The Korean Journal of Ceramics, **5** [2] 110 - 114 (1999)

Sensitivity of Ba_2WO_5 to NO_X gas at Elevated Temperature

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(Received February 27, 1998)

NO_x sensing properties of Ba_2WO_5 were investigated by varying the sintering temperature in an effort to study the effects of the neck-width on gas sensitivity. Ba_2WO_5 sintered at 800°C, which exhibits neck-controlled conduction provides highest sensitivity of 47 and 29 at 500°C to NO and NO_2, respectively. The samples sintered beyond 800°C show sintering temperature-independent gas sensitivity. This may be because the grain boundary control is dominant at lower sintering temperatures and open neck control is dominant at higher sintering temperatures than 800°C. The NO_x sensing mechanism of Ba_2WO_5 was briefly discussed.

Key words : Ba_2WO_5, NO_x, Gas Sensor, Combustion Exhausts

I. Introduction

NO_x is generated with CO, HC and H_2S from combustion facilities and all motor vehicles, and NO_x concentration contained in combustion exhausts generally ranges from 100 to 1000 ppm. In practice, it has been reported that the concentration of NO_2 is smaller than 5% of NO which is one of the most toxic components in the air pollutant.

Various materials have been used for the detection of NO_x: tin oxide,[1-4] tungsten oxide[5,6] and organometallic phthalocyanine.[7] Among various semiconductor materials, WO_3 is known to exhibit outstanding sensitivities to NO_x. But the sensitivity to NO remains one tenth of that to NO_2 at 300°C and moreover the sensitivities to both NO and NO_2 decrease steeply with increasing operating temperature, which becomes very modest at 500°C and above. Tamaki *et al.*[8] examined a series of WO_3-based mixed oxides for sensing NO_x at high temperature. They suggested that $BaWO_4$ mixed with $BaCO_3$ provided an excellent sensing properties with regard to NO and NO_2 at elevated temperature. However, Ba_2WO_5 is always present because of the negative free energy of the reaction, $BaWO_4+BaCO_3 \rightarrow Ba_2WO_5+CO_2$ during the high temperature calcination and sintering process above 700°C. In fact, large amount of Ba_2WO_5 was observed, instead of $BaCO_3$ when the mixture of $BaWO_4$ and $BaCO_3$ was calcined at 700°C. In this study, we examined the NO_x sensing properties of pure Ba_2WO_5, which was made by calcinating $BaCO_3$-WO_3 mixture at high temperature of 900°C.

The effects of particle size on the gas sensitivity was thoroughly studied and modelled by many authors in tin oxide system[9,10] and in tungstate system.[11] They used super fine particles of less than 10nm in diameter, which was, of course, unstable at high temperature over 400°C. Here, we tried to simulate the neck-controlled sensitivity using super large particles of Ba_2WO_5 with a diameter of about 2 μm.

II. Experimental procedures

WO_3(Strem Chemical Co.) and $BaCO_3$(Yakuri Pure Chemical Co.) were mixed at molar ratio of 1:2, and pulverized using a ball mill for one day. Mixed powder was calcined at 900°C for 2 hours in air, for ensuring the complete solid state reaction to form Ba_2WO_5. It was then pressed into disks with 14 mm in diameter by using a pressure of 650 kg/cm^2. The phase of the disk pellet was identified as Ba_2WO_5 by means of XRD. The disk specimens were then sintered at 750~900°C for 2 hours in air. The sintered disks were cut into small rectangular chips (3×4×1 mm^3). Each chip was attached with a pair of Pt electrodes 1.5 mm apart to form a sensor element shown in Fig. 1, before finally calcined at 800°C for 30

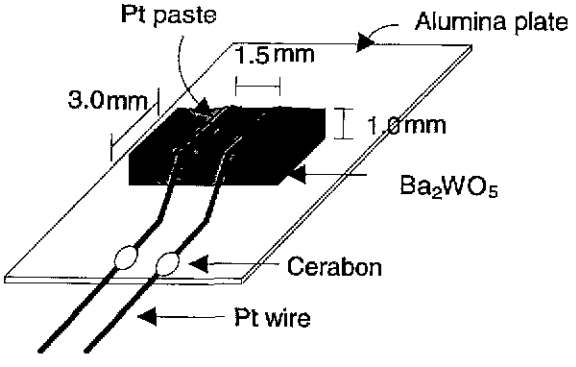

Fig. 1. The structure of the sensor.

min in air.

Measurements were carried out in a standard flow apparatus equipped with a heating facility, through which dry air or a sample gas was let to flow at a rate of 400 cm^3/min. The sample gas was prepared by diluting the parent source of NO(1000 ppm in N_2) or NO_2(200 ppm in air) with dry air. The concentration of NO and NO_2 were set to 200 ppm and 80 ppm, respectively.

The electrical resistance of the element was monitored and recorded by means of the electrometer(Keithley 617 electrometer) at various temperatures. The gas sensitivity was defined as R_a/R_g, where R_a and R_g are the resistance in air and in the sample gas, respectively.

III. Results and Discussion

1. Sintering properties

Fig. 2 shows the response transients of Ba_2WO_5 sintered at 800°C to 200 ppm NO(Fig. 2a) and to 80 ppm NO_2 (Fig. 2b) at various operating temperatures. Both gases exhibited oxidizing type response where the resistance of p-type semiconductor, Ba_2WO_5 fell markedly upon exposure to the gas. This is attributed to the chemisorption of NO_2 gas via the reaction:

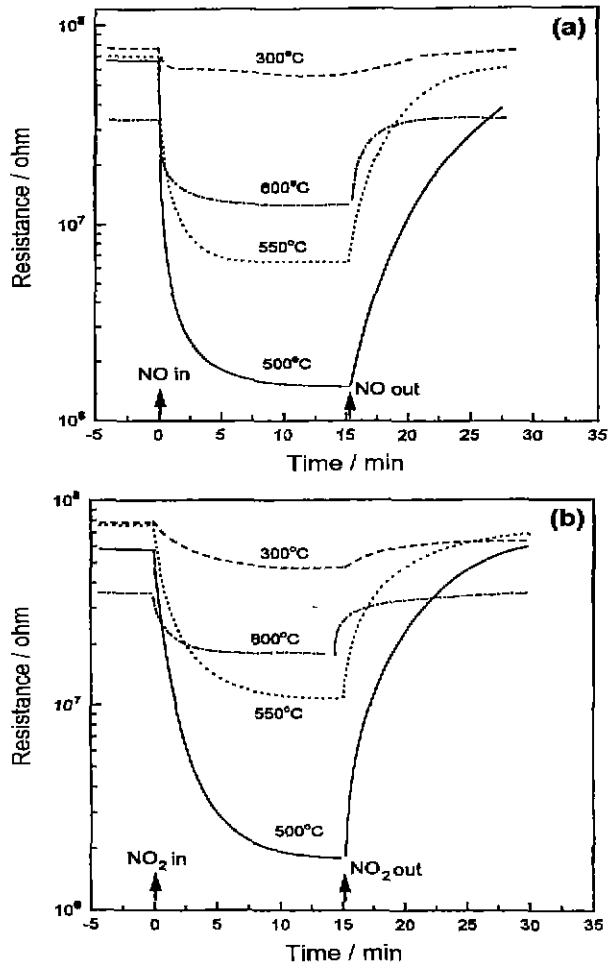

Fig. 2. Response transients of Ba_2WO_5 sintered at 800°C to (a) 200 ppm NO and to (b) 80 ppm NO_2 at various temperatures.

$$NO_{2(g)} + e \rightarrow NO^-_{2(ads)} \quad (1)$$

The capture of the conduction band electrons causes energy band bending at Ba_2WO_5-gas interface, which results in an increase of holes at interface. However, the chemisorption characteristics of NO which has been studied mostly in tin oxide system is not so simple, rather controversial. According to the XPS work done by Capehart and Chang,[12] the dissociative mechanisms occur on the surface of tin oxide such that the adsorbed NO molecules dissociate into N (which is subsequently desorbed as N_2) and atomic oxygen which diffuses into the bulk thus altering the concentrations of electrons available for conduction. On the contrary, Gutierrze *et al.*[13] proposed that adsorbed oxygen played an important role in the chemisorption of NO on tin oxide by the reaction:

$$NO_{(g)} + O_{(ads)} + e \rightarrow NO^-_2 \quad (2)$$

Both mechanisms give oxidizing type gas behavior, producing holes at interface to decrease the resistance of p-type semiconductor.

Sometimes, abnormal behavior was reported from the alio-valent ion doped SnO_2[14,15] where the resistance of the n-type semiconductor sensor decreased upon exposure to NO gas. However, this phenomena were not observed from pure SnO_2. Sberveglieri *et al.*[15] explained the abnormal decrease of resistance by the reaction:

$$NO_{(g)} + O^-_{(ads)} \rightarrow NO^-_2 \quad (3)$$

$$NO^-_{2(ads)} \rightarrow NO_{2(g)} + e \quad (4)$$

where the desorption of NO_2 turned back the conduction electrons to semiconductor which resulted in a decrease of the resistance of n-type semiconductor. In addition, Williams *et al.*[14] suggested that $O^-_{(ads)}$ in the above reaction could be a lattice oxygen from their resistance response experiment in nitrogen atmosphere where the available $O^-_{(ads)}$ is very limited. In the case of Ba_2WO_5, abnormal behavior was not observed as shown in Fig. 2a. Surprisingly, the sensitivity to NO 200 ppm was greater than that to NO_2 80 ppm as 47 and 29, respectively. Therefore, it is thought that the reaction of NO with $O^-_{(ads)}$ written above is not plausible on the surface of Ba_2WO_5. It is reasonable because the electron concentration in p-type semiconductor like Ba_2WO_5 is quite small compared with hole concentration, which reduces the concentration of $O^-_{(ads)}$ through the reaction

$$O^-_{(ads)} + h \rightarrow O_{(ads)} \quad (5)$$

The concentration of $O_{(ads)}$ may be much larger than that of $O^-_{(ads)}$ on the surface of Ba_2WO_5. Accordingly, reaction

$$NO_{(g)} + O_{(ads)} + e \rightarrow NO^-_{2(ads)} \quad (6)$$

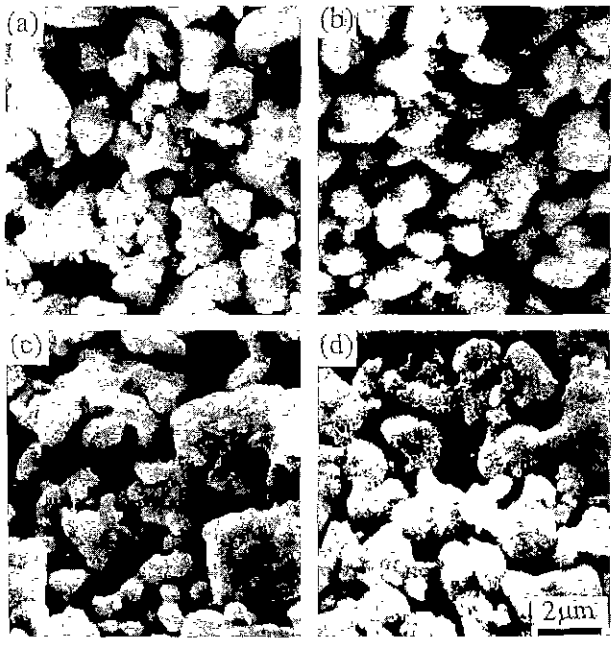

Fig. 3. SEM photographs of the surface of Ba_2WO_5 sintered at (a) 750°C, (b) 800°C, (c) 850°C and (d) 900°C.

is more probable on Ba_2WO_5 than the reaction involving $O^-_{(ads)}$.

Although tin oxide is resistive to sintering, Ba_2WO_5 gives a well developed shape of neck due to its high surface diffusivity of metal ions as shown in Fig. 3. As sintering temperature increases from 750°C to 900°C, it is apparently seen that the necks are formed between particles and the width of the neck becomes grow up to about 0.5 μm. Fig. 4 shows the gas sensitivity vs sintering temperature of the sensor tested at various temperatures from 300°C to 600°C. The samples sintered at temperatures less than 750°C as well as higher than 850°C exhibited sintering temperature-independent sensitivities. The maximum sensitivity appears at the sample sintered at 800°C.

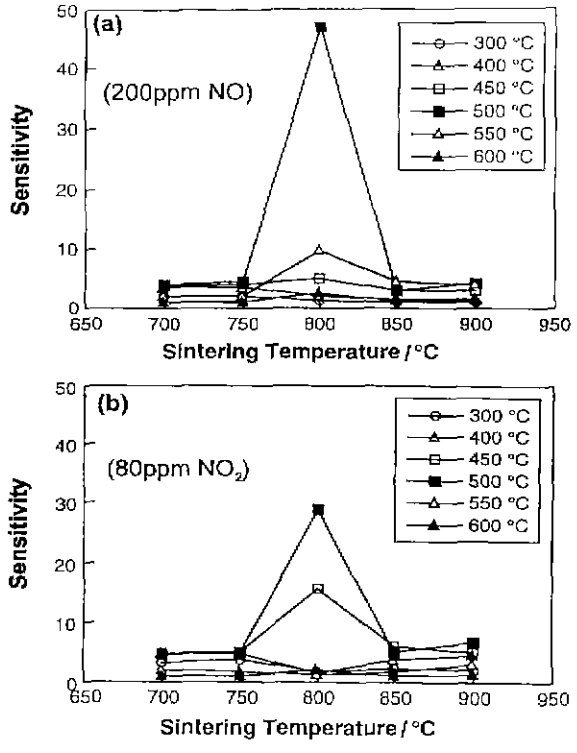

Fig. 4. Gas sensitivity vs sintering temperature tested at various temperatures in (a) NO (200 ppm) and (b) NO_2 (80 ppm).

The influences of the particle diamemter, D (which is equivalent to the width of the neck in this study) on gas sensitivity have been modeled for SnO_2-based devices[9,10] and WO_3-based devices.[11] According to those models, there are three different kinds of inter-grain contacts, depending on D and the length of the space charge layer, L. When D>>2L, the surface of the particle is covered with space charge layer across which electron conduction occurs. In this case, the resistance of the sensor is determined by the Schottky barrier height, eV_s at the grain boundary expressed as

$$R=R_0\exp(eV_s/kT) \quad (7)$$

Since Schottky barrier height is independent on D, D-independency of gas sensitivity is obtained (grain boundary control). When D≃2L, the resistance of the sensor is very sensitive to the variation of D as well as to the changes of the conductivity occurring in the space charge layer (neck control). This gives large gas sensitivity which depends on D. When D<<2L, the whole grains become a space charge layer and the resistance of the sensor is determined not only by the grain boundary contacts but also by the grain itself (grain control).

Adopting this model to Ba_2WO_5, the sintering at temperatures lower than 750°C is not enough to form a neck, which give D-independent grain boundary contacts of pressed pellet. However, sintering at 800°C give a neck diameter, D almost close to 2L such that the sensitivity go to maximum. Tamaki *et al.*[11] reported 0.033 μm for the critical diamemter of producing neck-controlled conduction in WO_3 system. In Ba_2WO_5, it is hard to tell the width of the neck from Fig. 3, but it must be larger in Ba_2WO_5 than in WO_3, having approximately 0.1 μm in diameter. As sintering proceeds further at higher than 850°C, the width of the neck becomes much larger than 2L, which gave D-independent electron conduction through the channel in the grain. The progress of the neck formation is schematically shown in Fig. 5.

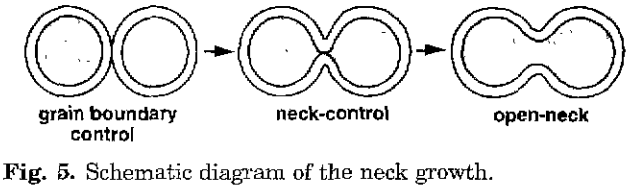

Fig. 5. Schematic diagram of the neck growth.

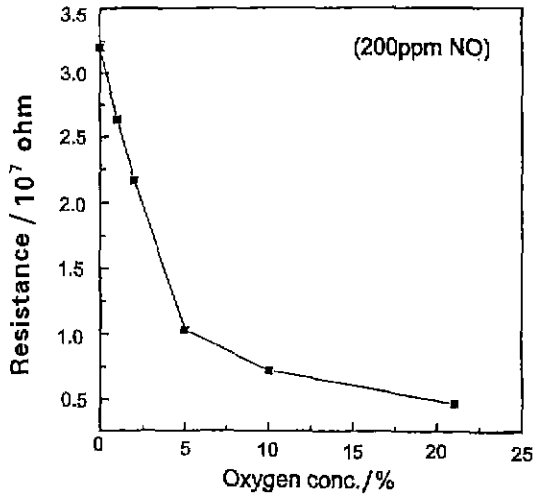

Fig. 6. The resistances of Ba_2WO_5 in 200 ppm NO mixed with various concentrations of oxygen measured at 500°C.

2. *Effects of O_2, CO and H_2*

It is known that O_2 in the atmosphere plays an important role in the adsorption of NO on $BaCO_3$[16] and on WO_3,[17] whereas NO_2 is hardly affected by the presence of oxygen. The electrical resistance of the present Ba_2WO_5 element (sintered at 800°C) under exposure to 200 ppm NO at 500°C changed largely with a change in O_2 concentration between 0 and 21% (N_2 balance), as shown in Fig. 6. As expected, the resistance fell remarkably with increasing oxygen content. This is because $O_{(ads)}$ which has to be involved for the chemisorption of NO on Ba_2WO_5, as mentioned above, increases with increasing oxygen in the atmosphere. This adsorbed oxygen increases again the amount of chemisorbed NO with increasing oxygen, which results in a large decrease in resistance.

CO and H_2 are reducing type gases in contrast with NO. Therefore, it is expected that the sensitivity to NO becomes reduced in the presence of CO and H_2. Fig. 7

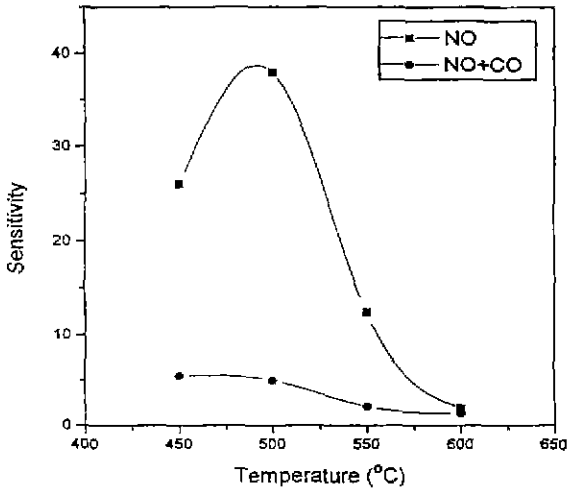

Fig. 7. The effects of CO on the sensitivity of Ba_2WO_5 to 200 ppm NO.

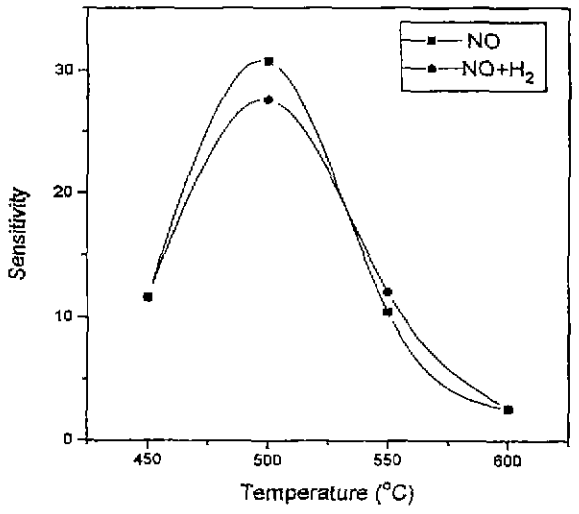

Fig. 8. The effects of hydrogen on the sensitivity of Ba_2WO_5 to 200 ppm NO.

shows the sensitivity to 200 ppm NO gas mixed with 600 ppm CO tested at various temperatures. Comparing with pure 200 ppm NO, the sensitivity considerably decreases from 38 to 5 upon mixed with CO at 850°C. This might result from the production of the electrons at the surface by the reaction:

$$CO + O_O^{\times} \rightarrow V_O^{\cdot} + n + CO_2 \quad (8)$$

However, CO did not affect the sensitivity at 600°C due to its limited adsorption at high temperature.

Fig. 8 shows the sensitivity values of Ba_2WO_5 element to 200 ppm NO in air in the absence and presence of 1000 ppm H_2 as a function of operating temperature. Even though the reducing nature of hydrogen gas, the sensitivity does not change upon exposure of 1000 ppm H_2. It is thought that the adsorption of hydrogen on Ba_2WO_5 is difficult at the temperature tested.

IV. Conclusions

Ba_2WO_5 exhibits p-type semiconductor which gives a decrease in resistance upon exposure of both NO and NO_2. The chemisorption of NO and NO_2 may follow the reactions:

$$NO_{2(g)} + e \rightarrow NO_2^- \quad (9)$$

$$NO_{(g)} + O_{(ads)} + e \rightarrow NO_2^- \quad (10)$$

The sintered Ba_2WO_5 provides a well developed neck and the sensitivity behavior is consistent with the neck model. Sintering at 800°C exhibits outstanding neck-controlled sensitivities of 47 and 29 to 200 ppm NO and 80 ppm NO_2, respectively at 500°C. Sensitivities to NO is higher than that to NO_2 at 500°C. This results show the possibility of using Ba_2WO_5 as sensing material for monitoring NO_x in combustion exhausts. O_2 and CO in the

atmosphere considerably interfere the sensitivity of the sensor while hydrogen doesn't give detrimental effects on sensitivity.

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