Determination of thermal expansion coefficient for thermoelectric $CaMnO_3$ with a shadow method

Chantira Boonsri, Pichet Limsuwan and Prathan Buranasiri

Department of Physics, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand
chantira.boonsri@gmail.com, opticslaser@yahoo.com

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Abstract. We have measured thermal expansion coefficient of a bulk $CaMnO_3$ thermoelectric module with a cylindrical shape, using a shadow method. The $CaMnO_3$ module has been heated from the room temperature up to 773 K. At each temperature, the shadow image has been recorded by a CMOS camera and reconstructed with a HoloViewer program in MATLAB. Then the diameters of the module have been obtained at different temperatures in the region 300–773 K. Finally, we have determined the linear thermal expansion and the thermal expansion coefficient for $CaMnO_3$. Our results demonstrate that the expansion coefficient for the bulk $CaMnO_3$ thermoelectric module depends linearly on the temperature in the region under study.

Keywords: thermoelectric materials, thermal expansion, shadow method

UDC: 535.8

1. Introduction

The field of thermoelectrics has started since the discovery of Seebeck and Peltier effects. Thermoelectric materials can directly convert heat into electrical energy, and vice versa [1]. Searches for oxides as candidates for thermoelectric materials have started in the late 1990s (see, e.g., the results for $NaCO_2O_4$ [2]). Perovskite oxides, $SiTiO_3$ and $CaMnO_3$, have also been studied in this relation [3, 4]. Note that a rapid progress in the development of thermoelectric devices in the recent years is due to their environmentally clean energy-transformation sources [1, 5].

Good thermoelectric materials should have large Seebeck coefficients, high electrical conductivity and low thermal conductivity [6, 7]. $CaMnO_3$ indeed exhibits a sufficiently large Seebeck coefficient and a relatively low thermal conductivity [8]. However, its drawback is low electrical conductivity [9]. A possible way out is to increase electronic conductivity of $CaMnO_3$ via doping [9, 10]. A solid-state reaction method is widely used for preparing thermoelectric materials [1, 8, 11], which requires high temperatures, somewhere in the range 750–1200°C. Then a thermal expansion effect occurring in the thermoelectric materials can affect their thermoelectric properties. In the past years, a number of researchers have studied the thermal expansion of thermoelectric materials [12–16].

Several methods have been employed for the measurement of thermal expansion, such as capacitance [13–15, 17–19], optical [20–25] and high-resolution powder-diffraction methods [16]. The capacitance methods are usually used for determining thermal expansion coefficients. In this method, the expansion coefficient is deduced through the change in capacitance of a capacitor, which appears due to sample dimension changes. The capacitance change is measured using two-terminal or three-terminal capacitance techniques. The two-terminal technique is used mainly in moderately high-temperature measurements, i.e. in the range from 50 to 150°C [26, 27]. On the contrary, the three-terminal capacitance technique developed by White [28], which provides high enough sensitivity, is often used for the low-temperature measurements in the range from 4 to 30 K. Among optical methods, interferometric techniques based on Fizeau and Fabry–Perot interferometers are also used for studying the thermal expansion effect.

In this work, the thermal expansion coefficient of a bulk n-type $CaMnO_3$ thermoelectric is determined using a simple optical method based on a shadow imaging and a diffraction occurring at the edges of bulk sample. The n-type $CaMnO_3$ thermoelectric has earlier been prepared by a solid-state reaction method and its thermoelectric properties have been studied extensively at the Smart Materials Research and Innovation Unit (Faculty of Science, King Mongkut's Institute of Technology Ladkrabang). Now a bulk n-type $CaMnO_3$ thermoelectric module has been prepared in order to measure its thermal expansion coefficient. The results obtained by us are expected to be useful for further improvement of the efficiency of thermoelectric materials.

2. Thermal expansion coefficient

When a solid material is heated, there is some change ΔT in its temperature and a change in its linear dimension, ΔL [29]. If the material is isotropic, then the changes along different directions are the same, and the mean linear thermal expansion coefficient is given by

$$\alpha_m = \frac{1}{L_0}\frac{\Delta L}{\Delta T}, \tag{1}$$

where L_0 is the initial length at the room temperature (300 K) and $\frac{\Delta \mathrm{L}}{\mathrm{L}_0} = \frac{L_T - L_0}{L_0}$ the relative length change, or the thermal expansion. The limiting value of this parameter (at a constant pressure P) at an infinitesimal temperature change is defined as a linear thermal expansion coefficient:

$$\alpha = \frac{1}{L_0}\left(\frac{\partial L}{\partial T}\right)_P . \tag{2}$$

Usually the thermal expansion coefficient is not measured directly. It is either calculated using its definition or is derived after differentiating the relation based upon its temperature-dependence expansion. If we have

$$\frac{L_T - L_0}{L_0} = \alpha_0 + \alpha_1 T + \alpha_2 T^2 + \alpha_3 T^3 + \ldots, \tag{3}$$

then the relation

$$\alpha = \alpha_1 + 2\alpha_2 T + 3\alpha_3 T^2 + \ldots \tag{4}$$

can be obtained. When the mean coefficient is determined over some temperature range ΔT, a curvature correction may be needed to obtain the true coefficient at the mean temperature. For instance, if the expansion can be represented by a third-power polynomial, then we have

$$\alpha = \alpha_m - \frac{\alpha_3}{4}(\Delta \mathrm{T})^2 . \tag{5}$$

3. Materials and methods

3.1. Sample preparation

A polycrystalline sample of n-type $CaMnO_3$ was prepared from a mixture of $CaCO_3$ and MnO_2, using a solid-state reaction method. The sample was kept at 1200°C for 12 h and then slowly cooled down to the room temperature. Then it was pressed in a cylindrical mold with an inner diameter of about 10 mm and a height of 20 mm. Finally, a bulk $CaMnO_3$ thermoelectric module was obtained.

3.2. Materials

This bulk $CaMnO_3$ thermoelectric module of a cylindrical shape was used for the measurements of thermal expansion coefficient. The initial diameter and length of the $CaMnO_3$ module were measured by a Vernier caliper. They were found to be equal to 10.05 and 20.16 mm, respectively.

3.3. Experimental setup

Fig. 1 shows the experimental setup for measuring thermal expansion coefficient of our bulk $CaMnO_3$ module. The light source was a diode laser emitting red light at the wavelength 636.4nm. The laser beam with the diameter of 1 mm was expanded by a concave lens and collimated by a collimator to obtain the laser-beam diameter of about 25 mm. It passed through the bulk $CaMnO_3$ module placed on an electric hot plate. It heated the module, which behaved as an obstacle for the light. Then the shadow of the module became visible on a screen behind. At the same time, the light beam diffracted at the edges of the bulk $CaMnO_3$ sample and diffraction patterns were also observed on the screen.

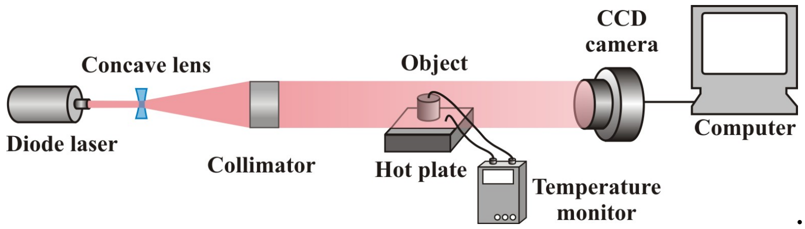


Fig. 1. Experimental setup used for measuring thermal expansion coefficient of a bulk $CaMnO_3$ module.

In this work, the shadow image and the diffraction pattern were recorded on a CMOS camera (Canon EOS 700D, 5184×3456 pixels, 4.29 μm pixel pitch). The shadow image and the diffraction pattern were reconstructed numerically using a HoloViewer program in MATLAB (Michigan Technological University), which is based on the Huygens–Fresnel principle. The electric hot plate can heat the bulk $CaMnO_3$ module from the room temperature (300 K) to the maximum temperature about 773 K. It was measured by a temperature monitor. As a result, the shadow image and diffraction pattern were recorded at the room temperature and at a number of higher temperatures, 373, 473, 573, 673 and 773 K.

If the $CaMnO_3$ module with the diameter d_0 at the temperature T_0 is heated up to the temperature T, the diameter of the object is enlarged. The diameter of the object at the temperature T denoted as d can be represented as

$$d = d_0 + d_0\alpha(T - T_0) , \tag{6}$$

$$\Delta d = d - d_0 = d_0\alpha\Delta T , \tag{7}$$

where Δd is the change in the diameter, ΔT the temperature change and α the thermal expansion coefficient.

4. Results and discussion

Fig. 2a shows the shadow images and the diffraction patterns obtained for the bulk $CaMnO_3$ module at the temperatures 300, 373, 473, 573, 673 and 773 K. It is seen from Fig. 2a that the edges of the shadow images are not sharp at all temperatures. It is therefore difficult to mark lines along the edges and the diameter of the shadow images cannot be determined accurately from the initial images. To obtain sharper edges in the shadow images, we have reconstructed these images using the HoloViewer program. The images thus reconstructed are shown in Fig. 2b.

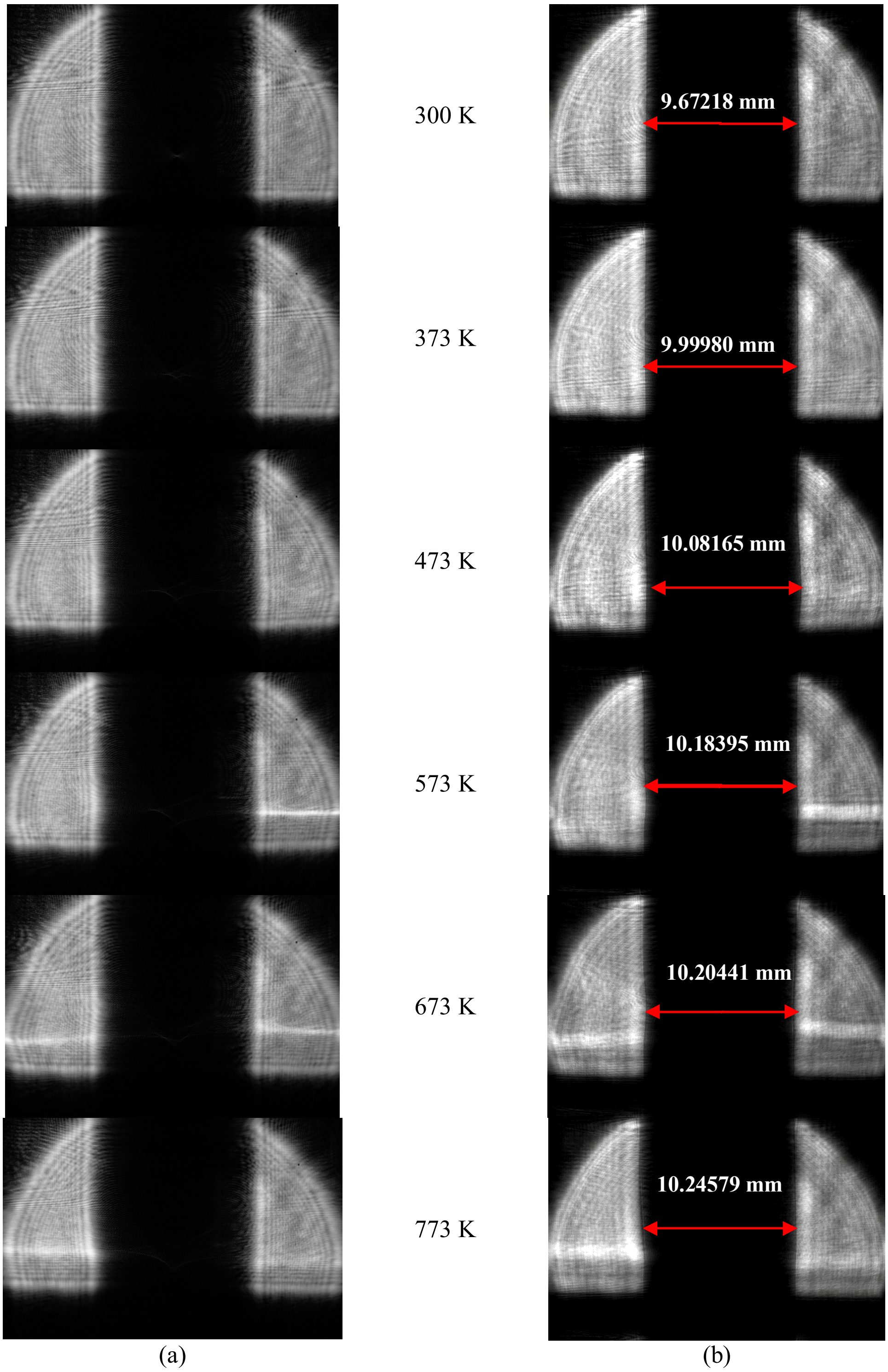


Fig. 2. Initial shadow images recorded with a CMOS camera (a) and reconstructed shadow images (b) at 300, 373, 473, 573, 673 and 773 K.

As seen from Fig. 2b, the edges in the shadow images are sharper than those in the original shadow images. Then the diameters of the bulk $CaMnO_3$ images at all temperatures can be determined using the distance function. The diameters of the object images obtained at 300, 373, 473, 573, 673 and 773 K are equal to 9.67218, 9.99980, 10.08165, 10.18395, 10.20441 and 10.24579 mm, respectively. These diameter values are indicated in Fig. 2b. However, the diameter obtained by this method still depends on the observer's eye and so is not reliable enough. To obtain the diameter with higher accuracy, it is necessary to investigate the transverse intensity profile of the reconstructed shadow images.

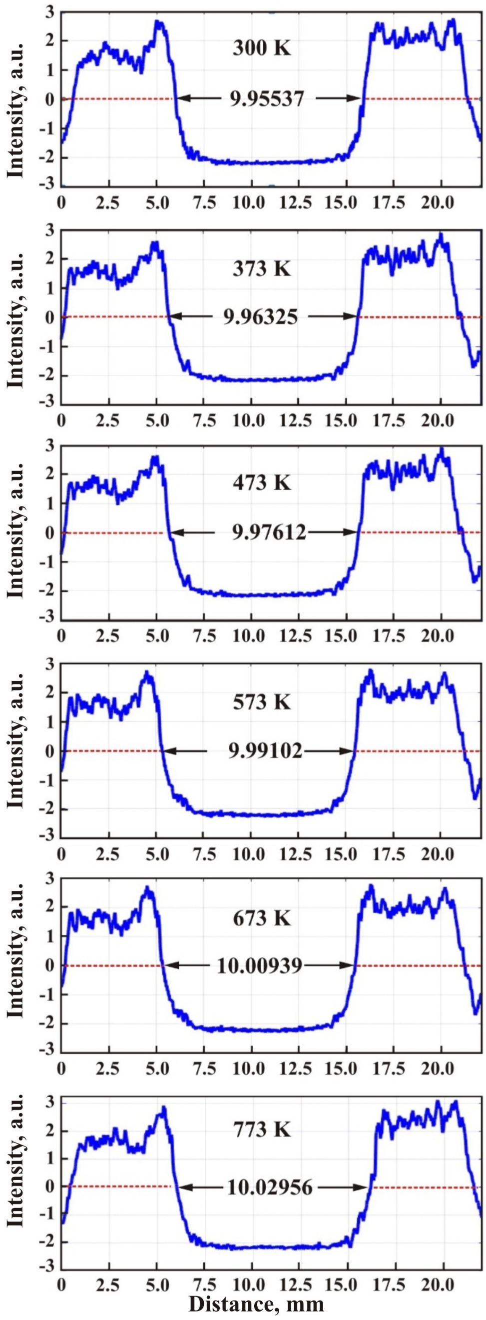
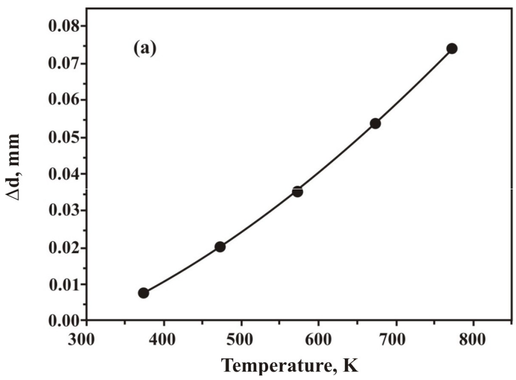


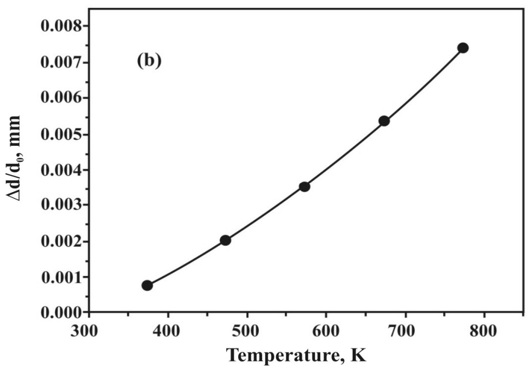
Fig. 3. Intensity profiles for the shadow images reconstructed at 300, 373, 473, 573, 673 and 773 K.

Fig. 3 shows the transverse intensity profiles for the reconstructed shadow images at different temperatures. The edges can be much more precisely marked from the intensity profiles and the diameters of the shadow can be easily determined. These values are indicated in Fig. 3 and gathered in Table 1. Since the light beam passing through the bulk $CaMnO_3$ module is parallel, the diameter of the shadow image is equal to that of the module. We remind that d_0 represents the diameter of the bulk $CaMnO_3$ thermoelectric module at the initial temperature T_0 and d is the diameter of the object at higher temperatures T (see Eq. (2)). The change in the diameter Δd, the thermal expansion $\Delta d/d_0$ and the thermal expansion coefficient α at different temperatures are also given in Table 1. Finally, temperature dependences of the diameter change Δd, the linear expansion $\Delta d/d_0$ and the thermal expansion coefficient α are shown in Fig. 4.

Table 1. Diameter d, diameter change Δd, thermal expansion $\Delta d/d_0$ and thermal expansion coefficient α, as obtained for the bulk $CaMnO_3$ thermoelectric module at different temperatures.

Temperature, K	Diameter d, mm	Δd, mm	$\Delta d/d_0$	Thermal expansion coefficient, 10^{-5} K^{-1}
300	9.95537	0	0	–
373	9.96325	0.00788	0.00079	1.08429
473	9.97612	0.02075	0.00208	1.20480
573	9.99102	0.03565	0.00358	1.31171
673	10.00939	0.05402	0.00542	1.45475
773	10.02956	0.07419	0.00741	1.57559





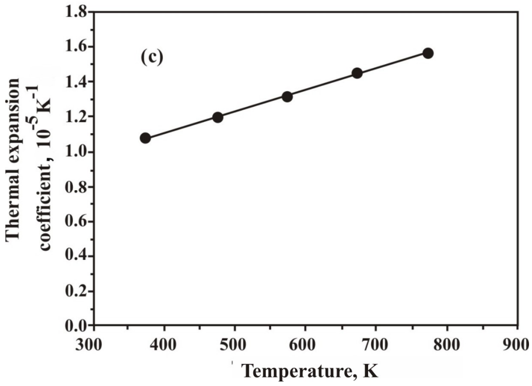


Fig. 4. Diameter change Δd, thermal expansion $\Delta d/d_0$ and thermal expansion coefficient α as functions of temperature.

It is seen from Fig. 4a and Fig. 4b that the diameter change Δd and the thermal expansion $\Delta d/d_0$ dependent quadratically on the temperature in the region from 373 to 773 K. This implies that the definition given by Eq. (3) is satisfied.

It is also clear from Fig. 4c that the thermal expansion coefficient α is a linear function of temperature, thus agreeing with the definition given by Eq. (2). In other words, the thermal expansion coefficient for the bulk $CaMnO_3$ thermoelectric module depends linearly on the temperature. Since the thermal expansion coefficient for $CaMnO_3$ has not yet been reported in the literature, we cannot compare our results with the data of some other authors. Nonetheless, our thermal expansion coefficient, which falls in the range $(1.1–1.6)\times10^{-5}\,K^{-1}$ at the temperatures 370–770 K, is of the same order of magnitude as those obtained for the others thermoelectric materials (see Refs. [1, 5, 12–14]).

5. Conclusion

We have developed the shadow method for measuring the thermal expansion coefficient of a bulk n-type $CaMnO_3$ thermoelectric module with a cylindrical shape. The initial diameter and length of the $CaMnO_3$ cylinder have been measured with the Vernier caliper. Then the shadow images of $CaMnO_3$ have been recorded in the region 300– 773 K using the CMOS camera. The recorded $CaMnO_3$ images have been reconstructed with the HoloViewer program. The diameters of the $CaMnO_3$ cylinder have been determined in this way. Finally, the diameter change Δd, the thermal expansion $\Delta d/d_0$ and the thermal expansion coefficient α have been calculated. Our method can be used for measuring linear dimensions with a very high accuracy, which is not worse than 10^{-5} mm.

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Анотація. *Ми виміряли коефіцієнт теплового розширення об'ємного термоелектричного модуля $CaMnO_3$ циліндричної форми, використовуючи тіньовий метод. Модуль $CaMnO_3$ нагрівали від кімнатної температури до 773 К. При кожній температурі було записано тіньове зображення CMOS-камерою, яке реконструювали за допомогою програми HoloViewer у MATLAB. Далі було одержано діаметри модуля при різних температурах у діапазоні 300–773 К. Нарешті, було визначено лінійне теплове розширення та коефіцієнт теплового розширення $CaMnO_3$. Наші результати засвідчують, що коефіцієнт розширення для об'ємного термоелектричного модуля $CaMnO_3$ лінійно залежить від температури в дослідженому діапазоні.*