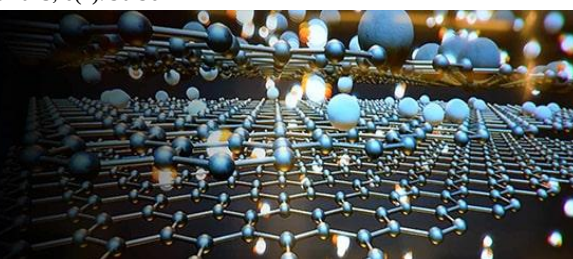


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Effect of Mn Addition at Low Temperature Sintering of BaTiO₃ PTCR ceramics

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Abstract

The main problem in preparing PTCR ceramics with multilayer structures is to reduce the sintering temperature of PTCR ceramics and, at the same time, to raise the PTC effect. We investigated the effect of BaO-B₂O₃-SiO₂-MnO₂ addition as a low temperature sintering additive on the electrical properties of PTCR ceramics prepared by solid state reaction method. To enhance the PTC effect in low temperature sintering, MnO₂ was added into the BaO-B₂O₃-SiO₂ sintering additive, the MnO₂ content varied from 0.02 mol% to 0.08 mol%. The PTCR ceramics adding sintering additives were sintered at temperature range of 970°C-1 250°C, the room-temperature resistance of PTCR ceramics had a minimum value at the sintering temperature of 1 050°C. According to the sintering temperature, the microstructures of PTCR ceramics were investigated using scanning electron microscopy. The PTCR ceramics with BaO-B₂O₃-SiO₂-MnO₂ sintering additive adding 0.06mol% MnO₂ at the sintering temperature of 1 050°C results in a relatively low room-temperature resistance and resistance jump of about 10⁴.

Keywords: BaTiO₃, BaO-B₂O₃-SiO₂-MnO₂ sintering additive, PTCR, Low temperature sintering

1. Introduction

It is well known that the resistance of n-doped BaTiO₃ semiconducting ceramics shows a considerably increase near the Curie temperature, T_c , which is called the positive temperature coefficient resistance (PTCR) effect. Currently, PTCR ceramics are widely applied in various fields and the need to improve their properties is increasing significantly. However, since the sintering temperature of BaTiO₃ ceramic materials is high above 1 300°C, it is rather difficult to fabricate PTCR ceramics with better performance, e.g. PTCR with multilayer structures.

Some authors have prepared PTCR chips with multilayer structures by varying sintering temperature, sintering soaking time, heating rate and cooling method ^[1].

The multilayer PTCR chips with average grain size of 1-2μm were prepared at 400°C/h heating rate, 1 260°C-1 280°C sintering temperature, soaking time 0.5 h, and 300°C/h cooling rate in reducing atmosphere, and then oxidized at 850°C for 1 h.

The room temperature resistivity of the fabricated multilayer PTCR chips is less than 100Ωcm and the resistance jump is more than 10⁴.

Most of the efforts have been undertaken to decrease the sintering temperature of BaTiO₃ ceramic materials.

B. Suherman *et al* reported the results of the synthesis of BaTiO₃ ceramics at low sintering temperatures of 700°C and 800°C using the co-precipitation technique ^[2].

The crystal size and tetragonality of BaTiO₃ ceramic have larger values at 800°C than at 700°C.

Matjaz Valant reported that an addition of 0.4 wt% Li₂O to (Ba_{0.6}Sr_{0.4}) TiO₃ powder was able to reduce the sintering temperature to ≤ 900°C and produce ceramics with a relative density of 97% ^[3].

Ying Luo studied the effect of Ba₂LaBiO₆ addition on the electrical properties of PTCR ceramics ^[4]. In the addition of Ba₂LaBiO₆, La³⁺ substituted for Ba ions in the lattices and Bi⁵⁺ substituted for Ti ions. As the amount of Ba₂LaBiO₆ increases, the room temperature resistance exhibited a U-shaped shape. A maximum of $\rho_{\max}/\rho_{\min}$ ratio was obtained at the sintering temperature equal to 1 270°C at a given content of Ba₂LaBiO₆. Also, the addition of BaBiO₃ significantly affected the grain size and the room temperature resistivity of samples

[5]. A maximum of $\rho_{\max}/\rho_{\min}$ ratio was obtained at the sintering temperature equal to 1 290 °C at a given content of BaBiO₃. P. Bomlai *et al.* analyzed the effect of TiO₂ and SiO₂ on the electrical properties of PTCR ceramics [6, 7]. A combined additive consisting of 3 mol% SiO₂ and 1 mol% TiO₂ was effective in reducing the sintering temperatures of Sb-doped BST ceramics, the SiO₂+TiO₂ additive enhanced the PTCR effect, and the room temperature resistivities were 14Ωcm. However, it was suggested that secondary phases in Sb-doped (Ba, Sr) TiO₃ ceramics containing 1 mol% excess TiO₂ and 3 mol% SiO₂ sintering additives were formed.

An effective way to reduce the sintering temperature of BaTiO₃ ceramics is to use sintering additives such as B₂O₃, BN, YB₆, etc [8-11].

At low temperature sintering using above sintering additives, it is emphasized that PTC effect is mostly due to B ions but not Mn ions.

Heywang reported that some 3d-transition elements, such as Mn, Fe and Cu, form Schottky barrier at grain boundary, which plays a very important role in determining the PTC effect [12, 13]. Low room-temperature resistance and a strong PTC effect are both critical parameters for PTCR ceramics application. In general, Mn is added to enhance the PTC effect at the grain boundaries of PTCR ceramics, and the role of Mn as acceptor has been reported widely in previous studies [14-17].

The Mn addition method introduced in most studies was added with the main raw materials according to the mixing conditions, and the sintering temperature was above 1 300°C. The diffusion of Mn into the grain boundaries in PTCR ceramics requires a high activation energy. From here, when the PTCR ceramics adding Mn sintered at low temperature than 1 200°C, that do not have a significant effect on the PTCR behavior, even exhibits an insulating property [18].

The aim of the work is to prepare PTCR ceramics which

have low room- temperature resistance and high resistance jump ($R_{\max}/R_{\min}$) at low sintering temperature. To reduce the room-temperature resistance of the PTCR ceramics sintered at low temperature, SiO₂ was added into the BaO-B₂O₃ sintering additive. In addition, MnO₂ was added into the BaO-B₂O₃-SiO₂ sintering additive to enhance the PTC effect. We analyzed the effect of sintering additives on the electrical properties of PTCR ceramics through experimental procedures.

2. Experimental

2.1 Preparation of Y-BaTiO₃ ceramic materials

The PTCR ceramics were prepared according to the formula of (Ba_{0.75}, Sr_{0.25}) Ti_{1.02}O₃ + 0.6 mol% Y₂O₃. The starting materials are analytical grade BaCO₃, TiO₂, SrCO₃ and Y₂O₃. These materials were weighted by the above formula and mixed in appropriate amounts of distilled water with zirconia grinding media by ball milling for 6 h, then dried and the mixed powders were pre-sintered at 1 150 °C for 2h in an alumina crucible.

2.2 Preparation of BaO-B₂O₃-SiO₂-MnO₂ sintering additive

BaO-B₂O₃-SiO₂-MnO₂ sintering additive was prepared by analytical grade BaCO₃, H₃BO₃, SiO₂ and MnO₂ as raw materials. Here, the ratio of B₂O₃ and BaO (B/Ba) is 2. The composition of sintering additive were based on the following formula:

$$0.5 \text{ BaCO}_3 + \text{H}_3\text{BO}_3 + 2\text{mol\%SiO}_2 + x \text{ MnO}_2 \quad (1)$$

And the content of MnO₂ in BaO-B₂O₃-SiO₂-MnO₂ sintering additive was changed to 0.02 mol%, 0.04 mol%, 0.06mol% and 0.08 mol%. The sintering additives weighed by above formula were prepared by quenching after being synthesized at 1 100°C for 30 min in an electric furnace.

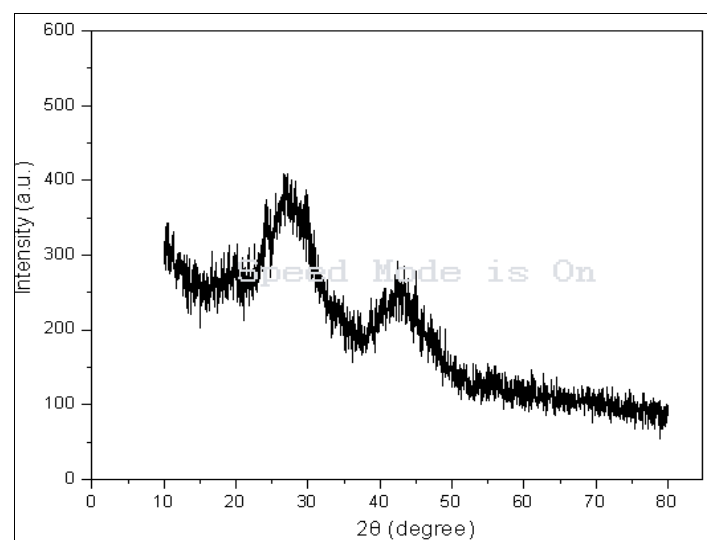


Fig 1: XRD analysis of synthesized BaO-B₂O₃-SiO₂-MnO₂ sintering additive

As can be seen in Fig. 1, two broad peaks are observed at $2\theta = 27^\circ$ and 43° , which shows the typical borate glass properties.

2.3 Processing

BaO-B₂O₃-SiO₂-MnO₂ sintering additives were added to the pre-sintered powder. The material compositions designed are shown in Table 1.

Table 1: The compositions of designed materials

Sample number	Composition
1	$(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1.02}\text{O}_3 + 0.006\text{Y}_2\text{O}_3 + (0.5\text{BaO} + \text{B}_2\text{O}_3)$
2	$(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1.02}\text{O}_3 + 0.006\text{Y}_2\text{O}_3 + (0.5\text{BaO} + \text{B}_2\text{O}_3 + 0.02\text{SiO}_2)$
3	$(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1.02}\text{O}_3 + 0.006\text{Y}_2\text{O}_3 + (0.5\text{BaO} + \text{B}_2\text{O}_3 + 0.0006\text{MnO}_2)$
4	$(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1.02}\text{O}_3 + 0.006\text{Y}_2\text{O}_3 + (0.5\text{BaO} + \text{B}_2\text{O}_3 + 0.02\text{SiO}_2 + 0.0002\text{MnO}_2)$
5	$(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1.02}\text{O}_3 + 0.006\text{Y}_2\text{O}_3 + (0.5\text{BaO} + \text{B}_2\text{O}_3 + 0.02\text{SiO}_2 + 0.0004\text{MnO}_2)$
6	$(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1.02}\text{O}_3 + 0.006\text{Y}_2\text{O}_3 + (0.5\text{BaO} + \text{B}_2\text{O}_3 + 0.02\text{SiO}_2 + 0.0006\text{MnO}_2)$
7	$(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1.02}\text{O}_3 + 0.006\text{Y}_2\text{O}_3 + (0.5\text{BaO} + \text{B}_2\text{O}_3 + 0.02\text{SiO}_2 + 0.0008\text{MnO}_2)$

For each component, the pre-sintered $(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1.02}\text{O}_3 + 0.006\text{Y}_2\text{O}_3$ powders and the sintering additive were mixed together by ball milling for 6 h. Here, the sintering additive content for each composition is 3 mol%.

The powders prepared above were mixed with a suitable amount of polyvinyl alcohol (8% PVA) and then pressed into disc-shaped pellets with 19 mm in diameter and 2.5 mm in thickness at a pressure of 100MPa. The samples were sintered at temperature ranging from 970°C to 1250°C for 3 h in air, then furnace-cooled.

To investigate the sintering behavior, scanning electron microscopy (SEM SX-40) was employed to observe the PTCR ceramics morphology and estimate the grain sizes. After both sides of the samples were painted with aluminium paste, the resistance change of the samples as a function of temperature were measured. The R-T characteristic curves are measured by the ZWX-B type PTCR R-T Automatic Test System

3. Results and discussion

The liquid phase sintering based on a capillary force between grains has faster bonding and densification as compared to solid-state sintering. Previous works reported that proper amount of the liquid phase addition promotes the grain growth during sintering, and facilitates uniform microstructures development^[7].

3.1 Influence of Si in sintering additive

Fig. 1 shows the resistance-temperature characteristics of the PTCR ceramics sintered at 1050°C temperature with $\text{BaO-B}_2\text{O}_3$ and $\text{BaO-B}_2\text{O}_3\text{-SiO}_2$ as the liquid phase sintering additives. Here, the content of $\text{BaO-B}_2\text{O}_3$ and $\text{BaO-B}_2\text{O}_3\text{-SiO}_2$ are 3 mol%, respectively. And the PTCR ceramics of sample 2 shown in Table 1 were used to evaluate the effect of SiO_2 at the low temperature sintering by $\text{BaO-B}_2\text{O}_3\text{-SiO}_2$ sintering additive, and the SiO_2 content are 2 mol%.

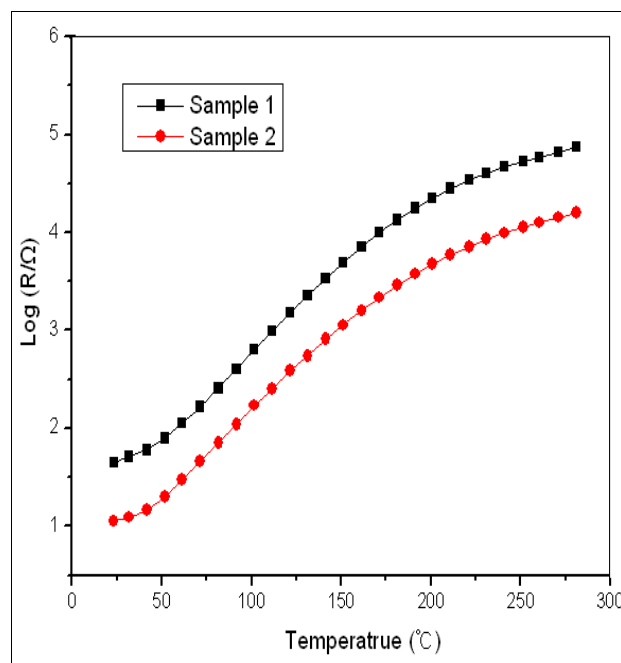


Fig 2: The resistance-temperature characteristics of PTCR ceramics (sample 1 and 2) sintered at 1050°C temperature with different sintering additives

As shown in the Fig. 2, $\text{BaO-B}_2\text{O}_3$ and $\text{BaO-B}_2\text{O}_3\text{-SiO}_2$ as liquid phase sintering additives significantly reduced the sintering temperature of the PTCR ceramics.

However, the electrical properties of the PTCR ceramics with the two sintering additives are different. At sintering temperature of 1050°C, the room-temperature resistance (R_{25}) of the PTCR ceramics with $\text{BaO-B}_2\text{O}_3$ is 42Ω and the resistance jump $\log(R_{\max}/R_{\min})$ is 3.5 while R_{25} of the PTCR ceramics with $\text{BaO-B}_2\text{O}_3\text{-SiO}_2$ sintering additive is 12.3Ω. It can be seen that the room-temperature resistance of PTCR ceramics with $\text{BaO-B}_2\text{O}_3\text{-SiO}_2$ sintering additive decreased

compared to that of PTCR ceramics with $\text{BaO-B}_2\text{O}_3$ without SiO_2 addition. This means that the addition of appropriate amount of SiO_2 can improve the purity of PTCR ceramics and provide favorable conditions for the uniform growth of the grains. However, the resistance jump ($R_{\max}/R_{\min}$) of PTCR ceramics with $\text{BaO-B}_2\text{O}_3\text{-SiO}_2$ sintering additive is near 3.

3.2 Influence of Mn in sintering additive

In the present work, we had added Mn as acceptor in $\text{BaO-B}_2\text{O}_3\text{-SiO}_2$ sintering additive in order to enhance the PTC

effect of Y-added BaTiO₃ ceramic materials at low temperature sintering.

Samples 4-7 designed in Table 1 were used to study the influence of Mn on the electrical properties of PTCR ceramics.

Fig. 3 shows the room-temperature resistance of the PTCR ceramics (samples 4-7) sintered at different temperature. It

can be seen that the room-temperature resistance of all PTCR ceramics in the considered Mn content range (0.02mol%-0.08mol%) reaches a minimum value at the sintering temperature of 1 050°C, and further increasing the sintering temperature results in an increase of room-temperature resistance.

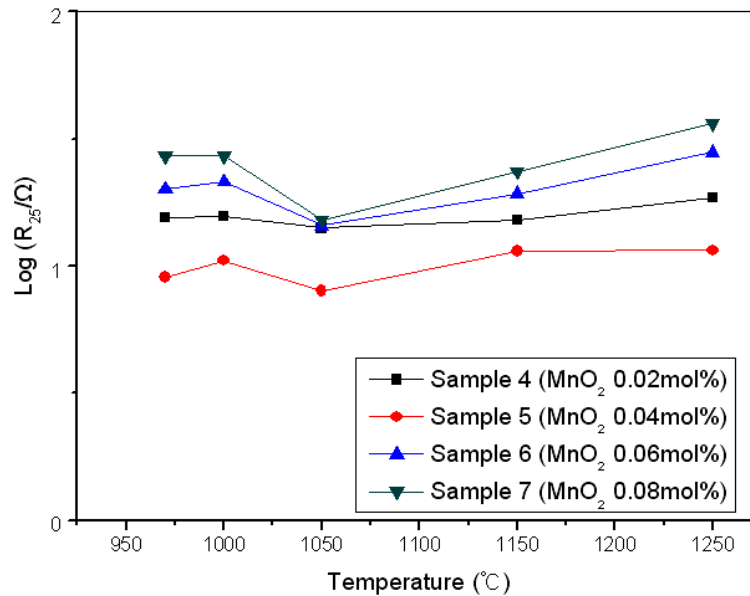


Fig 3: The room-temperature resistance of the samples (4-7) sintered at different temperature.

The relationship between the room-temperature resistance and sintering temperature observed above could also be seen from the microstructures of the PTCR ceramics. Fig. 4 shows the microstructures of PTCR ceramics sintered at different temperature. As can be seen in Fig. 4a, when the sintering temperature is 970 °C, the liquid phase distribution at the grain boundary is heterogeneous and sufficient growth of the grain is not achieved, thus increasing the room-

temperature resistance of the PTCR ceramics.

Also, when the sintering temperature is higher than 1 250°C (Fig. 4b), the grain boundary phase decrease, but the grain size distribution is heterogeneous and small grains exist between grains, reducing the mutual contact area of grains.

This results in a detrimental effect on the electrical performance of PTCR ceramics, thus increasing the room-temperature resistance.

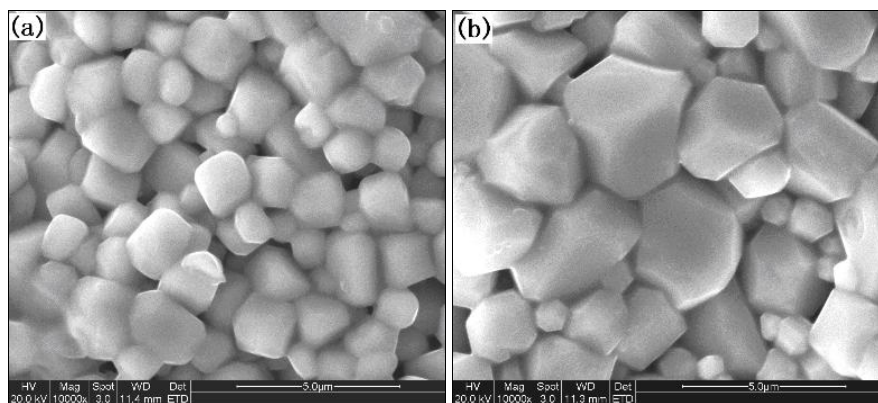


Fig 4: The microstructures of the PTCR ceramics sintered at different sintering temperature (a) 970°C, (b) 1250°C

Therefore, it can be seen that the optimum sintering temperature for low temperature sintering of PTCR ceramics is 1 050°C.

Fig. 5 shows the dependence of the room-temperature resistance and resistance jump of PTCR ceramics on the variation of Mn content in BaO-B₂O₃-SiO₂-MnO₂ sintering additive. As shown in the Fig, when the Mn content is 0.04 mol%, the room temperature resistance has a minimum

value of 11Ω, but the resistance jump also has a minimum value of 3.2. However, when the Mn content is 0.06 mol%, the room temperature resistance is 14.4Ω, and the resistance jump has a maximum value of 3.7.

With the increase of Mn content, the room-temperature resistance increases, and the resistance jump decreases. It can be seen that the optimum value of Mn content in the BaO-B₂O₃-SiO₂- MnO₂ sintering additive is 0.06 mol%.

All PTCR ceramics with BaO-B₂O₃-SiO₂-MnO₂ sintering additive show a dark- blue color and are semiconducting. This demonstrates that Mn in the BaO-B₂O₃-SiO₂-MnO₂ liquid phase sintering additive can reach the grain boundary very easily even at 1 050°C and form an acceptor state to capture electrons.

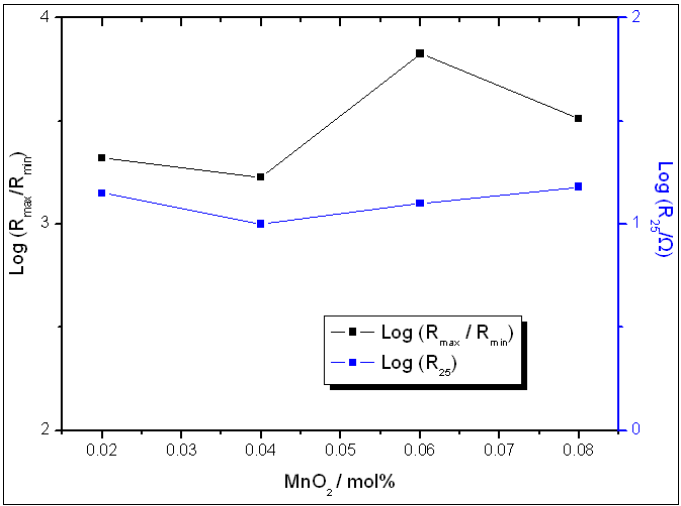


Fig 5: The room-temperature resistance and resistance jump of PTCR ceramics on the variation of Mn content

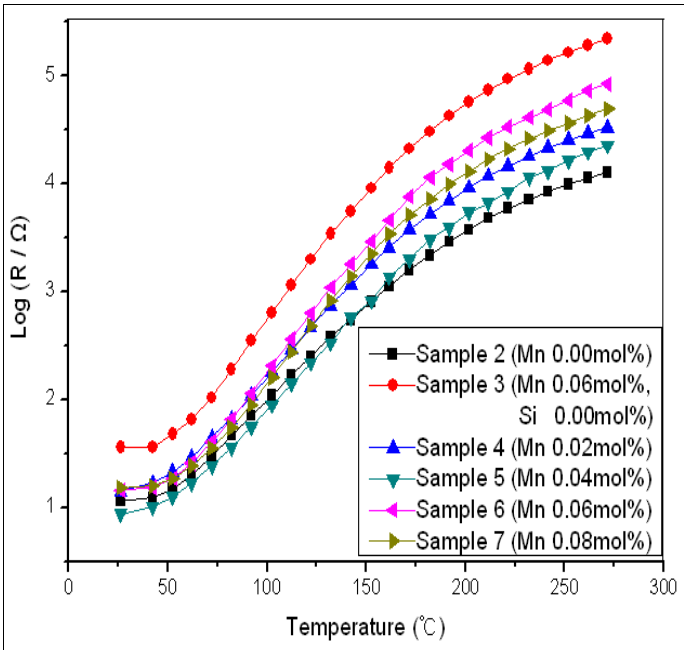


Fig 6: Resistance-temperature characteristics of the samples sintered at 1 050°C

Fig. 6 shows the resistance-temperature characteristics of the PTCR ceramics sintered at 1 050°C for 3 h. The room-temperature resistance of PTCR ceramics (sample 4-7) with BaO-B₂O₃-SiO₂-MnO₂ in Table 1 is almost identical to that of the PTCR ceramics (sample 2) with BaO-B₂O₃-SiO₂ without Mn addition, but the room-temperature resistance of the PTCR ceramics with BaO-B₂O₃-MnO₂ without Si the PTCR ceramics with BaO-B₂O₃-MnO₂ without Si is larger than that of PTCR ceramics with other sintering additives. The detailed results of R₂₅ and R_{max} /R_{min} of PTCR ceramics with sintering additives are listed in Table 2.

Table 2: R₂₅ and R_{max} /R_{min} of PTCR ceramics with sintering additive

Parameters	BaO-B ₂ O ₃	BaO-B ₂ O ₃ -SiO ₂	BaO-B ₂ O ₃ -MnO ₂	BaO-B ₂ O ₃ -SiO ₂ -MnO ₂
R ₂₅ (Ω)	42	12.3	38.1	14.4
Log(R _{max} / R _{min})	3.53	3.06	3.81	3.70

As shown in Table 2, the room-temperature resistance of the PTCR ceramics with BaO-B₂O₃-MnO₂ sintering additive is 38.1Ω, and the PTCR ceramics with BaO-B₂O₃-SiO₂ is 12.3Ω. Also, as mentioned above, the room temperature resistance of the PTCR ceramics with BaO-B₂O₃-SiO₂-MnO₂ is 14.4Ω. The difference in the room-temperature resistance of PTCR ceramics (sample 3) with same Mn content is thought to be due to the Si existing in BaO-B₂O₃-SiO₂- MnO₂ sintering additive. Si forms a secondary phase at the grain boundary of PTCR ceramics during sintering, which reduces the concentration of Mn for acceptor state formation, thus

leading to reduction of the room-temperature resistance [19, 20].

It also shows that the PTC effect of PTCR ceramics with BaO-B₂O₃-SiO₂-MnO₂ addition was significantly enhanced than that of PTCR ceramics with BaO-B₂O₃ and BaO-B₂O₃-SiO₂ addition.

The enhancement of the PTC effect at low temperature sintering by BaO-B₂O₃-SiO₂-MnO sintering additive cannot be explained by the B ions acting as acceptor in interstitial sites of PTCR ceramics. Obviously, the PTC effect of PTCR ceramics can be considered to be due to Mn ions.

This result indicates that even low temperature sintering of 1 050°C can provide relatively low room-temperature resistance and high resistance jump.

3.3 Influence of soaking time

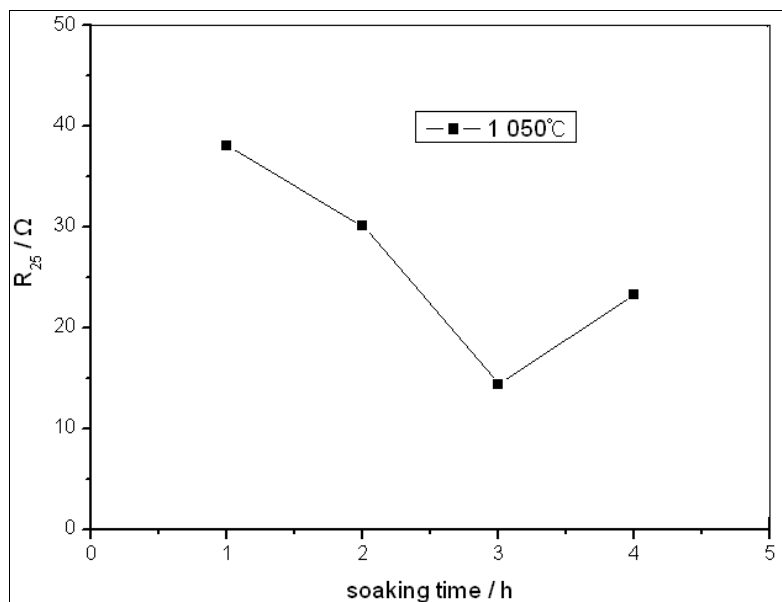


Fig 7: Room-temperature resistance of PTCR ceramics sintered at 1 050°C with different soaking time

The increase in room-temperature resistance in the PTCR ceramics with a soaking time of 4 h is attributed to the large possibility of electron capture by the diffusion of Mn ions into the grain interior.

From Fig. 7, it can be seen that the optimum soaking time at the sintering temperature of 1 050°C is 3 h.

4. Conclusions

To enhance the resistance jump of PTCR ceramics in low temperature sintering, MnO₂ was added into BaO-B₂O₃-SiO₂ sintering additive. Keeping the Y content fixed, the Mn content was varied to obtain the maximum resistance jump, when the Mn content is 0.06 mol%, the resistance jump is 3.7 and the room temperature resistance is 14.4Ω. With increasing Mn content, the room temperature resistance has a U-type change, but the resistance jump is reversed. This clearly shows that the PTC effect of PTCR ceramics is strongly dependent on Mn ions than B ions. The sufficient sintering soaking time is beneficial for the growth and semiconducting of the grain by realizing a uniform distribution of liquid phase sintering additives in PTCR ceramics. In particular, Si in sintering additives acts to reduce the room temperature resistance of PTCR ceramics. The optimum soaking time of PTCR ceramics at a sintering temperature of 1 050°C is 3h.

The sintering soaking time is a very important factor determining the electrical properties of PTCR ceramics. It reduces the room-temperature resistance of PTCR ceramics by providing sufficient substitution of Y³⁺ ions as semiconducting ions with Ba²⁺ ions of the BaTiO₃ ceramics during the soaking time. Also liquid phase sintering additives form a fully liquid phase, which homogenizes the growth of the grains.

Therefore, the reasonable soaking time provides a favorable condition for making PTCR ceramics semiconducting. We have investigated the electrical properties of PTCR ceramics adding 3 mol% sintering additive with different soaking time at 1 050 °C. As can be seen in Fig. 7, the room-temperature resistance of PTCR ceramics exhibited the U-type curve with increasing soaking time.

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