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Infrared sensing properties of positive temperature coefficient thermistors with large temperature coefficients of resistivity

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Infrared (IR) detecting elements were prepared using positive temperature coefficient (PTC) thermistors with large temperature coefficients of resistivity (α). Their compositions were denoted as $Ba_{1-x}Sr_xNb_{0.003}Ti_{0.997}O_3$ + 1 mol%TiO_2 + 0.07 mol% MnO ($x = 0$, 0.2), and their temperature coefficients of resistivity were 78 and 50% K^{-1}, respectively. Their IR sensing properties were measured under the self-regulating heating conditions, and were compared with those of a detector with small α (18% K^{-1}). It was shown that large α was effective for controlling the element temperature by self-regulating heating and for improving sensitivity. The responsivity, R_v, of the element with $x = 0.2$ was 980 V W^{-1}, and was as large as those of pyroelectric detectors. Expressions which normalize the sensitivity and the thermal time constant were derived. From these expressions, criteria for improving some IR sensing properties were obtained.

1. Introduction

Thermal type infrared (IR) detectors have slower response rates and smaller sensitivities than photon type detectors. Nonetheless, they are of practical value because they can be operated under uncooled conditions and have sensitivities independent on wavelength [1].

Thermistor bolometers are one category of the thermal detectors. Negative temperature coefficient (NTC) thermistors have been used for many years in this category. Their sensitivities, however, are not so large, normally because of their low temperature coefficients of resistivity, about $-4\%\ K^{-1}$ [2].

Semiconducting $BaTiO_3$ ceramics are well known for their large positive temperature coefficients of resistivity (PTC). The resistance increases by several orders of magnitude in the vicinity of the Curie point (T_c), and the temperature coefficient of resistivity reaches 15–100% K^{-1} [3]. Infrared detectors made of PTC thermistors are expected to have higher sensitivities than those made of NTC thermistors. However, the operating temperature of the detector must be controlled carefully because the large temperature coefficient is brought about only in a narrow temperature range near the Curie point.

One promising method for controlling the element temperature near the Curie point is to use the self-regulating heating of PTC thermistors [4]. When sufficiently high voltage is applied to the PTC thermistor, its temperature is kept constant in the vicinity of the Curie point. We reported IR sensing properties of an IR detector made of a PTC thermistor, the Curie point of which was 122 °C, under the self-regulating heating conditions [5]. We also discussed theoretical expressions for some IR sensing properties under the self-regulating heating conditions. As for the sensitivity (the ratio of the change in resistance to the resistance before irradiation $\Delta R/R$) and the thermal time constant (τ'), the following expressions were obtained:

$$\Delta R/R = \alpha\eta WA/(G + VI\alpha) = \alpha\eta WA/G\{1 + (T - T_a)\alpha\} \quad (1)$$

$$\tau' = H/G' = G\tau/G' = G\tau/(G + VI\alpha) \quad (2)$$

where α is the temperature coefficient of resistance (/K), η is the fraction of incident energy absorbed (the absorption efficiency), W is the incident IR energy (W cm^{-2}), A is the receiving area of the detector (cm^2), G is the thermal conductance to the surroundings (W K^{-1}), V is the applied voltage (V), I is the current before irradiation (A), T is the temperature of the detector element (K), T_a is the ambient temperature (K), H is the heat capacity, and τ is the thermal time constant when the joule heating is negligible. From Equation 1, it was considered that the following factors may improve the sensitivity:

1. A small $VI\alpha$ (a low Curie point).
2. A large temperature coefficient of resistivity.
3. A low thermal conductance.
4. An absorption coefficient close to unity.

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Our previous report [6], which was concerned with IR sensing properties of a low Curie point PTC thermistor with a Curie point of 25 °C, confirmed the effect of the reduction in $VI\alpha$ on the sensitivity.

In the present study, we prepared IR detectors made of PTC thermistors with large α, the Curie points of which were 125 and 60 °C, and investigated their IR sensing properties under the self-regulating heating conditions. Expressions which normalize the sensitivity and the thermal time constant were derived, and the calculated results were compared with the experimental ones.

2. Experimental procedure

2.1. Preparation of the detector elements

The sintered bodies of PTC thermistors were prepared by the usual ceramic processing technique. The compositions were denoted as $Ba_{1-x}Sr_xNb_{0.003}Ti_{0.997}O_3$ + 1 mol %TiO_2 + 0.07 mol %MnO (x = 0–0.3). $BaCO_3$, $SrCO_3$, Nb_2O_5 (Rare Metallic Co. Ltd, 99.99 %), TiO_2 (Fuji Titanium Co. Ltd, rutile, 99.97 %), and $Mn(NO_3)_3 \cdot 6H_2O$ (Wako Pure Chemical Industry Co. Ltd) were used as starting materials. The mixture of the powders was wet-milled with ethanol, calcined at 1100 °C for 2 h, and then 0.07 mol % $Mn(NO_3)_3$ was added in order to improve the PTC effect. The powder obtained was pressed into pellets of 2.5 mm thickness and 10 mm diameter at a pressure of 700 kg cm^{-2}. The pellets were sintered in air at 1350 °C for 2 h. The cooling rate was controlled at 100 °C h^{-1} to 800 °C.

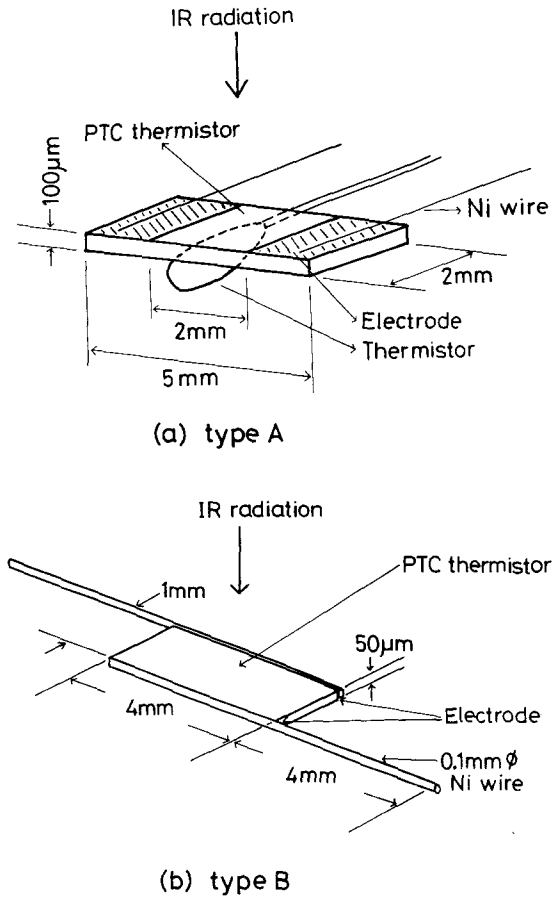

Figure 1 PTC thermistor detectors.

The pellet was cut into detector elements as illustrated in Fig. 1. Two types of the element were prepared in this study. One (type-A) had the size of 2 mm × 5 mm × 100 μm and another (type-B) had the size of 1 mm × 4 mm × 50 μm. Ohmic silver paste (Dometoron Co., 61900781/347) as electrodes was fired with nickel wires (0.1 mm diameter) as leads. For the type-A element, a small thermistor (Shibaura Electronics Co. Ltd, PT5-25E5) was attached on the element to measure the temperature of the element. For type-B element, the element temperature was not measured directly, but was calculated from the element resistance using the resistance–temperature characteristic of the element.

2.2. Measurement of IR sensing properties

A blackbody furnace (Chino Co. Ltd, IR-R24) was used as an IR source. The detectors were placed 15 cm away from the aperture of the blackbody furnace. The type-A element was placed in an electrical furnace (Gold furnace, Transtemp Co.) with a polyethylene IR transmitting window (15 μm thickness), and the ambient temperature was controlled in the furnace. The type-B element was mounted in a holder made of polyvinyl chloride with the IR transmitting window. The ambient temperature was controlled with a thermostat (Lo Temp Incubator IL-60, Yamato Science Co. Ltd). Incident IR energy upon the detector was measured with a thermopile IR detector (Mitsubishi Yuka Co. Ltd, MIR-100S), and was 1.51×10^{-2} W cm^{-2} from a 600 K blackbody furnace.

Constant voltages were applied to the detectors, and the currents passed through them were measured, using a power supplier (HIOKI Co. Ltd, Model 7005) and a digital multimeter (ADVANTEST Co. Ltd, TR-6878). The current change by IR radiation (20 s) was measured when the steady state was attained. The sensitivity S_n was expressed using the following expression:

$$S_n = (\Delta R/R)(G/WA) \quad (3)$$

which is the normalized ratio of the resistance change to the resistance before irradiation. The factor G/WA normalizes the configuration of the element and the incident IR energy.

3. Results

3.1. IR sensing properties of a large α element

A type-A element was prepared from a PTC thermistor with a composition of $BaNb_{0.003}Ti_{0.997}O_3$ + 1 mol %TiO_2 + 0.07 mol % MnO. The resistance–temperature characteristic of the element is shown in Fig. 2. The temperature coefficient of resistance was 78 % K^{-1} at 125 °C (B = − 121000 K). The Curie point was determined from the temperature at which the element showed the maximum capacitance, and was 125 °C. The resistance–temperature characteristic of the element whose α was 18 % K^{-1} in the previous study [5] is also shown in Fig. 2. Fig. 3 shows the temperature of the element as a function of applied

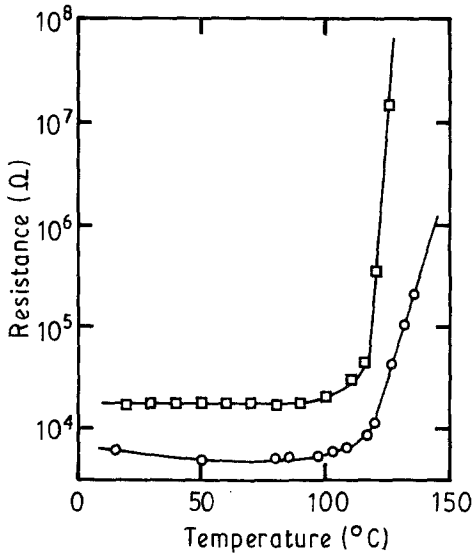

Figure 2 Resistance–temperature characteristics of the elements: (□) $BaNb_{0.003}Ti_{0.997}O_3$ + 1 mol % TiO_2 + 0.07 mol % MnO, α = 78 % K^{-1}; (○) $Ba_{0.997}La_{0.003}TiO_3$ + 2 mol % SiO_2 + 0.07 mol % MnO, α = 18 % K^{-1}.

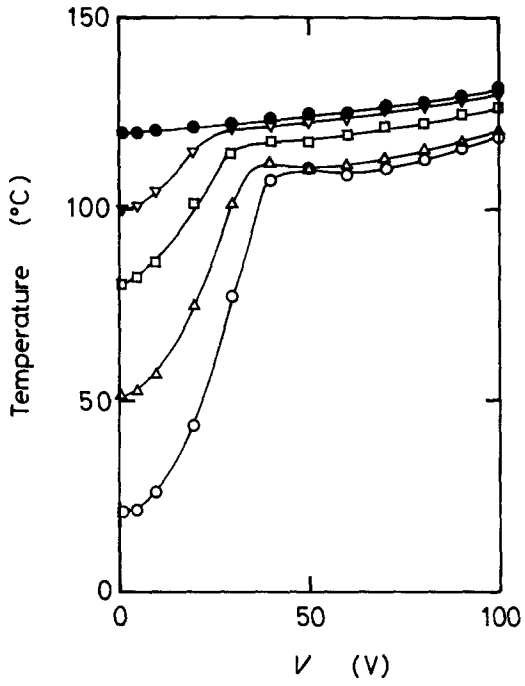

Figure 3 Surface temperature of the detector element as a function of applied voltage measured at (○) 20, (△) 50, (□) 80, (▽) 100, and (●) 120 °C.

voltage at various ambient temperatures. At sufficiently high voltage, the element temperature reached the self-regulating region (the PTC region). When the ambient temperature was changed in the range from 20–100 °C, the temperature change of the element was suppressed within 20 °C in this region. The increase in the element temperature at high voltages was also suppressed, compared with the element with α = 18 % K^{-1} in the previous study [5]. The thermal conductance, G, estimated from the relation between the element temperature and the power consumption was 1.02×10^{-3} W K^{-1}.

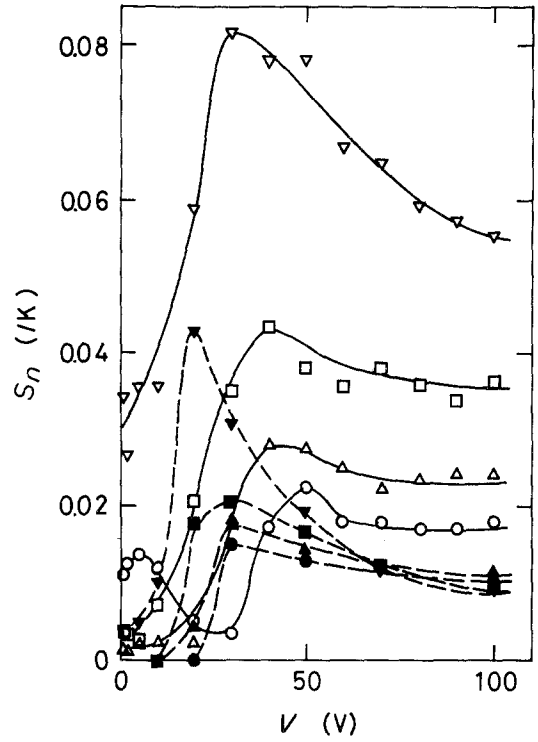

Figure 4 Sensitivity, S_n, of $BaNb_{0.003}Ti_{0.997}O_3$ + 1 mol % TiO_2 + 0.07 mol % MnO element to 600 K blackbody radiation measured at (○) 20, (△) 50, (□) 80, and (▽) 100 °C, and S_n of $Ba_{0.997}La_{0.003}TiO_3$ + 2 mol % SiO_2 + 0.07 mol % MnO element (α = 18 % K^{-1}, T_c = 122 °C) measured at (●) 15, (▲) 45, (■) 67 and (▼) 95 °C in the previous study [5].

Fig. 4 shows the sensitivities of the element to 600 K blackbody radiation measured at various ambient temperatures. The sensitivities in the previous study [5] are also shown in Fig. 4. The sensitivity of the element with α = 78 % K^{-1} in the PTC region measured at each ambient temperature was several times larger than that of the element with α = 18 % K^{-1} at the comparable ambient temperature. It was therefore shown that large α is effective for improving the sensitivity.

The sensitivity decreased as higher voltages were applied in the PTC region, but the decrease was also suppressed in the element with α = 78 % K^{-1}, compared with that of the element with α = 18 % K^{-1}. This is because the rise in the temperature of the element with α = 78 % K^{-1} at higher voltages was suppressed as shown in Fig. 3, i.e., the increase in $VI\alpha$ in Equation 1 was smaller than that of the element with α = 18 % K^{-1}. Fig. 5 shows the thermal time constant τ' measured at 20 °C as a function of applied voltage. The thermal time constant decreased suddenly when the element temperature went into the PTC region as shown in the previous study [5].

3.2. IR sensing properties of a large α, low T_c element

It is effective for improving the sensitivity to use the detectors with low Curie points as well as with large α. Sr^{2+}-substitution for a part of Ba^{2+} is known to lower the Curie point of barium titanate [7]. PTC thermistors having various Curie points were prepared by

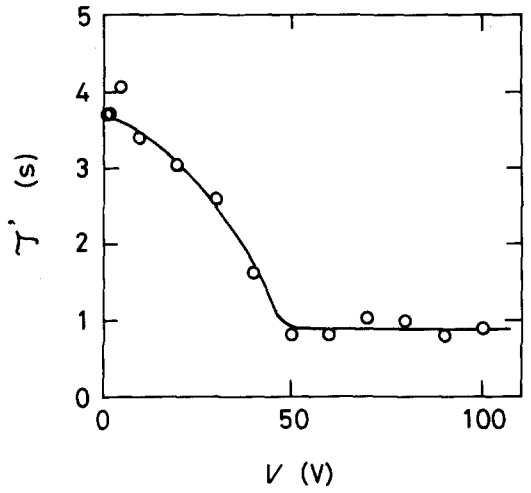

Figure 5 Thermal time constant measured at 20 °C.

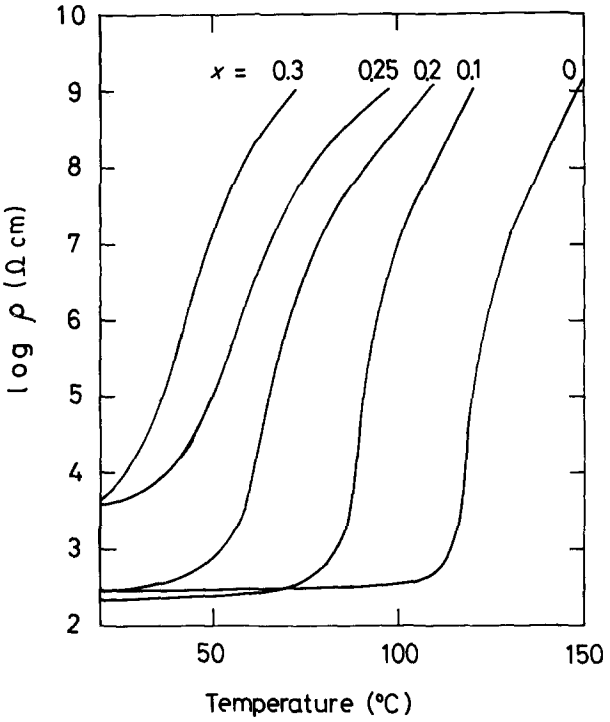

Figure 6 Resistivity–temperature characteristic of $Ba_{1-x}Sr_x Nb_{0.003}Ti_{0.997}O_3$ + 1 mol %TiO_2 + 0.07 mol % MnO.

Sr^{2+}-substitution. The resistivity–temperature characteristics of the Sr^{2+}-substituted PTC thermistors are shown in Fig. 6. The temperature coefficients of resistivity and the resistivities at room temperature ρ_{25} are summarized in Table 1. The temperature coefficient α decreased as the Curie point was shifted to a lower temperature by the substitution of Sr^{2+} ions. On the other hand, ρ_{25} increased simultaneously, in particular, in $x > 0.2$. The decrease in α reduces the sensitivity and the controllability of the element temperature. The increase in the resistance needs a high voltage to control the element temperature in the vicinity of T_c. Taking these factors into account, the detector with $x = 0.2$ was favourable for IR detectors.

A type-B element was prepared from the Sr^{2+}-substituted PTC thermistor with $x = 0.2$. The Curie point was 60 °C. The temperature coefficient of resistance was 50 % K^{-1}, which was slightly smaller than that of the original sintered body (58 % K^{-1}). The thermal conductance was 9.60×10^{-4} W K^{-1}. Fig. 7 shows the sensitivity and the thermal time constant as a function of applied voltage measured at 20 °C. The sensitivity in the PTC region was larger than that measured at the same ambient temperature (20 °C) in Fig. 4 in the previous section. The responsivity, R_v, which means the output signal per received IR energy and is widely used for IR detectors, was calculated using the following expression [8]:

$$R_v = (V/2WA)(\Delta R/R) \quad (4)$$

R_v was 980 V W^{-1} at an applied voltage of 40 V, and was as large as that of the pyroelectric detectors [9].

The response rate ($\tau' = 300$ ms) was a few times faster than that of the type-A element, which was ascribed to its small heat capacity.

TABLE I Effect of Sr^{2+}-substitution on α and ρ_{25}.

x	α (% K^{-1})	ρ_{25} (Ω cm)
0	97	270
0.1	79	210
0.2	58	110
0.25	29	3400
0.3	36	3500

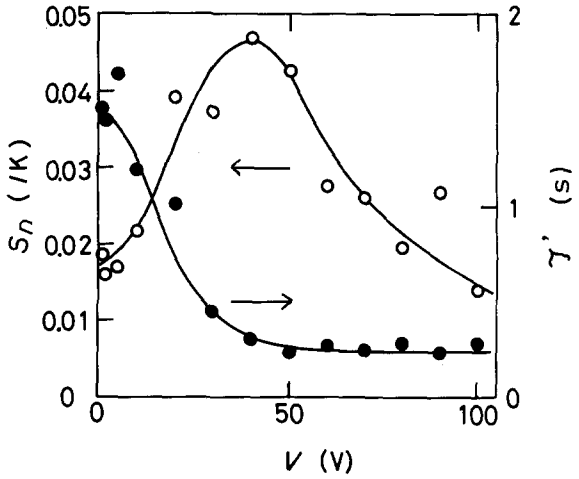

Figure 7 Sensitivity and thermal time constant of the detector with a composition of $Ba_{0.8}Sr_{0.2}Nb_{0.003}Ti_{0.997}O_3$ + 1 mol %TiO_2 + 0.07 mol %MnO measured at 20 °C.

4. Discussion

The sensitivity S_n in this study is derived from Equation 1 as

$$S_n = (\Delta R/R)(G/WA) = \alpha\eta/\{1 + (T - T_a)\alpha\} \quad (5)$$

Since T is kept near T_c by self-regulating heating, Equation 5 can be approximated to

$$S_n = \alpha/\{1 + (T_c - T_a)\alpha\} \quad (6)$$

where η is assumed to be unity. It is shown that S_n is

dependent on only α and T_c of the element, that is, the inherent constant in the material. The sensitivity, S_n, can therefore be used as the figure of merit for PTC type detectors, like the pyroelectric figure of merit F_v for pyroelectric detectors [10].

The sensitivity, S_n, measured for elements having different α and T_c at various T_a are shown in Fig. 8 as a function of $T - T_a$. Calculated S_n for α = 10, 20, 40 and 80 % K^{-1} are also shown in Fig. 8, where η is assumed to be unity. The calculated results are in good agreement with the experimental ones. The deviations between them are ascribed to the obscurity in the estimated values of the thermal conductance and the element temperature in calculating S_n. Elements with large α have high sensitivities as shown in this study. The temperature difference $T - T_a$ affects S_n significantly. When $T - T_a > 50$ °C, S_n hardly depends on α or $T - T_a$. However, S_n increases abruptly when $T - T_a$ becomes smaller. It is therefore confirmed that small $T - T_a$, i.e., using a PTC thermistor with a low Curie point or operating at high T_a is favourable for improving the sensitivity. On the other hand, for suppressing the dependence of the sensitivity on T_a, large $T - T_a$, i.e., using a PTC thermistor with a high Curie point is effective.

The thermal time constant is an important factor for IR detectors as well as the sensitivity. The normalized thermal time constant τ_n is derived from Equation 2 as

$$\tau_n = \tau'/\tau = \eta/\{1 + (T - T_a)\alpha\} \quad (7)$$

In the same way as Equation 6, Equation 7 can be approximated to

$$\tau_n = 1/\{1 + (T_c - T_a)\alpha\} \quad (8)$$

It is shown that the τ_n is also dependent on only α and T_c of the element. Fig. 9 shows τ_n as a function of $T - T_a$. The experimental values are also shown in Fig. 9. The experimental values are slightly larger than the calculated ones, but both tendencies are consistent with each other. Large α and $T - T_a$ are effective for fast response.

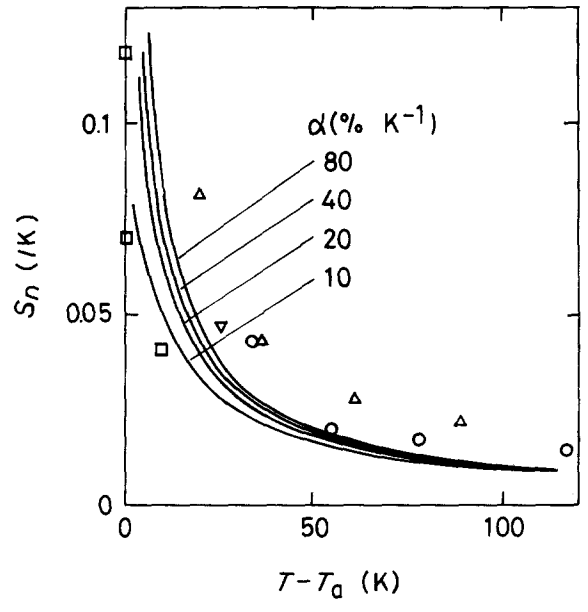

Figure 8 Sensitivity, S_n as a function of $T - T_a$: (○) α = 18 % K^{-1}, T_c = 122 °C; (□) α = 13 % K^{-1}, T_c = 25 °C in the previous studies [5, 6]. (△) α = 78 % K^{-1}, T_c = 125 °C; (▽) α = 50 % K^{-1}, T_c = 60 °C in this study. (——) calculated curves for α = 10, 20, 40, and 80 % K^{-1}.

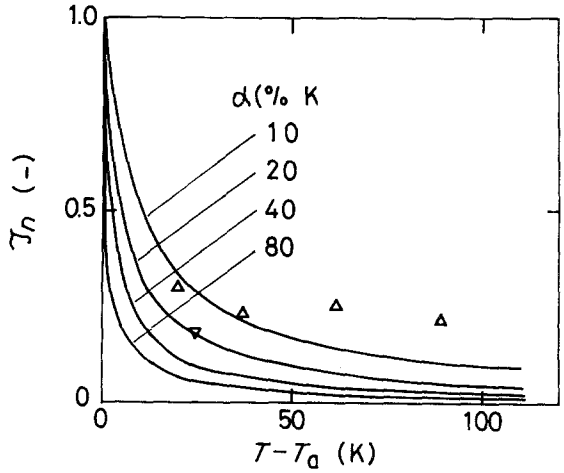

Figure 9 Thermal time constant, τ_n, as a function of $T - T_a$: (△) α = 78 % K^{-1}, T_c = 125 °C; (▽) α = 50 % K^{-1}, T_c = 60 °C in this study. (——) calculated curves for α = 10, 20, 40, and 80 % K^{-1}.

TABLE II Criteria for designing PTC thermistors as IR detectors

Parameter	Large α	Low Curie point
Sensitivity	Increase	Increase
Dependence of sensitivity on T_a	Increase	Increase
Thermal time constant	Decrease	Increase

As mentioned above, criteria for improving some IR sensing properties were derived from Equations 5 and 7, and are summarized in Table 2. The characteristics required for IR detectors depend on the conditions where they are operated. Equations 5 and 7 can therefore be used for designing PTC thermistors as IR detectors.

5. Conclusions

(1) Infrared detectors were prepared from PTC thermistors with large temperature coefficients of resistivity (α), whose compositions were $Ba_{1-x}Sr_xNb_{0.003}Ti_{0.997}O_3$ + 1 mol % TiO_2 + 0.07 mol % MnO (x = 0, 0.2) and αs were 78 and 50 % K^{-1}, respectively. Their IR sensing properties were measured under the self-regulating heating conditions, and were compared with those of an element with small α (18 % K^{-1}). It was shown that large α was favourable for controlling the temperature of the element and for improving the sensitivity. The responsivity, R_v, of the element with x = 0.2 was 980 V W^{-1}, and was as large as those of pyroelectric detectors.

(2) Normalized expressions for sensitivity, S_n, and thermal time constant, τ_n, were derived. They were not dependent on the configuration of the element and the incident IR energy, but dependent only on the temperature coefficient of resistivity and the Curie point of the element. These normalized expressions can be used for designing PTC thermistors as IR detectors.

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