THERMO-POWER OF HIGHLY ANISOTROPIC OXIDE MIXTURES

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Abstract – Thermoelectric properties of complex oxide mixtures have been studied to achieve high figure-of-merit. It is shown that for mixtures of oxide having highly anisotropic thermopower, near the percolation thresholds, Seebeck coefficient can be larger than the highest one of the components.

Keywords: thermo-power, oxide, percolation, figure-of-merit, Seebeck coefficient

1. Introduction

Recently oxide materials are considered to be promising for future thermoelectric applications such as refrigeration, heat to electrical energy conversion and electromagnetic wave power sensors [1-3]. The efficiency of thermoelectric materials is governed by figure-of-merit, Z [K^{-1}].

$$Z = \frac{S^2 \sigma}{\kappa}, \qquad (1)$$

where S [V/K] is the Seebeck coefficient, σ [S/m] is the electrical conductivity, κ [W/(m·K)] is the thermal conductivity which is the sum of carrier and phonon components. In order to achieve high figure-of-merit it is necessary independently control both electron and phonon transports to realize large thermo-power, low electrical resistivity, and low thermal conductivity simultaneously. In the limit of single type oxide, the change of stoichiometry, substitutions and doppand provide improvement of one of the parameters in figure-of-merit, but simultaneously provide the degradation of other parameters. In case of two or more kinds of oxides with different compositions and structural symmetries, after integration into one mixture, each subsystem can invest its own contribution and hence electron and phonon systems can be independently controlled by concentration of mixture in order to achieve high figure-of-merit [4,5].

2. Experiment

Investigated samples was prepared from bi-component mixtures $(R_1$-Ba-Cu-o$)_x$/$(R_2$-Ba-Cu-O$)_{1-x}$, where R_1=Nd,Gd; R_2=Y,Pr. Mixed samples were prepared from based powders Y-Ba-Cu-O; Sm-Ba-Cu-O; Nd-Ba-Cu-O and Pr-Ba-Cu-O. Powder samples were synthesized by the usual solid-phase reaction of initial oxides at temperatures 900÷920°C. These powders were mixed at various proportions, pressed to cylinders (d=6mm) and annealed at T=900°C in the air atmosphere within 12 hours. Then the samples were annealed in vacuum at 10^{-3} Torr within an hour at various temperatures T=450÷650°C. Since the annealing in base compositions at the same temperature results in various values of electro-conductivity and thermo-power, the annealed samples represent the mixture of two subsystems with various concentrations, having the inner sets of (σ_1, S_1) and (σ_2, S_2). The samples containing Pr-Ba-Cu-O already represent such a mixture skipping vacuum annealing, because Pr-containing base composition possesses the high value of thermo-power without oxygen deficit. We have prepared also mono-phase stoichiometric samples from some initial oxides, to control the absence of chemical interaction during sintering.

Both thermo-power and electrical conductivity were measured at 300K via standard methods. Figure 1 shows the measured results of thermo-power of such ceramics versus concentration of initial components. As it can be seen, some of general peculiarities, common to all mixtures, are listed below:

- curves, corresponding to high difference of thermo-power in the limiting points c=0 and c=1, have narrow maximum near the percolation point c≈10÷20%;

- there are local minimums on all curves of thermo-power at medium values of concentrations of the order of 60÷40%;

- character of dependencies remains unchanged for the same composition at various vacuum annealing conditions;

- thermo-power of stoichiometric mono-phase samples $(R_1)_x$-$(R_2)_{1-x}$-Ba-Cu-O sufficiently differs from one of non-stoichiometric simple mixtures $(R_1$-Ba-Cu-O$)_x$/$(R_2$-Ba-Cu-O$)_{1-x}$, i.e. there is no chemical interaction between two subsystems during sintering.

Complex composition of such oxide ceramics allows controlling the value of thermo-power by means of more quantity of independent parameters compared with mono-component mixture.
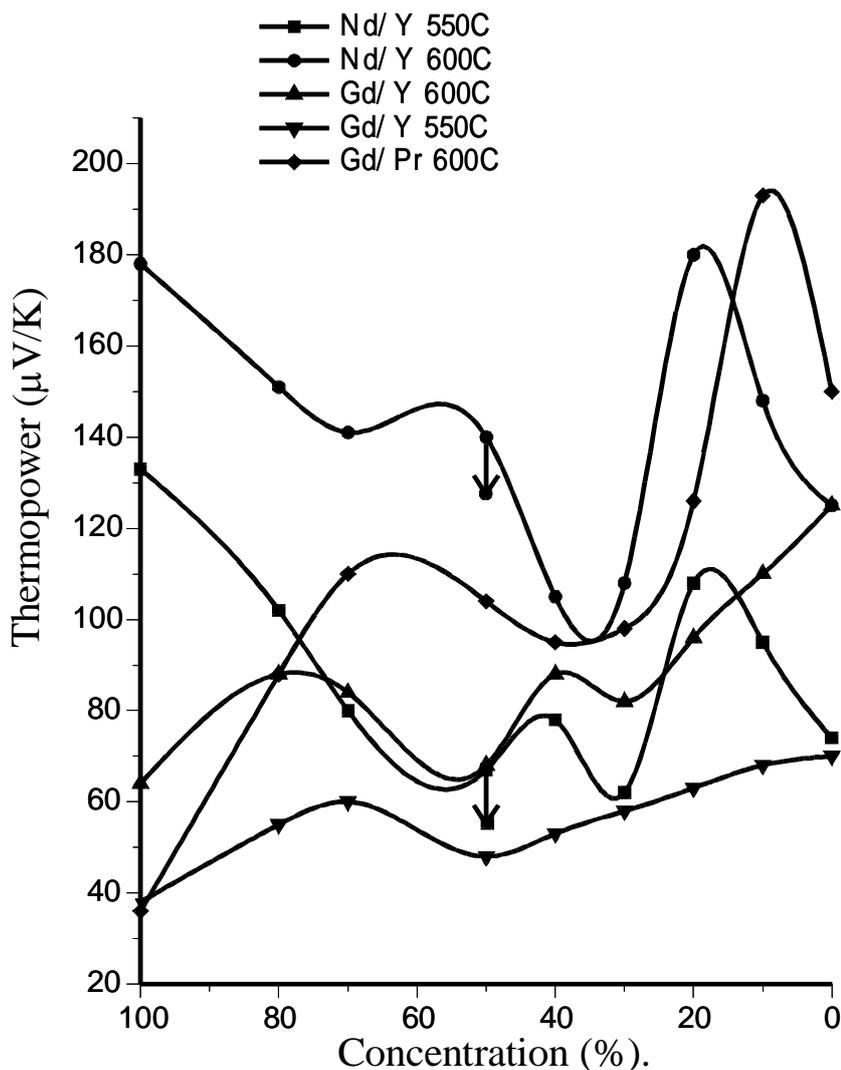
Fig. 1 Measured thermo-power versus concentration of initial components. Arrows indicate stoichiometric samples

Experimental results are in substantial disagreement with those predicted by bi-component mixtures model [6-10], according to which the bi-component mixture thermo-power

$$S_e = \frac{(\mu S_1 - S_2) f(\lambda) - (\lambda S_1 - S_2) f(\mu)}{(\mu \sigma_1 - \sigma_2) f(\lambda) - (\lambda \sigma_1 - \sigma_2) f(\mu)}$$

where

$$\left\{ \begin{matrix} \mu \\ \lambda \end{matrix} \right\} = \frac{1}{4\sigma_1 \kappa_1} \left\{ \left[\left(\sqrt{\sigma_1 \kappa_2} + \sqrt{\sigma_2 \kappa_1} \right)^2 + \sigma_1 \sigma_2 T (S_1 - S_2)^2 \right]^{1/2} \pm \left[\left(\sqrt{\sigma_1 \kappa_2} - \sqrt{\sigma_2 \kappa_1} \right)^2 + \sigma_1 \sigma_2 T (S_1 - S_2)^2 \right]^{1/2} \right\}^2,$$

and *f(x)* function reflects the dimensionality of the preeminent geometry of crystallites.

Figure 2 shows calculated curve for thermo-power of Bi-component mixture versus concentration for $S_2/S_1 = 100$
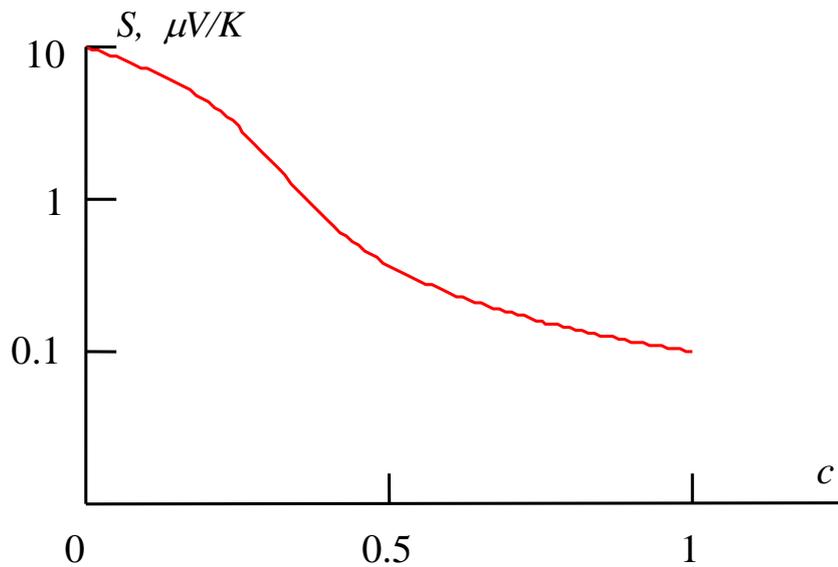
Fig. 2. Calculated thermo-power versus concentration of initial components.

To explain this disagreement, one should be noted, that this compound formally represents four-component mixture of isotropic grains. Hence, we cannot simply apply the aforementioned bi-component model to describe the transport properties of these materials.

3. Conclusion

Near the percolation threshold value of bi-component oxide mixture approx. $20 \div 30\%$, the significant improve in figure-of-merit can be achieved. This indicates that the percolation phenomena can provide a new strategy to optimize properties of thermoelectric materials, especially for disordered materials.

Acknowledgment

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