YTTRIUM, STRONTIUM DOPED BaTiO3 PEROVSKITE	PEROVSKITE BaTiO3 PHA TẠP YTTRIUM,

AS MATERIAL FOR GAS SENSOR ABSTRACT New gas sensors of Yttrium, Strontium- doped BaTiO3, perovskite oxides were studied. The n-type semiconducting BaTiO3 ceramics compounds: Ba1-x-ySrxYyTiO3 (x= 0.04 - 0.07; y = 0.004) were prepared by conventional ceramic technology. The electrical properties of produced samples (carrier type, its density, mobility…) were studied. The sensitivity of the ceramics samples to CO gas in the concentration of 0.5% at, the temperature of phase transition and middle temperature region was also studied. The strong influence of reducing CO gas on resistivity of the ceramic samples above metallic to semiconducting transition (MST) temperature was found. It's able to detect CO gas in the concentration range of 0.1% - 1.5% at middle temperature region (100o-200oC). The application principle is based on the extreme reactivity of grain oxygen atoms just above the phase transition temperature. The studying positive thermoresistive coefficient (PTC) ceramics can be used as CO gas sensors because of high stability in thermal, atmospheres and low cost.	STRONTIUM ỨNG DỤNG TRONG CẢM BIẾN KHÍ TÓM TẮT checked 2 Bài báo nghiên cứu loại cảm biến khí mới, oxit perovskite BaTiO3 pha tạp Yttrium, Strontium. Chúng tôi chế tạo hợp chất gốm bán dẫn BaTiO3: Ba1-x-ySrxYyTiO3 (x= 0.04 - 0.07; y = 0.004) bằng công nghệ gốm thông thường. Sau đó nghiên cứu các tính chất điện của các mẫu được chế tạo bao gồm loại hạt tải, khối lượng riêng, độ linh động. Đồng thời chúng tôi cũng nghiên cứu độ nhạy của các mẫu gốm với khí CO ở nồng độ 0.5% at, nhiệt độ dịch chuyển pha và vùng nhiệt độ giữa (trung gian). Kết quả cho thấy khí khử CO có ảnh hưởng mạnh đến độ nhạy của các mẫu gốm ở trên nhiệt độ dịch chuyển kim loại-bán dẫn (MST). Nó có thể phát hiện khí CO ở nồng độ 0.1% - 1.5% ở vùng nhiệt độ giữa (trung gian) (100o-200oC). Nguyên lý hoạt động dựa trên độ phản ứng cực mạnh của các nguyên tử oxy dạng hạt ngay trên nhiệt độ dịch chuyển pha. Gốm có hệ số nhiệt điện trở dương (PTC) đang nghiên cứu có thể được sử dụng làm cảm biến khí CO do có độ ổn định cao trong nhiệt độ, môi trường và giá

1. INTRODUCTION

Some perovskite oxide ceramics have been used as gas sensor materials for the last decade. The gas sensor ceramics could be classified into two groups: the electrochemical ceramics and semiconducting ceramics [1]. The semiconducting perovskite oxide ceramics were widely used in the detection of reducing gases, such as: CO [2-4], H_2S, Cl_2, NO_2 [5], C_2H_2, C_2H_4, C_3H_6 [7], O_2 [9-11]. Among these gases, CO is the most interesting because it can damage the human body [1]. So, the metal oxide semiconductors have been studied for detecting CO, such as: $BaSnO_3$, HfO_2, TiO_2, In_2O_3 [1]. Some authors have been studying to reduce the working temperature of materials by means of promotion of the activity of CO reaction on the surface [12, 13] and some of them have been working on low price CO gas sensor by means of new application of doped $BaTiO_3$ with PTC effect [14]. Recently, the PTCR ceramics have developed to be a new multifunctional semiconducting ferroelectric ceramics [8]. They are widely used in industries and civilian as a control device because of high stability in thermal, atmospheres and low cost [1]. The semiconducting

thành thấp.

[redacted]

BaTiO3- based ceramics are considered to be good adsorbing material as it has specific selectivity to CO, CO2… [6]. The purpose of this paper was an investigation the electrical properties of prepared samples (electrical carrier nature, its density, mobility…), CO influence on conductivity of the PTC ceramics. The influence of temperature on gas sensitivity of the n-type semiconducting Ba1-x- ySrxYyTiO3 (x = 0.04 - 0.07; y = 0.004) ceramics compounds for concentrations of 0.1%-1.5% CO gas was studied.

2. EXPERIMENTS

Semiconducting BaTiO3 material was synthesized by conventional ceramic semiconducting technology with initial materials: BaCO3 (99,0%), Y2O3(99,99%), MnCO3(96,0%), TiO2(99,0%), SrCO3(99,0%). The prepared perovskite powders were pressed into pellets of 1 mm thickness an d 8 mm in diameter at high pressure. The pellets were sintered in air at varied temperatures from 1200oC to 1400oC for 4 hours. Both the surfaces of some samples were coated with Ag-Zn alloy by sputtering cathode method to form the electrodes. The structure of sintered bodies was analyzed by X-ray diffractometer D-5005 (Brucker). The Hall measurements were carried out in

the presence of a magnetic field up to 1.3 T. The relation between the Hall voltage and the current, the Hall mobility, the majority carrier density, the resistivity and the magnetic flux density of the samples were studied by examining the Hall effect in air at room temperature, and in CO environment.

The high temperature dependence of the sample resistance was measured using two- probe method in concentration of 0.5% CO gas and in air. To examine the sensitivity of the ceramics samples to CO, the prepared per ovskite powder s wer e milled and annealed for 10 hours then the samples were coated with Ag-Zn. The measurements were performed in the tubular flow quartz- glass chamber with thermocouple, first in air and then successively under the reducing CO gas. The sensitivity-temperature relation for concentration 0.5% of CO gas in ceramics was defined by following equation:

Where □gas and □air are resistivities in 0,5 vol% CO and air respectively.

3. RESULT AND DISCUSSION

Fig. 1 shows the X-ray diffraction pattern for the sample. It is seen from fig. 1 that the doping sample

has the same structure as BaTiO3, it indicates that the sample is single- phase. At room temperature the sample has a tetragonal structure.

Fig. 2 shows the relation between Hall voltages and the applied current. It is seen that, when the current increased, the Hall voltage increased non-linearly in constant magnetic field. The Hall resistance of the sample can be determined from the Hall voltages and the applied currents. The Hall resistance of the sample was about 6 k□ in air and a little smaller in CO gas at room temperature. The resistance is rather high comparing with the standard resistance.

The relation between the bulk carrier density and magnetic flux density in air was shown in Fig. 3. From this figure we can see that, the bulk carrier density of the sample in air at room temperature is low order of □1015.cm-3, the maximum of carrier density is □ 5.1015.cm-3. This is typical density of carriers in PTC semiconducting materials.

Fig. 3: Bulk carrier density versus magnetic field strength in air.

Fig. 1: X- ray diffraction pattern of samples

Fig. 4 shows the Hall mobility calculated from sheet carrier

density and the sheet resistivity. The Hall mobility is given by the product of the Hall constant and the conductivity for the given sample. In general, the greater the carrier mobility in the sample, the greater the Hall mobility. The carrier mobility depends on the applied magnetic field. From this figure, we can see that, the Hall mobility decreases with increasing of applied magnetic field strength.

Fig. 2: Dependence of the Hall voltage on applied current through the sample30

Fig. 4: The Hall mobility versus Magnetic field

Studying the Hall effect, we found that the electrical majority carriers are electrons and materials presented n-type semiconductor. The Hall mobility □H □ 70 (cm2/Vs) at room temperature and in zero magnetic field. In the 0,5 vol.% concentration of CO gas, the carrier density increases a little because of the oxygen adsorption on the grain surface.

It was seen in Fig. 5 and Fig.6 the resistivity - temperature characteristics of the doping BaTiO3 perovskite (Ba0.936Sr0.07Y0.004TiO3) sample in air and in CO gas. The reduction of sample's resistivity in CO environment is observed clearly.

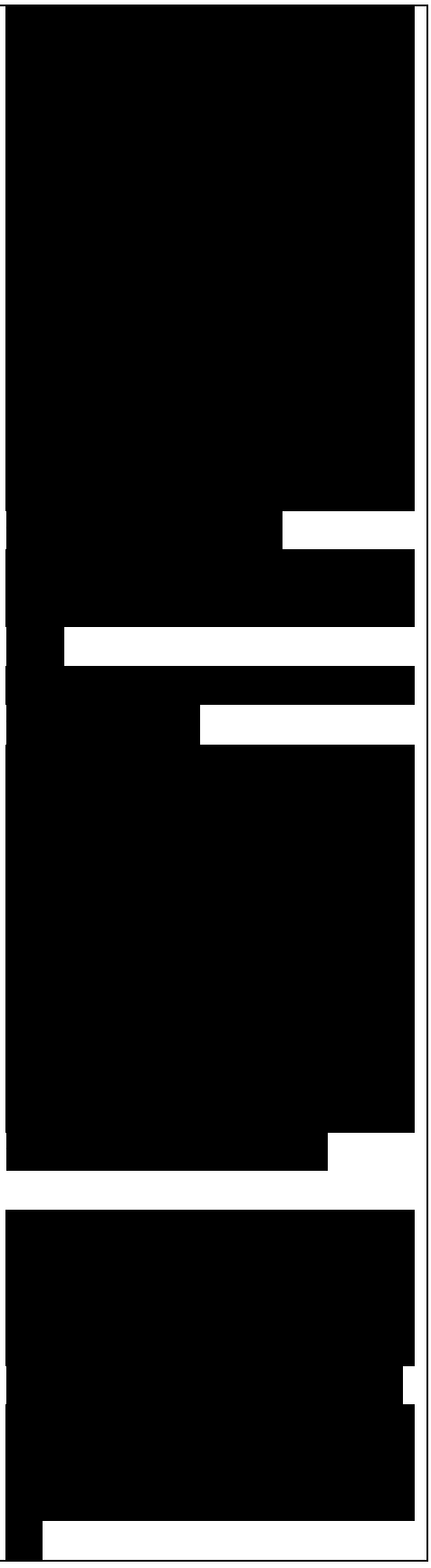

Fig. 5. Resistance- temperature in air and CO gas for sample above Tc to 2000C

The change of resistivity is sensitive especially above the Curie temperature of ferroelectric-paraelectric phase transition (TC~ 125oC) in the interval from 125oC to 170oC (see Fig. 5). The CO gas sensitivity of the sample is expressed via the ratio of the resistivities and plotted in Fig. 6. We note that the sensitivity of the sample to the CO gas strongly depends on temperature. It has the maximum 20% near 130oC and reduces to

Fig. 6. Resistance- temperature in air and CO gas for sample Ba0.946Sr0.06Y0.004TiO3

5% around 1600C. Figure 7 shows the resistivity - temperature characteristics of another doping BaTiO3 (Ba0.946Sr0.06Y0.004TiO3) in air and in CO, the temperature in this examination was above the Tc (1300C). We can see it's the same to the sample: Ba0.936Sr0.07Y0.004TiO3. The reduction of the sample's resistivity in CO environment is also observed clearly in the interval from 125oC to 170oC.

The PTC effect is stipulated by specific structure of a surface of a grain formed under special technological conditions. The substitution of Ba2+ ions in perovskite lattice by Y3+ causes conductivity rises of the doped material. It could be explained by the following equation in Kroeger Vink notations [14]:

On the grain surface, at low temperature the adsorbed oxygen may exist in not charged forms of O2(ads) or O (ads), or the lattice ternary atoms of oxygen on the surface may be present in the form of O0. The raise of temperature prior to the beginning of Tc promotes an establishment of the surface with adsorbed oxygen
[14] :

Their reactions with CO molecules on the grain surfaces by following equations:

Fig. 6. Sensitivity-temperature in PTCR ceramics: Ba0.936Sr0.07Y0.004TiO3

These reactions happen when the molecules CO diffuse in intergranular space. We consider that, the influence of small concentration of CO gas on conductivity of materials Ba1-x-ySrxYyTiO3. (x = 0.04 - 0.07; y = 0.004) can be explained by

equations (1)-(2).

4. CONCLUSION

The sensing mechanism for the adsorption between CO gas and PTC ceramics are based on the reactivity of grain oxygen atoms above MST. The reduction of resistivity of PTC ceramic above MST in CO gas invironment is caused by the increasing of carrier concentration due to CO absorption. The n-type semiconducting PTC ceramics doped with strontium and yttrium is a perspective material for creation gas sensors.