

## New Thermoelectric Materials and New Applications

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*Thermoelectricity in general is of strong scientific and technological interest due to its application possibilities ranging from clean energy to photon sensing devices. Recent developments in theoretical studies on the thermoelectric effects, as well as the newly discovered thermoelectric materials provide new opportunities for wide applications. One type of these materials is based on the strongly correlated electron systems; typical examples are the transition metal oxides, which were not regarded as very promising for thermoelectric applications. In this paper, we discuss some recent progress in this field, and special emphasize is on the new application of thin films grown on vicinal cut substrates. The thermoelectric effect is based on the anisotropic Seebeck components in crystals. Upon radiation of heat and/or light on the film surface, there will be an induced voltage, hence device which can detect the heat and/or light radiation can be made. We'll show that this type of detector demonstrates novel properties: broad optical response, very fast time response and at the same time it does not need any bias, therefore it is extremely energy saving. The performance of three typical compounds  $YBa_2Cu_3O_7$ ,  $LaCaMnO_3$  and  $LaSrCoO_3$  are presented.*

### 1. Introduction:

Thermoelectricity was discovered in 1821, and has been interesting from the point of view of basic science since then. After about 100 years of efforts, it was found that the effect can be applied to refrigeration and power generation in very special cases in 1950's. There were great efforts to explore more effective materials, especially among the semiconductors [1-4] The theory predicted at that time that the figure of merit for thermoelectric application is  $ZT = S^2/\kappa\rho$ , with  $S$  being the Seebeck coefficient,  $\kappa$  the thermoconductivity and  $\rho$  the resistivity. A large  $S$ , low  $\rho$  and low  $\kappa$  should be found in semiconducting materials with carrier densities of about  $10^{19}/\text{cm}^3$ . Recently, due to the discovery

of high  $T_c$  superconductor, new group materials have been studied widely and deeply. These are the strongly correlated transition metal oxides, which demonstrate novel properties not only in superconductivity but also in magnetic, thermoelectric and other related properties. The progress in theory of transport properties in these transition metal oxides predicts at the same time new direction for searching new thermoelectric materials[5-9]. On the other hand, the new discovery of a laser induced voltage effect (LIV) in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO)[10-13] and colossal magneto resistance (CMR) materials such as  $\text{LaCaMnO}_3$  (LCMO) thin films[14-16] has trigged new interests in the study and application of thermoelectricity, since this new effect was proved to be based on the off-diagonal components of the Seebeck tensor in single crystals. This principle and application are very different from the early concepts.

In this paper, we report recent progress in the study of new thermoelectric materials and their new applications. Special emphasis is on the single crystal and single crystal type thin film materials, which posses anisotropic Seebeck tensor components.

## 2. Results and Discussion:

The equations to describe the flow of electric and heat currents in an unisotropic solid are

$$j_i^e = -\alpha_k \frac{\partial \bar{\mu}}{\partial x_k} - \beta_{ik} \frac{1}{T} \frac{\partial T}{\partial x_k}, \quad (1)$$

$$k_i = -\beta_{ki} \frac{\partial \bar{\mu}}{\partial x_k} - \gamma_{ik} \frac{1}{T} \frac{\partial T}{\partial x_k}, \quad (2)$$

where  $j_i^e$  and  $h_i$  are the electric current and the heat flow density respectively, and,  $\bar{\mu} = \mu - e\phi$ , with  $\phi$  and  $\mu$  are the electrical and chemical potential. The coefficients  $\alpha_{ik}$ ,  $\beta_{ik}$ ,  $\beta_{ki}$ ,  $\gamma_{ik}$  are tensors for case of single crystals. The thermoelectric potential is produced and expressed as along certain direction in unitary length, when there is no electric current:

$$-\frac{\partial \phi}{\partial x_i} = -\frac{1}{e} \left( \varepsilon_{ik} \frac{\partial T}{\partial x_k} + \frac{\partial \mu}{\partial x_i} \right), \quad (3)$$

where  $e$  is electron charge,

$$\varepsilon_k \equiv \alpha_{ik}^{-1} \beta_{ik} \frac{1}{T} \quad (4)$$

is Seebeck tensor (or thermoelectric tensor). It is easy to prove that  $\alpha_{ik} = \sigma_{ik} / e^2$ , where  $\sigma_{ik}$  is the electrical conductivity tensor of the crystal. For homogenous media  $\partial\mu / \partial x_i = 0$ , then

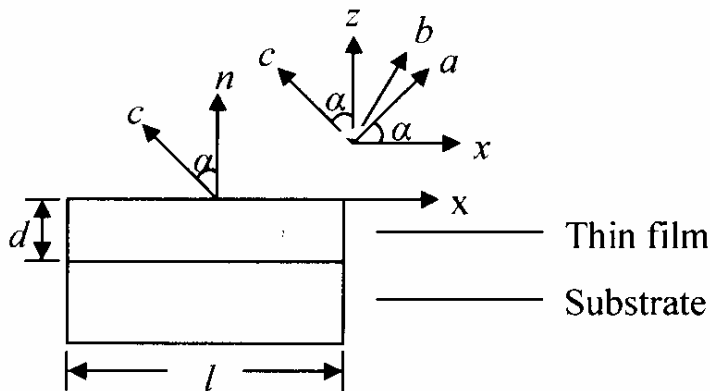
$$\frac{\partial\phi}{\partial x_i} = \frac{1}{e} \varepsilon_{ik} \frac{\partial T}{\partial x_k}, \tag{5}$$

and this means that the direction of temperature gradient is not necessary to coincide with that of potential gradient due to the tensors feature of a crystal. The expression of Seebeck tensor varies according to the crystal symmetries.

YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> crystal is of orthorhombic structure, and its Seebeck tensor is

$$\begin{pmatrix} S_{xx} & 0 & 0 \\ 0 & S_{yy} & 0 \\ 0 & 0 & S_{zz} \end{pmatrix}, \tag{6}$$

For YBCO,  $S_{xx}=S_{yy}=S_{ab}$ , and  $S_{ab}$  is the Seebeck coefficient in CuO<sub>2</sub> plane, it is different from the c-axis component  $S_c = S_{zz}$ . For a YBCO thin film grown on vicinal cut substrate the normal of the thin film surface ( $z$ ) does not coincide with the main axis  $c$  of the  $S$  crystal, and the angle  $\alpha$  between them (Fig.1) is given by the angle of the vicinal cut. Under this condition, (6) is transformed to



**Fig.(1):** A YBCO or LCMO thin film grown on a tilted substrate and the coordinate systems.

$$\begin{pmatrix} S_{11} & 0 & S_{13} \\ 0 & S_{22} & 0 \\ S_{31} & 0 & S_{33} \end{pmatrix}, \quad (7)$$

where  $S_{33} = S_{11} = S_{ab} \sin^2 \alpha + S_c \cos^2 \alpha$ ,  $S_{22} = S_{ab}$ , and  $S_{31} = S_{13} = 1/2 \sin(2\alpha)(S_{ab} - S_c)$ .

When the surface of the thin film absorbs a radiation, a temperature difference  $\Delta T$  along  $z$  direction is generated, and  $\Delta T_x = \Delta T_y = 0$ , if the film is heated from top homogeneously. Supposing that the thickness of the thin film is  $d$ , and the temperature distribution is homogeneous along  $z$  direction, the temperature in the thin film is  $(\partial T / \partial z) = (\Delta T_z / d)$ . Substituting the tensor components of (7) into (5), one obtains

$$\frac{\partial \phi}{\partial x} = \frac{1}{2} \sin(2\alpha)(S_{ab} - S_c) \frac{\Delta T_z}{d}, \quad (8)$$

$$\frac{\partial \phi}{\partial y} = 0 \quad (9)$$

$$\frac{\partial \phi}{\partial z} = (S_{ab} \sin^2 \alpha + S_c \cos^2 \alpha) \frac{T_z}{d} \quad (10)$$

Therefore, the temperature difference  $\Delta T_z$  induced by laser radiation can generate not only the potential along  $z$  direction but also the potential along  $x$  direction. The integration of (8) along  $x$  direction and (10) along  $z$  direction leads to

$$V_x = \int_0^1 \frac{\partial \phi}{\partial x} dx = \frac{1}{2} \frac{\Delta T_z}{d} (S_{ab} - S_c) \sin(2\alpha), \quad (11)$$

$$V_z = \int_0^1 \frac{\partial \phi}{\partial z} dz = \Delta T_z (S_{ab} \sin^2 \alpha + S_c \cos^2 \alpha). \quad (12)$$

Equations (11) and (12) show that the transverse thermoelectric potential  $V_x$  and vertical thermoelectric potential  $V_z$  are directly proportional to the temperature difference  $\Delta T_z$  and relate to the tensor components. Especially  $V_x$  is directly

proportional to  $(S_{ab} - S_c)$  and increases with  $\alpha$ . Equ.(11) can explain many phenomena, however it failed in explaining the relation between  $V_x$  and the film thickness  $d$ . In fact,  $V_x$  cannot be increased with  $1/d$  as  $d$  goes to zero. Furthermore, (11) supposes that  $\Delta T_z$  is a constant, and does not vary with time, hence it is difficult to discuss the time dependent LITV signals.

Using a micro-cell network model, based on the atomic layer thermopile model, we deduced a formula which describes the time-dependence of LITV. The formula is[18]

$$U(t) = \frac{\alpha_0 E l \sin(2\alpha)}{4d \rho c_0 \sqrt{\pi D t}} (S_{ab} - S_c) \left( e^{-\frac{\delta^2}{4dt}} - e^{-\frac{d^2}{4dt}} \right), \quad (13)$$

where  $E$  is the laser energy density per pulse,  $\alpha_0$  is the laser absorption coefficient,  $\rho$  is the mass density,  $c_0$  is the specific heat,  $\delta$  is the laser penetration depth, and  $D$  is the thermal diffusion constant of the thin film. Ref. [18] describes the time evolution of the induced signals and explain the measured result between the peak voltage and the film thickness  $d$  in YBCO thin films [3].

We can see from ref. [18] that LITV signal at any time  $t$  is directly proportional to  $\alpha_0, E \sin(2\alpha), l$  and  $S_{ab} - S_c$ , and inversely related with  $\rho$  and  $c_0$ . We now discuss the influence of parameters  $\delta, D$  and  $d$  on LITV signals. With the increasing of penetration depth  $\delta$  the peak value of LITV  $U_p$  decreases and the time constant  $\tau$  increases monotonously.  $\delta$  is related to the character of thin film and the wavelength of the incident laser. In practical applications, in order to obtain a device with higher  $U_p$  and smaller  $\tau$ , that is with higher sensitivity and fast time response, one can select materials with smaller  $\delta$  at the used wavelength, or take measure to spread another material on top of the thin films, which is with small  $\delta$ .

With decreasing the thermo-diffusion constant  $D$ , the  $\tau$  increases and  $U_p$  shifts to large value in time. This is easy to understand because  $D$  embodied the diffusion speed of heat, so the higher  $D$ , the faster the thermal equilibrium is reached, hence a smaller  $\tau$  is reached.

It can be shown that there exists an optimum thin film thickness  $d$  in order to obtain largest peak voltage  $U_p$ . Small  $d$  can decrease the time constant  $\tau$  but reduce the peak intensity, while large  $d$  will reduce the peak intensity as well increase the time constant, hence is more harmful to the performance of the device.

It should be mentioned that the time response of these thin films to pulsed laser is very fast. The voltage is produced in an atomic layer thermopile, as long as there is a temperature gradient generated by what means, there is a voltage produced, and the carriers move only a very short distance, a scale of the lattice parameter. This is different from the traditional thermal devices, say bolometers, which function with long time constant, because to reach thermal equilibrium needs time. In LCMO thin films the rising time (for the signal rising from 0 to the peak) of LITV can reach the *ns* order, and in YBCO thin films, can reach the *ps* order[15].

This type of detector does not need any electric bias like traditional semiconductor or bolometers, since they are based on the principle of atomic layer thermopile. Therefore it is extremely energy saving.

### 3. Conclusions:

In conclusion, laser induced thermoelectric voltage (LITV) effect had been found in YBCO, LCMO and LaSrCoO<sub>3</sub> thin films, and this effect is originated from the anisotropic Seebeck effect in the crystals. This is an intrinsic property of crystals; hence many other crystals may demonstrate the effect. Due to the different properties, these crystals can be used for different purpose or at different wavelengths. According to the time dependent LITV relation one can design light or heat detectors working in wide spectrum range with fast time response. To obtain a detector with fast time response, the thermal diffusion constant *D* of the thin films must be big. Moreover, to obtain the optimum performance of the thin film the penetration depth  $\delta$  under the working wavelength must be as small as possible, and the optimum thin film thickness *d* must be reached.

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