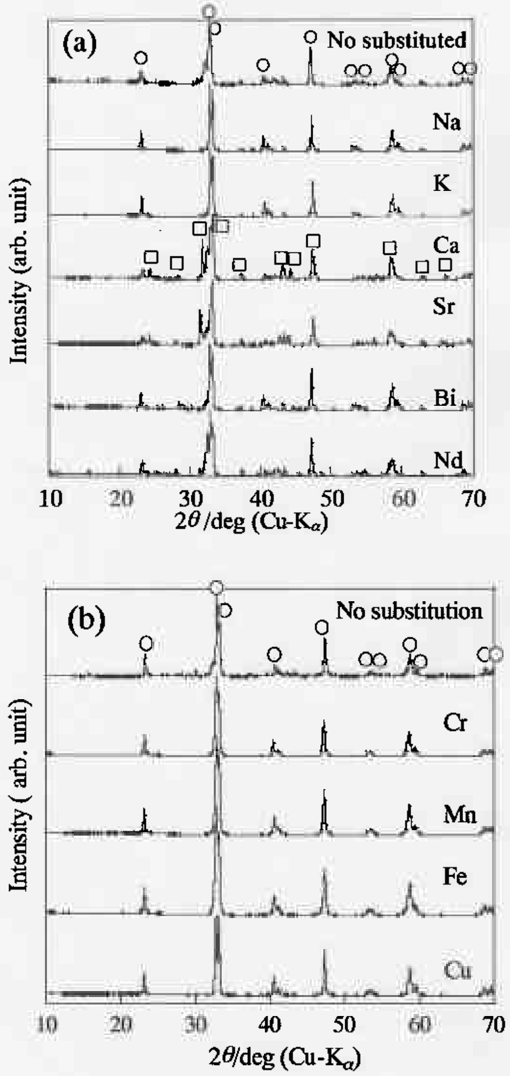

Figure 7 Powder XRD patterns for (a) (La, M^1)NiO_3 and (b) La(Ni, M^2)O_3 bulks. Diffraction peaks for $LaNiO_3$ and La_2NiO_4 are indicated by ○ and □.

Figure 8 indicates temperature dependence of ρ. All samples show a metal-like behavior. Only Bi-substitution is effective to reduce ρ in the $La_{0.9}M^1_{0.1}NiO3$ systems. If oxygen composition is not changed by Bi-substitution, average Ni valence is same between no-substituted and Bi substituted samples. The reduction of ρ seems to be caused by structural change or improvement of electrical property at grain boundaries. On the other hand, K-substitution increases ρ of the $LaNiO_3$ system. In these samples, the average Ni valence is calculated as 3.2, if the oxygen composition is 3.0. This is an incredible high valence for Ni. Therefore, the oxygen deficiency may be present in the K substituted sample. Because no secondary phases are observed in the XRD pattern, the increase in ρ is due to a decrease in carrier (electron) concentration, which induces the increase in S (Fig. 6 (a)). No-substituted sample would also include the oxygen deficiency, so that the average Ni valence is lower than 3.0. Substitution for Ni with other 3d transition metals increases S, even in these samples ρ is reduced (Fig. 8). Strikingly, the Cu substitution is much more effective for reducing ρ values.

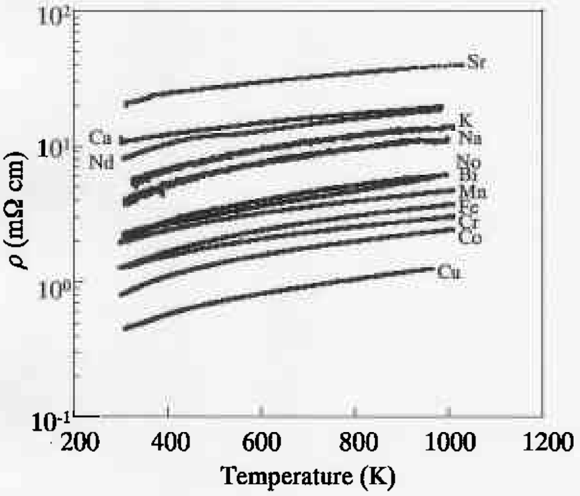

Figure 8 Temperature dependence of ρ for $La_{0.9}M^1_{0.1}NiO_3$ and $LaNi_{0.9}M^2_{0.1}O_3$ bulks.

Figure 9 shows power factors ($PF = S^2/\rho$) plotted against temperatures. Only the Bi-substituted sample possesses higher PF values than the non-substituted sample in the $La_{0.9}M^1_{0.1}NiO_3$ systems (Fig. 9 (a)). On the other hand, PF of all substituted samples are basically higher than the non-substituted samples in the $LaNi_{0.9}M^2_{0.1}O_3$ systems (Fig. 9 (b)). It is interesting to note that substitution at Ni sites with 3d transition metals reduces ρ in spite of the rather substantial increase in S. Secondary phases existing in the non-substituted sample seem to be reduced by substitution of Ni. Moreover, it would seem valuable to give further consider to the difference between the effects on thermoelectric properties due to substitution at the La and Ni sites.

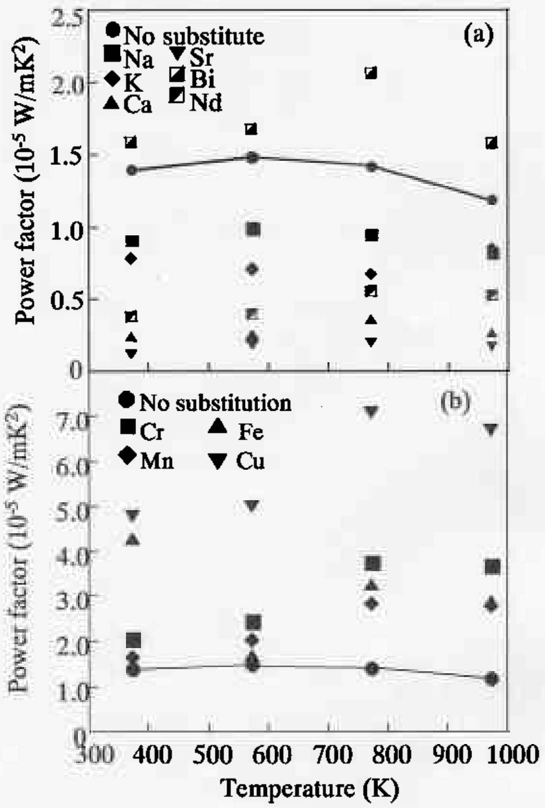

Figure 9 Temperature dependence of PF for (a) $La_{0.9}M^1_{0.1}NiO_3$ and (b) $LaNi_{0.9}M^2_{0.1}O_3$ bulks.

Conclusion

In order to discover a good n-type oxide, high throughput screening of (La, M^1)NiO_3 and La(Ni, M^2)O_3 systems was carried out. K-, Bi-, and Nd-substitution for La and Cr-, Mn-, Fe-, and Cu-substitution for Ni is effective to enhance S. ρ is reduced only by Bi-substitution for La and by Cr-, Mn-, Fe-, and Cu-substitution for Ni. As a result, PF is increased in these substituted samples.

References

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