ORIGINAL ARTICLE

The new types of positive temperature coefficient effect based on SnO_2+2CoO and SnO_2+Cr_2O_3 ceramics used as temperature sensor

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Abstract

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The SnO_2+2CoO and SnO_2+Cr_2O_3 materials were prepared by standard ceramic techniques and the phase identified by XRD techniques. The PTC effect was tested. Both samples were applied as temperature sensors. Sample 1 exhibited PTC effect from 25 to 110ºC and the positive temperature coefficient of the resistance (α) was +18.2 %/ºC. The maximum resistance was 28.5 MΩ at 110ºC. Sample 2 exhibited PTC effect from 35 to 85ºC and the positive temperature coefficient of the resistance (α) was +28.6 %/ºC. The maximum resistance was 91.8 MΩ at 85ºC. The PTC effect was seen to have its origins in the resistance of the grain boundary region. The PTC effect in both samples was discovered for the first time. The prepared samples and temperature monitoring with a computer system can measure the temperature in the range 22ºC to 70ºC (sample 1) and 40ºC to 120ºC (sample 2). The working temperature of these sensors are near the PTC region and they are very sensitive to heat.

Key words : PTC thermistor, temperature sensor

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บทคัดย่อ

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ปรากฏการณ์พีทีซีชนิดใหม่ที่พบในสาร SnO_2+2CoO และ SnO_2+Cr_2O_3 ที่ประยุกต์ใช้เป็นหัววัดอุณหภูมิ

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ได้เตรียมสารที่ 1: SnO_2+2CoO และสารที่ 2: SnO_2+Cr_2O_3 โดยวิธีเทคนิคเซรามิกส์มาตรฐานและชี้บ่งเฟส ด้วยเครื่อง XRD ได้ทดสอบปรากฏการณ์ PTC สารทั้งสองสามารถนำไปประยุกต์ใช้เป็นหัววัดอุณหภูมิ สารที่ 1 แสดงปรากฏการณ์ PTC ในช่วง 25 ถึง 110°C โดยมีสัมประสิทธิ์อุณหภูมิที่เป็นบวก (α) เท่ากับ +18.2 %/°C ความต้านทานสูงสุดมีค่า 28.5 MΩ ที่ 110°C สารที่ 2 แสดงปรากฏการณ์ PTC ในช่วง 35 ถึง 85°C โดยมีสัมประสิทธิ์อุณหภูมิที่เป็นบวก (α) เท่ากับ +28.6 %/°C ความต้านทานสูงสุดมีค่า 91.8 MΩ ที่ 85°C ปรากฏการณ์ PTC มีจุดกำเนิดจากความต้านทานในย่านขอบเขตของเกรน ได้ค้นพบปรากฏการณ์ PTC ในสารทั้งสองนี้เป็นครั้งแรก สารตัวอย่างที่เตรียมได้และระบบการวัดอุณหภูมิด้วยคอมพิวเตอร์สามารถวัดอุณหภูมิได้ในช่วง 22°C ถึง 70°C (สารที่ 1) และ 40°C ถึง120°C (สารที่ 2) อุณหภูมิใช้งานของหัววัดอยู่ใกล้ย่าน PTC ซึ่งมีความไวต่อความร้อนมาก

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Thermistor is the temperature dependent resistor (Moulson, 1990). PTC thermistor is the device whose resistance increases as the temperature decreases. This thermistor had high value of α (positive temperature coefficient of resistance, PTCR) (Buchanan, 1991). PTCR value is involves the ferroelectric Curie point or Curie temperature (T_c) or ferroelectric-paraelectric transition temperature. The Curie temperature is involved with microstructure. The resistance of a PTC thermistor will increase rapidly as temperature increases due to the transformation of lattice from tetragonal to cubic and the changing of the electronic properties at the grain boundaries. $BaTiO_3$ is the ferroelectric semiconductor which shows PTC effect. T_c of $BaTiO_3$ is about 120-130ºC and is changed with dopant content. Dopant is added to $BaTiO_3$ for changing of the potential barrier at grain boundaries. Then the PTC behaviour is changed. PTC thermistors are $BaTiO_3$+0.01 La_2O_3 (BLT), $BaTiO_3$ +0.01 Y_2O_3, $BaTiO_3$+0.01Nb_2O_5, $BaTiO_3$+0.01 Ta_2O_3 and $BaTiO_3$+0.01Sb_2O_3, etc. This thermistor can be used as a temperature sensor, constant temperature heater (PTC heater), honeycomb air heater (hair dryer), auto fuel evaporator, current limiter, circuit timer, sensor for motor protection, motor start assist and high temperature material.

Research groups that have studied the PTC thermistors are as follows. Klaus Dostert reported that PTC thermistor can be operated as a thermostat for heat flowing (Klaus Dostert, 1983). Issa prepared $BaTiO_3$+0.4 mol% Ho_2O_3 and the resistivity, dielectric constant, dissipation factor versus frequency and Curie temperature were measured for PTCR effect study (Issa, 1992). Masalu Miyayama in Japan, prepared $(Ba_{1-x}Sr_x)(Nb_{0.003}Ti_{0.997})O_3$ + 1 mol% TiO_2 + 0.07 mol% MnO (x=0, 0.2). The electrode was fabricated from silver paste. The resistance versus temperature was measured and applied to an infrared detector (Masalu Miyayama, 1992). Padmini in India prepared $BaTiO_3$ + 0.3 at% Nb_2O_5 ; $BaTiO_3$ + 0.3 at% Nb_2O_5 + 0.2 at% Bi_2O_3. The resistivity versus dopant content, the resistivity versus temperature and the dielectric constant versus temperature were measured (Padmini, 1994). Horng-Yi Chang in Taiwan, prepared $(Sr_{0.2}Ba_{0.8})TiO_3$ and the material was tested for PTC effect and the Curie temperature (T_c) was measured (Horng-Yi Chang, 1997). Wang in China, prepared $(Sr,Pb)TiO_3$. The resistivity at different temperature and Curie temperature were measured and the PTCR value was calculated (Wang, 1997). Shibagaki in Japan, prepared Ca-doped $SrTiO_3$ capacitor and α was measured (Shibagaki, 1997). Xue in China, prepared MnO-doped $BaTiO_3$ with $Al_2O_3.SiO_2$ as the sintering-aid material and the PTC efficiency was studied (Xue, 1997). Igor in Slowenia had found that the PTCR effect in TiO_2-doped $BaNb_2O_6$ was in the range 70 to 300ºC (Igor, 1999). AI-Shahran in Saudi Arabia prepared Ho-doped $BaTiO_3$ ceramics and the Curie temperature was 110ºC (AI-Shahran, 2000). He in Singapore reported about PTC effect in the Cr/(Ba,Pb)TiO_3 material for overcurrent protection application. The structural model was used to explain the PTC effect (He, 2000). Meier in England, found that the PTC thermistor could be used as overtemperature protectors (Meier, 2001). Jingchang in China, prepared the (Y, Mn) co-doped $Sr_{0.5}Pb_{0.}5TiO_3$ thermistors and studied the PTCR effect (Jingchang, 2002).

Tin oxide (SnO_2) has found applications in high-temperature conductors, ohmic resistors, transparent thin-film electrodes and gas sensors. It crystallizes in the tetragonal rutile structure with cell dimensions a=474 pm and c=319 pm. It is a wide band gap semiconductor, with the full valence band derived from the O 2p level and the empty conduction band from the Sn 5s level. The band gap at 0 K is approximately 3.7 eV. Doping the crystal with group V elements also induces n-type semiconductivity (Moulson, 1990).

Chromium oxide (Cr_2O_3) is used in recording tapes (Moulson, 1990). Bulk chromium oxide Cr_2O_3 is an antiferromagnetic material (Salah, 2004). Chromium oxide has been reported to have good response as an electrode in a potentiometric NO sensor. Cr_2O_3 is a p-type semiconducting metal oxide which has been proposed as a potentially attractive electrode material for resistive sensors due to high melting point, excellent corrosion resistance, and good high temperature electrical conductivity (Peter Martin, 2003).

Cobalt oxide (CoO) like other transition metal oxide, is electrically insulating, antiferromagnetic and has the rocksalt structure. There are several interesting works on CoO previously such as X-ray and ultraviolet photoemission and electron energy loss studies of its electronic structure (Sindhu, 2004).

$SnCo_2O_4$ has spinel structure (Depero, 1995). The behaviour of precipitated $SnCo_2O_4$ phase in 2 mol% CoO-doped SnO_2 ceramics was investigated for changes of sintering and heat treatment atmospheres (Bong-Chull kim, 2001).

Nobody has studied the PTC effect in SnO_2 +2CoO and SnO_2+Cr_2O_3 samples. So, in this study, the SnO_2+2CoO and SnO_2+Cr_2O_3 samples were prepared from powder starting materials and the sample phases were identified with XRD apparatus. The dependence of resistance on temperature of the PTC effect was studied. The PTCR value was calculated. The sample was applied to be a temperature sensor.

Materials and Methods

1. Preparation, phase identification and electroding of the samples

Samples were prepared by standard ceramic techniques as shown in Figure 1 (Buchanan,1991). The samples had two compositions, sample 1: SnO_2+2CoO and sample 2: SnO_2+Cr_2O_3. Sample powders of SnO_2, CoO and Cr_2O_3 with 99.5% purity were collected. Sample powders were calculated and weighed. Powders were mixed with mortar and then mixed again by containing the powders in a plastic can and rotated with a mixer. PVA (polyvinyl alcohol) and distilled water were added to the powders as a binder for forming granulation. These powders were taken in a press mold and were pressed with hydraulic pressor (Rllk 25 tons) into small discs. The samples were fired with furnace that used temperature controller (FCR-13A-R/M) and type S thermocouple as a temperature sensor. The samples 1 and 2 were fired at 1200ºC. Both samples used a heating rate of 5ºC/min and a soaking time of 1 h. Finally, we obtained the as-fired samples. The prepared samples were identified with XRD apparatus (X-ray diffractometer, Philip PW1730). The sample thickness and diameter were measured with micrometer. The samples were electroded with silver paste by

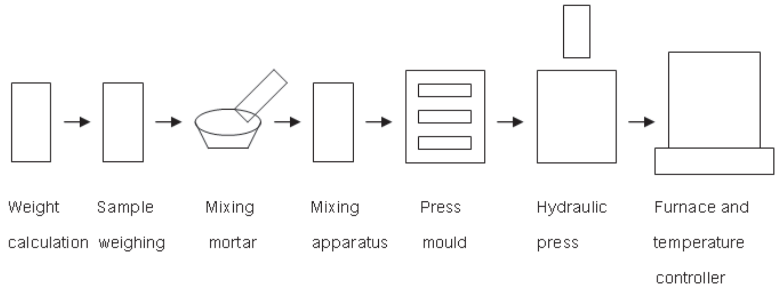


Figure 1. The schematic diagram for sample preparation.

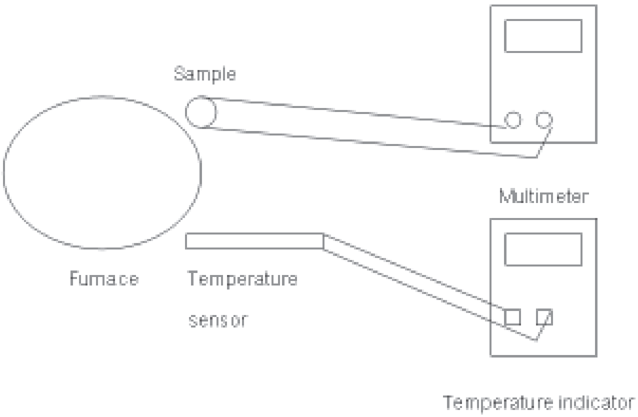


Figure 2. The experimental set up for the resistance versus temperature measurement.

smearing onto the surface, together the metallic pin and fired at 120ºC for 20 min.

2. PTC property measurement

The sample was held in a stand above the furnace about to obtain the proper temperature increasing rate as shown in Figure 2. The resistance (R) was measured with a multimeter (Fluke 45) and the temperature (T) with temperature apparatus (AVD M890C^{+}). After that the sample temperature was varied slowly from 25 to 150ºC (sample 1) and 35 to 140ºC (sample 2). The resistance and temperature relationships were recorded and the R vs T graphs were plotted. The positive temperature coefficient of the resistance and negative temperature coefficient of the resistance were calculated from the formula, $\alpha = (1/R)(dR/dT)$.

3. Temperature sensor testing

After the sample was measured for the resistance versus temperature relation, the samples were tested as the temperature sensor using the following steps:

1) Computer interfacing system for temperature measurement with the prepared sample as a temperature sensor was prepared as shown in Figure 3. This system is comprised an ADC0809, 74LS244, ET-PT8255 card and computer. After that this circuit was tested for correct operation.

2) Measurement and control program was written and was calibrated for computer reading the temperature with the prepared sample used as a temperature sensor.

```
Program Temperature_Sensor_Testing;
uses   crt ;
var    i, ,j, x, y, DV :  integer;
       AV, Ttrue       :  real;
       const  PA         =  $0304;
              Pcontrol   =  $0307;
```

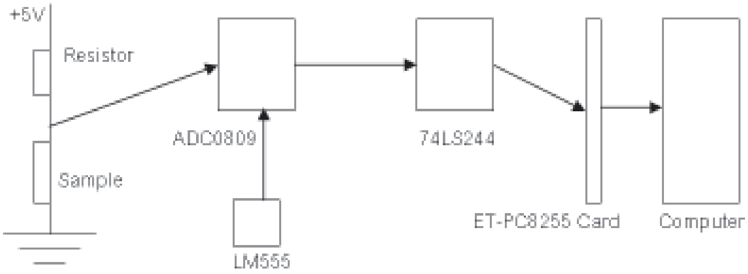


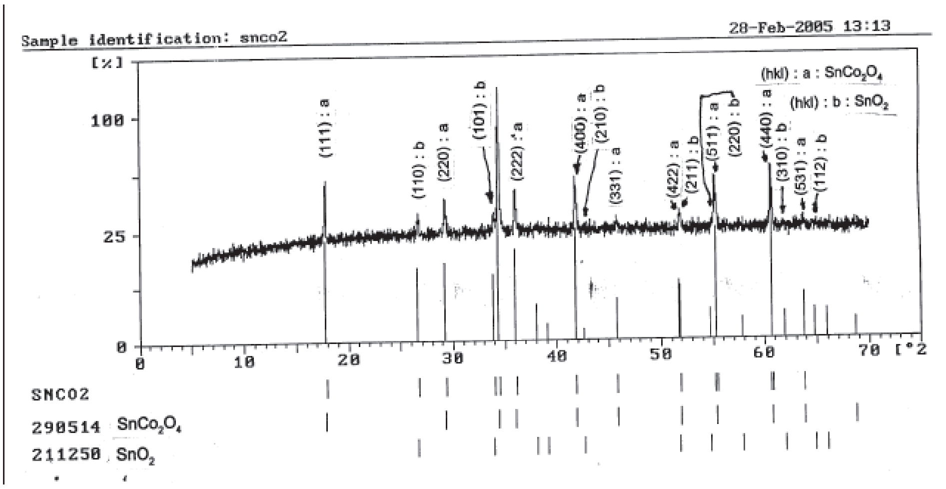
Figure 3. Block diagram for temperature measurement system with computer with the prepared sample as a temperature sensor.

```
begin
        clrscr;
        port[Pcontrol]: = $90;
        gotoxy(25,2); writeln('TEMPERATURE
                        MEASUREMENT');
        gotoxy(25,3); writeln('..................');
        DV : = 0 ; AV : = 0 ; Ttrue : = 0;
        for  i : = 1 to 255 do
begin
        DV : = port[PA];
        gotoxy(27,15); writeln('Digital Voltage =',
                         DV : = 3);
        AV : = (5/225)*DV;
        gotoxy(27,20); writeln('Analog Voltage =',
        AV:3:2,'V');
        delay(100);
        Ttrue : = (39.919*AV+5.5948);
        gotoxy(27,22); writeln('Measure Temper-
                         ature =',
        Ttrue : 3, 'deg C');
        delay(200);
        end;
end.
```

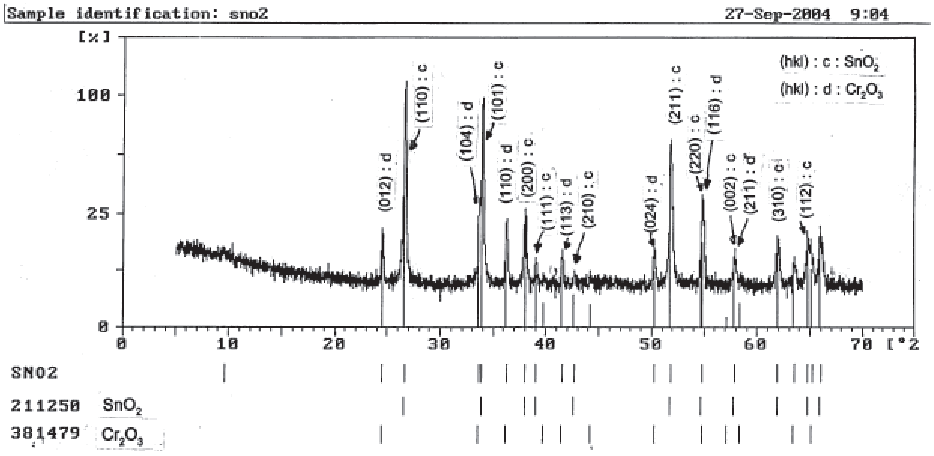
3) To do the instrument calibration, the electric current was supplied from a d.c. 5 V power supply through the sample and resistance and then the sample was voltage dropped. This voltage (V) was supplied to ADC 0809 for conversion from analog voltage (AV) to digital voltage (DV). 74LS244 was used as a buffer. The voltage from this buffer was sent through port A of ET-PC8255 card, slot and then to RAM. The voltage (DV) was read and displayed on the screen. The DV was converted to AV. The sample temperature was increased with the electric furnace. To do the calibration, the true temperature (Ttrue) was read with commercial temperature apparatus (Union 305) with type K thermocouple as a temperature sensor and the voltage drop on the resistor (AV) which was related to the sample was read from the value on the screen from 25 to 65ºC for the sample 1 and 24 to 120ºC for the sample 2. These data (Ttrue, AV) were recorded into a table and plotted with EXCEL. The Ttrue versus AV was obtained and then was input into the written program. After RUN, the computer read the temperature (Tmeasure). For the final calibration step, the Ttrue and Tmeasure were read, recorded and plotted as a bar graph for comparison. Finally, we obtained the temperature apparatus with computer display and the prepared sample as a temperature sensor.

Table 1. Sample dimensions, composition and phase for the sample 1 and sample 2.

Sample No.	Diameter (mm)	Thickness (mm)	Composition	Sample phases from XRD
1	12.97	3.06	SnO_2+2CoO	$SnCo_2O_4$ and SnO_2
2	13.02	3.31	SnO_2+Cr_2O_3	SnO_2 and Cr_2O_3



a) SnO_2+2CoO



b) SnO_2+Cr_2O_3

Figure 4. X-ray diffraction patterns of the SnO_2, Cr_2O_3 and CoO.

Results

1. Sample phase

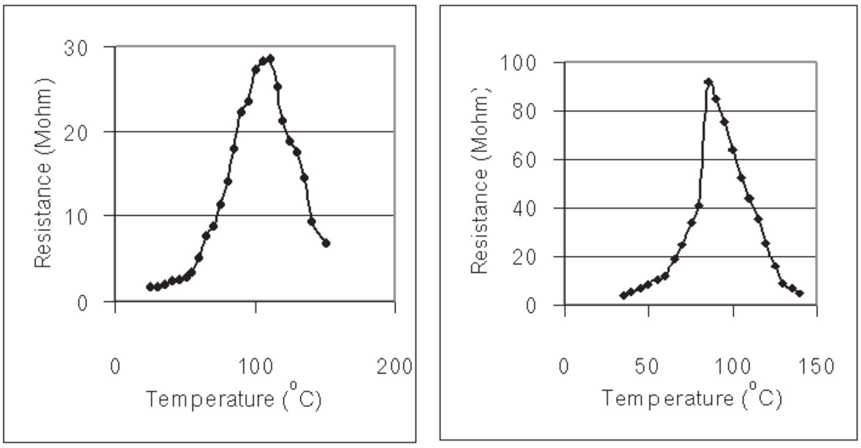
The x-ray diffraction patterns of the samples after firing are shown in Figure 4. Composition and sample phase from XRD patterns are shown in Table 1.

2. The resistance versus temperature characteristics of the samples

The resistance versus temperature relation of the samples were shown in Figure 5. The resistance of the sample 1 increased as the temperature increased or showed the PTC effect from 25 to 110°C and the resistance decreased as the temperature increased or showed NTC effect from 110 to 150°C. But, the sample 2 showed PTC effect from 35 to 85°C and NTC effect from 85 to 140°C.

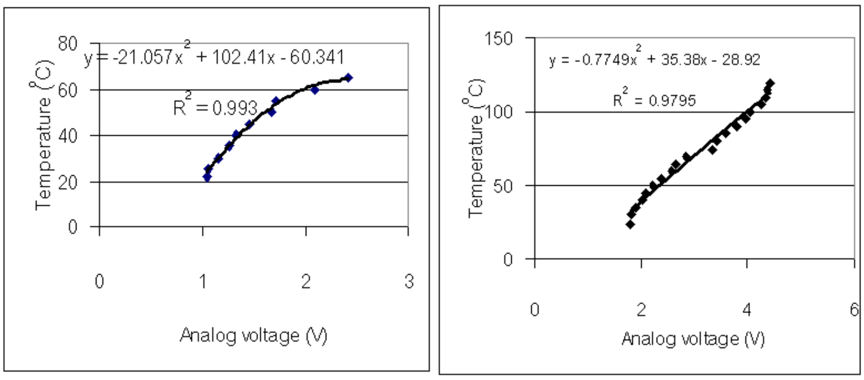
3. The constructed temperature apparatus with computer display and the prepared sample as a temperature sensor

The relationships of true temperature (Ttrue) and the voltage (V) is shown in Figure 6 and



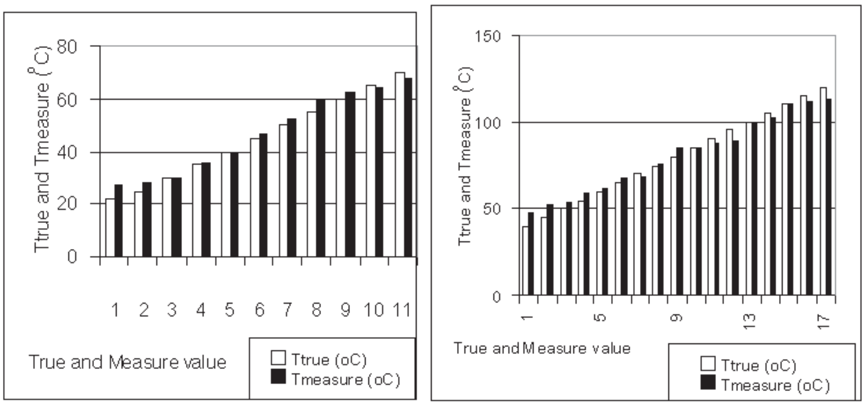
a) Sample 1 b) Sample 2

Figure 5. The resistance versus temperature of the sample 1 and sample 2.



a) Sample 1 b) Sample 2

Figure 6. Temperature vs analog voltage of the sample 1 and sample 2.



a) Sample 1 b) Sample 2

Figure 7. Comparison between true temperature (Ttrue) and measured temperature (Tmeasure) of the sample 1 and sample 2.

correspond to the equation:

Sample 1: Ttrue = -21.057(V)2+102.41(V) -60.341
(R^2=0.9930) (22-65ºC)

Sample 2: Ttrue = -0.7749(V)2+35.38(V) -28.92
(R^2=0.9795) (24-120ºC)

This equation was used for calibration to use the prepared sample as a temperature sensor. Figure 7 shows the comparison between True temperature (Ttrue) and measure temperature (Tmeasure). From the picture,the sample 1 and 2 showed the physical properties of PTC thermistor and can be used as temperature sensor from 22 to 70ºC and 40 to 120ºC, respectively.

Discussion and Conclusion

The samples were disc-shaped. The composition of the prepared sample were SnO_2+2CoO and $SnO_2+Cr_2O_3$. Both samples were two phase materials. The objectives of fabrication were to produce a material with specific properties and a body of a required shape and size. The material properties are basically controlled by the composition.

The resistance of the sample 1 increased with increasing temperature. The sample exhibited PTC effect in the range of 25 to 110ºC. The positive temperature coefficient of the resistance (α) was +18.2 %/ºC. The relation between the resistance (R) and the temperature (T) corresponds to the equation : $R=0.0043(T)^2-0.2124(T)+3.67567$ (R^2=0.979). However, the resistance of the sample decreased with increasing temperature from 110 to 200ºC. The sample exhibited NTC effect in the range of 110-150ºC. The negative temperature coefficient of the resistance (α) was -1.9 %/ºC. The relation between the resistance (R) and the temperature (T) corresponds to the equation : $R= 1619.6e^{-0.036T}$ (R^2=0.9573). The maximum resistance was 28.5 MΩ at 110ºC. The maximum/minimum resistance ratio was 16.5.

The resistance of the sample 2 increased with increasing temperature. The sample exhibited PTC effect from 35 to 85ºC. The positive temperature coefficient of the resistance (α) was +28.6 %/ºC. The relation between the resistance (R) and the temperature (T) corresponds to the equation : $R=0.0509(T)^2-4.8295(T)+117.47$ (R^2=0.8932). However, the resistance of the sample decreased with increasing temperature from 85 to 140ºC. The sample exhibited NTC effect. The negative temperature coefficient of the resistance (α) was -1.9 %/ºC. The relation between the resistance (R) and the temperature (T) corresponds to the equation : $R=13602e^{-0.0545T}$ (R^2=0.9471). The maximum resistance was 91.8 MΩ at 85ºC. The maximum/minimum resistance ratio was 20.5.

The positive temperature coefficient of the resistance (α) of PTC material made from $BaTiO_3$ was the range from +10 to +100 %/ºC (25-100ºC) and the negative temperature coefficient of the resistance (α) of the NTC material was in the range from α = -6.0 to -1.0 %/ºC (25-300ºC) (Buchanan, 1991). Comparing compare these α values with the results of both prepared sample, they showed similar properties.

The SnO_2, CoO and Cr_2O_3 exhibit only NTC effect in the entire temperature range. But, $SnCo_2O_4$ +SnO_2 and $SnO_2+Cr_2O_3$ samples that were two phase materials exhibited both PTC and NTC effect. The both prepared samples showed PTC effect in a certain temperature range. The PTC effect is seen to have its origins in the resistance of the grain boundary region which increases with temperature above the ferroelectric-paraelectric transition temperature. The grain boundaries capture the flowing electron, the electric current decreases and the resistance will increase in the same way as the PTC effect in $BaTiO_3$ (Moulson, 1990). NTC effect involves band structure with electrons promoted from the valence to the conduction band as temperature increases. The samples can conduct and then the sample resistance decreases (Moulson, 1990).

The PTC effect in the SnO_2+2CoO and $SnO_2+Cr_2O_3$ samples were discovered for the first time at the Material Physics Laboratory, Department of Physics, Faculty of Science, Prince of Songkla University, Thailand. The samples were a very sensitive to temperature in the PTC region.

Thus, the samples can be used as temperature sensors which are suitable for learning and teaching work. The prepared samples and the temperature monitoring with a computer system can measure the temperature in the range 22ºC to 70ºC (sample 1) and 40ºC to 120ºC (sample 2). The working temperature of these sensors are at the PTC region, and they are very sensitive to heat.

The advantages and characteristics of the PTC thermistors made from this two materials are as follows: The firing temperature is not high which needs only a low temperature furnace. The samples have good electrical stability ($\Delta R/\Delta t$). The samples are not responsing to light. The samples are a very sensitive to heat. The shapes of the resistance versus temperature curves are smooth. The samples are PTC thermistors and can be used as temperature sensors and displayed with the computer. The samples are semiconducting ceramics because they exhibit thermal response. Thus, these PTC materials are important for electronic industrial application and further research.

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