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ZrO_2–TiO_2 ceramic humidity sensors

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Ceramics based on $0.5ZrO_2$–$0.5TiO_2$ were evaluated as humidity sensors. The variation of phase change, microstructure, and conductivity with relative humidity were investigated for base ceramics doped with additives such as $CrO_{1.5}$, $FeO_{1.5}$ and MgO. It was found that $FeO_{1.5}$ enhanced the formation of $ZrTiO_4$. The addition of MgO and $FeO_{1.5}$ increased conductivity and its humidity sensitivity. Open porosity was not affected much by the addition of the three dopants. Nitrogen treatment of sintered ceramics at 900 °C was found to increase conductivities and humidity sensitivity of the ceramics.

1. Introduction

There have been increased applications of humidity sensors, such as in the production process of fibres, electronic materials, precision instruments, and foodstuffs, as well as in humidity controlling systems in air conditioning and other domestic electrical facilities. The reported humidity sensors include electrolytes [1, 2], organic polymers [3, 4], and metal oxides [5–14]. However, electrolytes and organic polymers can only be applied in the temperature range between about 0 and 90 °C; for humidity sensors for use above 100 °C, such as drying machines and combustion controlling systems, metal oxides must be used. Many kinds of metal oxides have been widely investigated as humidity sensing materials. Two types of humidity sensing mechanisms are recognized. The first is proton-type in which ionic conductivity increases as water physisorption or capillary condensation in the micropores occurs [5, 10]. The second is semiconductive type in which electronic conductivity changes with water chemisorption [8, 14].

$MgCr_2O_4$–TiO_2 [5] and TiO_2–V_2O_5 porous ceramics are typical proton-type humidity sensors; perovskite-type oxides such as $CaTiO_3$ and $CaSnO_3$ are representative of semiconductive humidity sensors. The ZrO_2–TiO_2 ceramic which was found to be sensitive to the environment, is a good catalyst [15] and electrolytic material [16, 17]. However, its sensitivity to humidity has not been investigated. In the present paper, we evaluate the potential of ZrO_2–TiO_2-type ceramics as humidity sensors. In addition, the effect of dopants as well as the effect of nitrogen atmosphere treatment at high temperature on its humidity sensitivity are studied.

2. Experimental procedure

The basic composition studied was 50 mol % ZrO_2–50 mol % TiO_2 (ZT). Small amounts of dopants, such as $CrO_{1.5}$ (1 mol %), MgO (1 mol %), and $FeO_{1.5}$ (0.25, 1, 5 mol %) were also added. The powders were prepared by using reagent grade chemicals: TiO_2 (Wako), ZrO_2 (Cerac), Cr_2O_3 (Merck), MgO (Merck) and Fe_2O_3 (Merck). The chemicals were weighed and milled together in a polyethylene bottle with ZrO_2 balls for 10 h. The milling medium was alcohol with 1.5 wt % stearic acid added. After drying and passing through 100-mesh sieves, the powders were dry-pressed to form discs, 10 mm diameter and 1 mm thick. The discs were sintered at 900, 1000, 1100, and 1200 °C for 2 h, at a heating rate of 10 °C min^{-1} and furnace cooled. The duration of sintering at 1200 °C was also varied: 0.5, 1, 2, 4, 8, and 16 h. The open porosities of the sintered compacts were determined by Archimedes method after measuring the dry weight, (W_d), wet weight, (W_w), and weight in the water, (W_h). The open porosity was calculated as follows:

$$\text{open porosity}(\%) = (W_w - W_d)/[(W_w - W_d) + (W_d - W_h)]$$

The crystal phases were detected by X-ray powder diffraction, and the microstructures were investigated by scanning electron microscopy. For evaluation of humidity sensitivity, the sintered compacts were sputtered gold on both surfaces, then the variations of conductivity with relative humidity were determined by an a.c. impedance analyser (HP4192A). The measurements were performed in a chamber with controlled temperature and realtive humidity. Owing to limited ability to control the accuracy of the humidity at temperatures higher than 90 °C, the measurements were taken at 40, 60, and 80 °C. The relative humidity (r.h.) varied from 20% to 95%.

In addition, two systems, ZT and ZT–5 mol % $FeO_{1.5}$, were selected to study the effect of nitrogen treatment on the humidity sensitivity.

3. Results

3.1. X-ray diffraction and microstructures

Fig. 1 shows the typical results of X-ray powder

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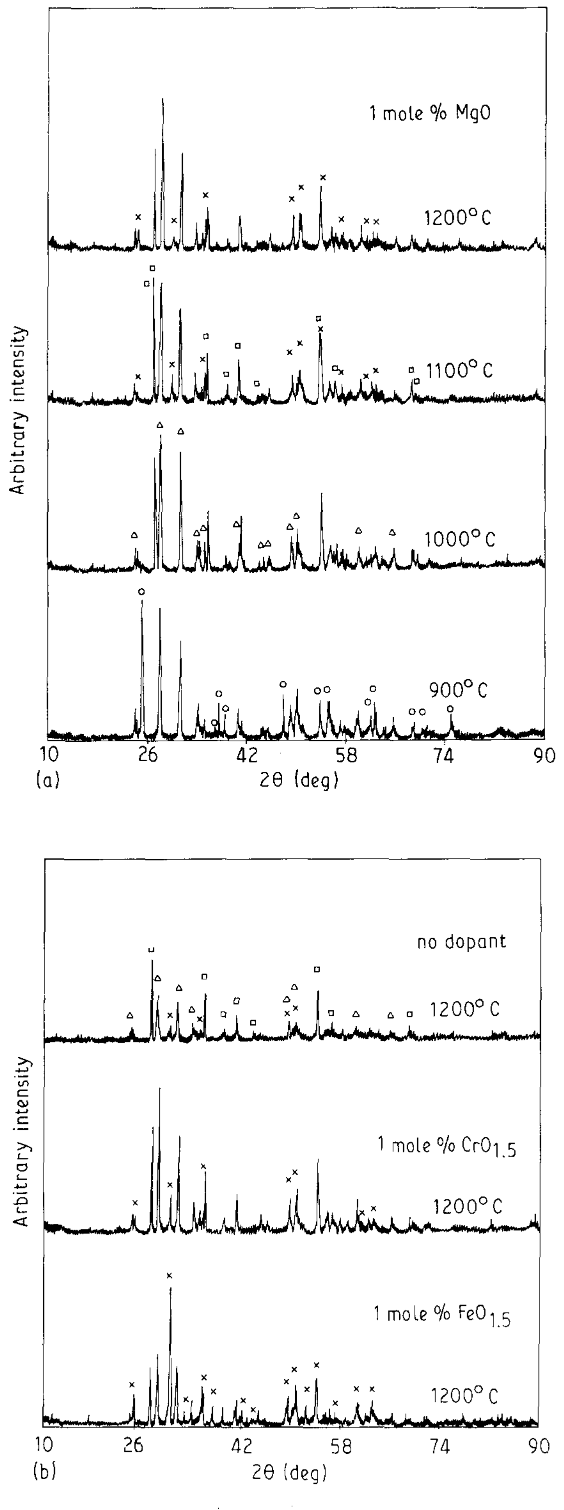

Figure 1 X-ray powder diffraction patterns of sintered ceramics doped with various additives. (□) TiO_2, rutile; (△) ZrO_2, monoclinic, (○) TiO_2, anatase, (×) $ZrTiO_4$, columbite.

diffraction. It was found that the reactions occurring during sintering were

$$TiO_2\,(\text{anatase}) \rightarrow TiO_2\,(\text{rutile}) \qquad (1)$$

$$ZrO_2 + TiO_2 \rightarrow ZrTiO_4 \qquad (2)$$

Reaction 1 occurs between 900 and 1000 °C for all powders doped with different dopants. Reaction 2 strongly depends on the type and amount of dopant. For samples containing no dopant, Reaction 2 takes place at 1200 °C after 2 h heating, but only a small amount of $ZrTiO_4$ (columbite) compound is formed. For the 1 mol % $CrO_{1.5}$ dopant, Reaction 2 starts at 1100 °C, but the amount of $ZrTiO_4$ formed at 1200 °C is still small. The effect of MgO on Reaction 2 is similar to that of $CrO_{1.5}$. In contrast, iron oxide is found to enhance Reaction 2, the amount of $ZrTiO_4$ becoming the major reaction compound at 1200 °C sintering. As the amount of $FeO_{1.5}$ increases to 5 mol %, only traces of rutile and ZrO_2 (monoclinic) remain; the main phase is $ZrTiO_4$.

The variation of open porosities with sintering temperature for different dopants is shown in Fig. 2, illustrating that the porosities after sintering for 2 h at temperatures lower than 1100 °C are all greater than 50%. The reduction in porosities with sintering temperature is not prominent until 1200 °C. The porosities are still high, about 37% to 50%, even at 1200 °C. The high porosities make these samples easy to interact with the environment.

Fig. 3 shows the microstructure of the sample containing no dopant and sintered at 1200 °C for 2 h. It illustrates high porosity of the ceramics. The small bright particles are $ZrTiO_4$, the large bright ones are

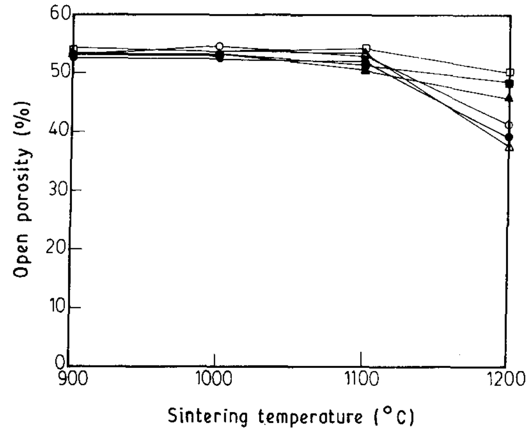

Figure 2 Variation of open porosities with sintering temperature for ceramics with different dopants added. (□) 1 mol % $CrO_{1.5}$, (△) 1 mol % MgO, (○) 0.25 mol % $FeO_{1.5}$ (■) 1 mol % $FeO_{1.5}$, (▲) 5 mol % $FeO_{1.5}$, (●) undoped.

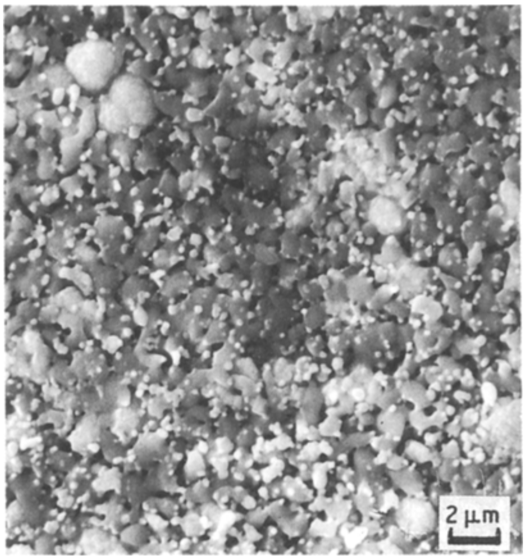

Figure 3 Typical microstructure of $0.5ZrO_2$–$0.5TiO_2$ ceramic.

ZrO_2, and the large grey particles are rutile. Samples doped with different dopants have similar microstructures and will not be shown.

3.2. Frequency dependence of r.h. sensitivity

Fig. 4 shows the dependence of humidity sensitivity on a.c. frequency for the sample doped with 1 mol% MgO and sintered at 1200 °C for 2 h. The variation in conductivity with a.c. frequency is relatively small if compared with its variation with r.h. All other samples doped with different dopants show the same behaviour. Therefore, all data are given at 1 kHz frequency in the following sections.

3.3. Effect of dopants on r.h. sensitivity

Fig. 5 shows the effect of dopants on the humidity sensitivity of ZrO_2–TiO_2-type porous ceramics sintered at 1200 °C for 2 h. It illustrates that the ZrO_2–TiO_2 porous ceramic without dopant is not sensitive to the humidity variation. The addition of 1 mol% $CrO_{1.5}$ reduces the conductivity of the ceramics, thus most of the data are below the limit of measurement and cannot be obtained. For 1 mol% $FeO_{1.5}$ addition, the sensitivity and the conductivity are increased. The effect of 1 mol % MgO is even more prominent; the conductivities are higher than those of $FeO_{1.5}$-doped ceramics. Both MgO- and $FeO_{1.5}$-doped samples have three orders of magnitude variation in conductivity as humidity increased from 20% to 95% r.h.

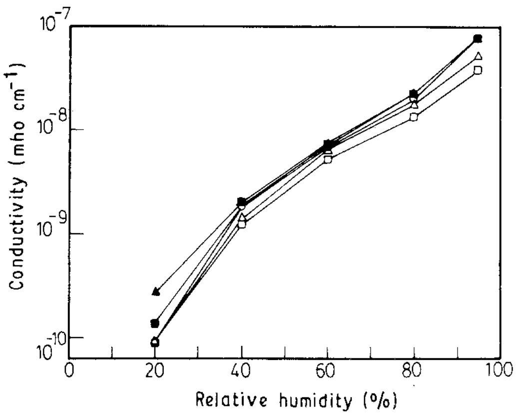

Figure 4 Frequency dependence of humidity sensitivity at 40 °C of ceramics doped with 1 mol% MgO. (□) 10 Hz, (△) 100 Hz, (○) 1 kHz, (■) 10 kHz, (▲) 100 kHz.

3.4. Effect of sintering temperature on r.h. sensitivity

Fig. 6 shows the effect of sintering temperature on the humidity sensitivity of the conductivity of the porous ceramics doped with 1 mol% MgO. The conductivities of ceramics sintered at temperatures lower than 1100 °C are very low; therefore, they are not able to be measured except in the high r.h. region. Generally, the conductivities increase with sintering temperature. However, the conductivities of the ceramics sintered at 1100 °C are always the lowest, even in ceramics doped with $FeO_{1.5}$. This is tentatively correlated with the initial occurrence of $ZrTiO_4$ which causes volume change and grain separation, resulting in lower conductivities.

3.5. Effect of sintering time on r.h. sensitivity

Fig. 7 shows the change of open porosity with sintering time at 1200 °C for samples doped with 5 mol% $FeO_{1.5}$ and samples without dopant, illustrating that porosities generally decrease with time but only slightly. The crystal phases do not vary significantly with time. Samples containing no dopants consist mainly of rutile and monoclinic ZrO_2 with a small amount of $ZrTiO_4$ after sintering at 1200 °C from 0.5 to 16 h. In samples doped with 5 mol% $FeO_{1.5}$ the

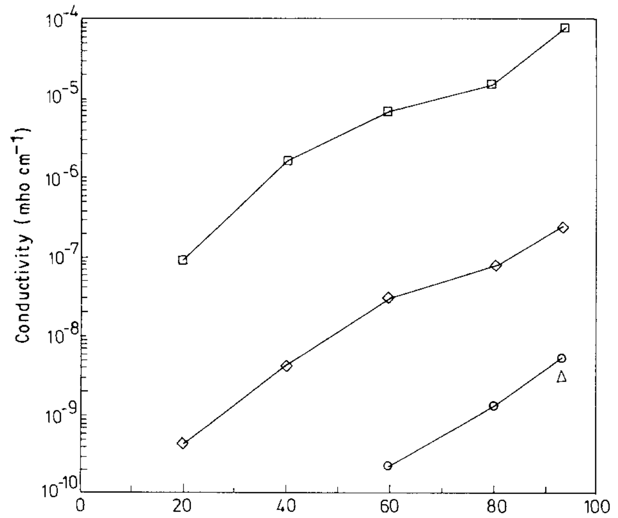

Figure 5 The effect of dopants on the humidity sensitivity at 40 °C of $0.5ZrO_2$–$0.5TiO_2$ ceramic. (○) Undoped, (△) 1 mol% $CrO_{1.5}$, (□) 1 mol% MgO, (◇) 1 mol% $FeO_{1.5}$.

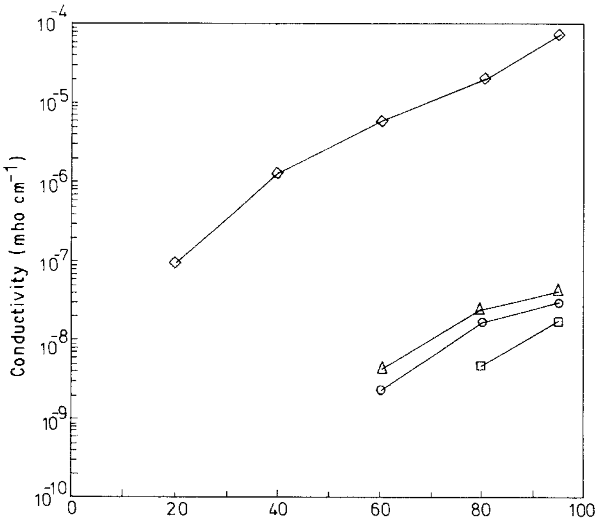

Figure 6 The effect of sintering temperature on humidity sensitivity at 40 °C of ceramics doped with 1 mol% MgO. (○) 900 °C, (△) 1000 °C, (□) 1100 °C, (◇) 1200 °C.

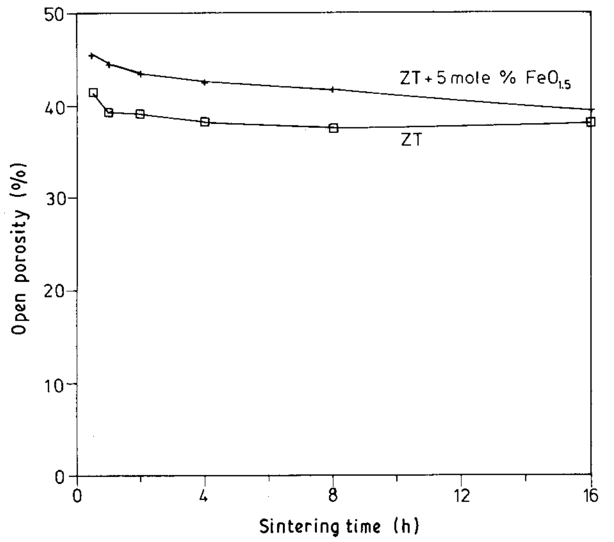

Figure 7 The variation of open porosity with sintering time at 1200 °C for ceramics undoped and doped with 5 mol % $FeO_{1.5}$.

crystal phase is mostly $ZrTiO_4$ (columbite) after 0.5 to 16 h sintering at 1200 °C. Figs 8a to d show the microstructures after sintering at 1200 °C for 0.5 and 16 h, respectively, for samples without and with 5 mol % $FeO_{1.5}$ dopant. There is apparent grain growth in the 16 h sintered samples. Samples sintered between 0.5 and 16 h possess similar variation and will not be shown here. Figs 9a and b show the effect of sintering duration on the r.h. sensitivity of conductivity for ceramics without dopants and doped with 5 mol % $FeO_{1.5}$, respectively. It was found that lengthening the sintering time raised the conductivity and its r.h. sensitivity in both ceramics. Higher conductivity is desirable because the measured values are more reliable. The conductivities of both samples sintered for 0.5 h are low and below the detection limit in the low r.h. region. As sintering time increases to 16 h the r.h. sensitivity of the sample doped with 5 mol % $FeO_{1.5}$ is high.

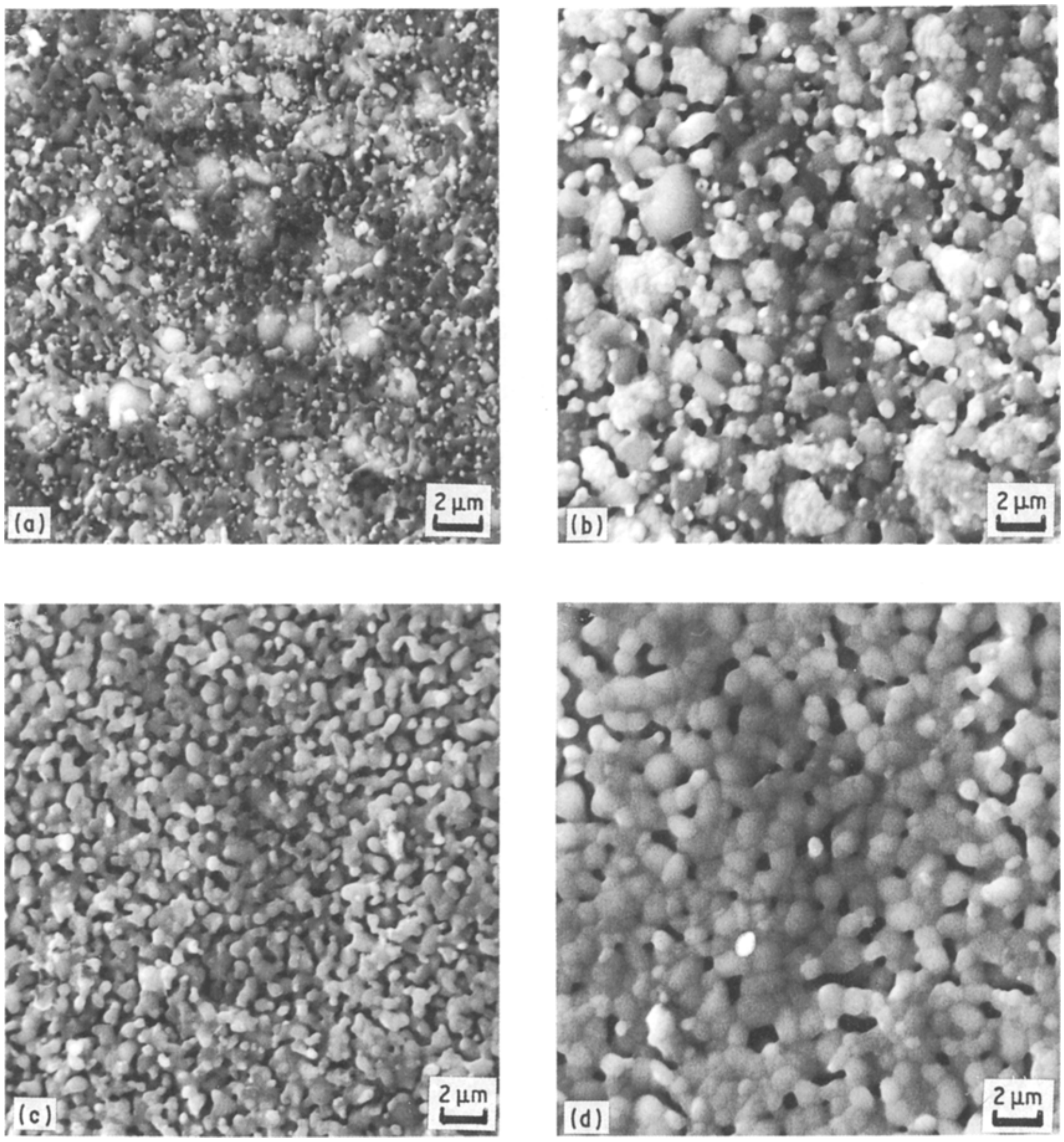

Figure 8 Microstructures of doped and undoped samples after sintering at 1200 °C for different times. (a) No dopant, 0.5 h; (b) no dopant, 16 h; (c) 5 mol % $FeO_{1.5}$, 0.5 h; (d) 5 mol % $FeO_{1.5}$, 16 h.

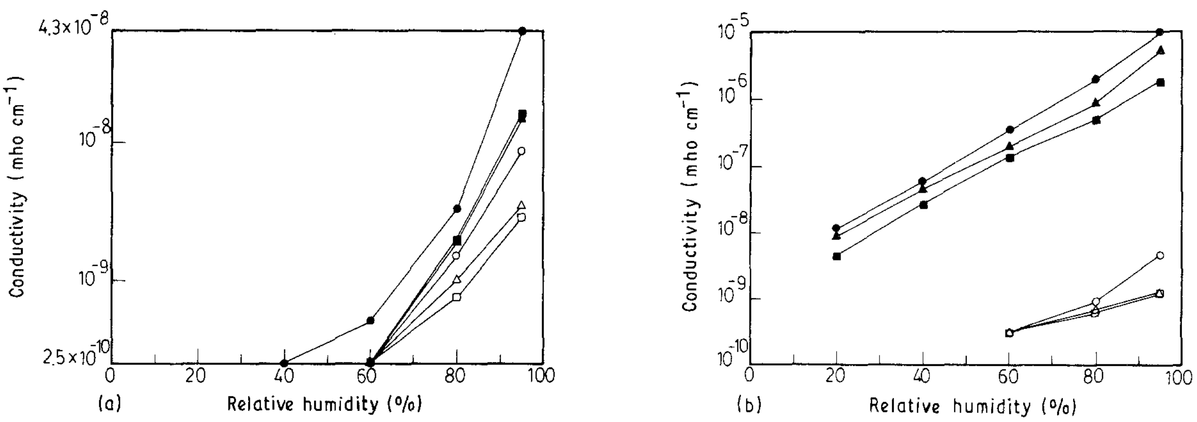

Figure 9 The effect of sintering time on the humidity sensitivity of ceramics (a) undoped and (b) doped with 5 mol % $FeO_{1.5}$. 0.5 h at: (□) 40 °C, (△) 60 °C, (○) 80 °C 16 h at: (■) 40 °C, (▲) 60 °C, (●) 80 °C.

3.6. Effect of nitrogen treatment

Figs 10a and b show the effect of nitrogen treatment at 900 °C for 2 h on the r.h. sensitivity of conductivity for the same ceramics as shown in Figs 9a and b. Several changes were observed after nitrogen treatment. The conductivity of all samples was increased depending on the porosity of the ceramics. It was found that the larger the porosity of the ceramics, the higher the increase of conductivity is obtained after nitrogen treatment. For samples sintered for only 0.5 h, the conductivity is increased by three to four orders of magnitude. In contrast, for those sintered for 16 h, the increase is only about one order of magnitude. The sensitivity of conductivity to r.h. increases only slightly for long-term sintered samples, while it increases significantly for short-term sintered samples which show poor r.h. sensitivity before the nitrogen treatment. Although samples sintered for 0.5 h possess higher conductivity, those samples sintered for 16 h have slightly better r.h. sensitivity.

3.7. Effect of measurement temperature

Figs 9 and 10 also show the variation of conductivity and r.h. sensitivity with the measuring temperature. It illustrates that the change in conductivity from 40 to 80 °C is relatively small compared with that due to humidity change. This property is considered an advantage because the ceramics are employed as humidity sensors in an environment undergoing temperature changes.

3.8. Effect of ageing

Fig. 11 shows the stability of conductivities with ageing time when samples doped with 5 mol % $FeO_{1.5}$

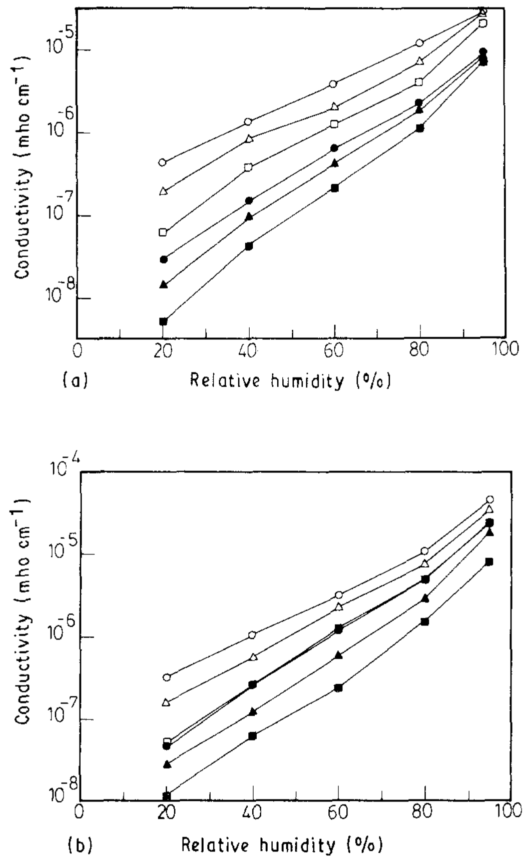

Figure 10 The effect of nitrogen treatment on the humidity sensitivity of ceramics (a) undoped and (b) doped with 5 mol % $FeO_{1.5}$. For key, see Fig. 9.

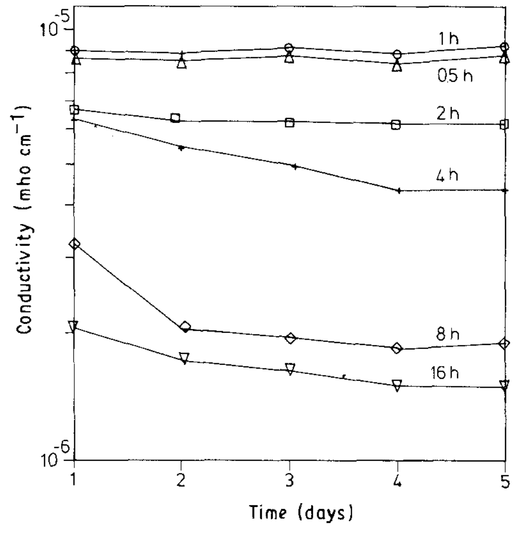

Figure 11 Variation of conductivity with ageing time at 40 °C, 95% relative humidity.

and sintered for various times were aged in a 40 °C, 95% r.h. environment. Samples sintered for 0.5, 1 and 2 h are stable with no change, during ageing over a period of 5 d. Samples sintered for longer times, show obvious decreases in conductivities within the first 1 to 2 d, then the conductivities become stable with ageing. The r.h. sensitivity of conductivity is essentially unchanged.

4. Discussion

The conductivity changes as relative humidity varies from 20% to 95% are about three orders of magnitude for ZrO_2–TiO_2 ceramics doped with 1 mol % MgO and $FeO_{1.5}$. The variation in conductivity with humidity change is relatively high and advantageous for applications as humidity sensors. The achieved humidity sensitivities of ZrO_2–TiO_2 ceramics are comparable with those of commercial $MgCr_2O_4$–TiO_2 ceramics [5] and a little better than those of TiO_2–V_2O_5 ceramics [18]. In addition the observed effect of a nitrogen atmosphere treatment on conductivity is interesting, and can be employed to enchance the humidity sensitivity of ZrO_2–TiO_2 ceramics. Furthermore, the porous ZrO_2–TiO_2 ceramics sintered at 1200 °C possess relatively high strength from a simple abrasion test as compared with that of TiO_2–V_2O_5 ceramics under similar sintering conditions.

The conduction mechanism is still not clear and needs more investigation. It is tentatively considered to be related to oxygen vacancy, because both nitrogen atmosphere treatment and dopants such as MgO and $FeO_{1.5}$ create oxygen vacancies in ZrO_2–TiO_2 porous ceramics. The presence of oxygen vacancies may enchance the chemisorption of water vapour on the necks of grains such as V_0–OH^- and they, in turn, provide mobile protons. When more water is present, the water molecules physically adsorb on the surface hydroxyl groups to increase the dielectric constant, which was observed and was not reported in previous sections, thereby decreasing the dissociation energy and promoting dissociation and higher carrier concentration as proposed in [5].

5. Conclusion

1. $FeO_{1.5}$ enhances the formation of $ZrTiO_4$. The major phase is $ZrTiO_4$ after $0.5ZrO_2$–$0.5TiO_2$ ceramics doped with 5 mol % $FeO_{1.5}$ were sintered at 1200 °C for 2 h.

2. MgO and $FeO_{1.5}$ dopants increase the humidity sensitivity of $0.5ZrO_2$–$0.5TiO_2$ ceramics, there being three orders of magnitude of variation in conductivity as relative humidity varies from 20% to 95%.

3. Conductivity and humidity sensitivity generally increase with sintering temperature, except at 1100 °C. Only samples sintered at 1200 °C are good for humidity sensor application, others are not.

4. Nitrogen treatment at 900 °C for 2 h after the samples were sintered at 1200 °C for various times increases conductivities and humidity sensitivity of $0.5ZrO_2$–$0.5TiO_2$ ceramics doped without and with 5 mol % $FeO_{1.5}$.

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