Sintering and humidity-sensitive behaviour of the ZnCr$_2$O$_4$–K$_2$CrO$_4$ ceramic system

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Solid state reaction at elevated temperatures and the sintering behaviour of zinc chromite formed by zinc oxide and chromite oxide were investigated. Crystalline structure, surface and fractured morphologies and humidity-sensitivity characteristics of ZnCr$_2$O$_4$–K$_2$CrO$_4$–CuO were studied. The fired ceramic body, which proved to be mainly constructed from ZnCr$_2$O$_4$ spinel grains, was porous. The humidity characteristics of the sensor showed that the resistance decreased as a logarithmic function with an increase in humidity. The resistance values obtained were about $6 \times 10^9 \, \Omega$ and $3 \times 10^4 \, \Omega$ at 25 and 93% relative humidity (RH), respectively. Based on a.c. impedance measurements, an equivalent circuit associated with a network of resistors together with series capacitors has been suggested. It is assumed that such an equivalent circuit model of the sensor under the moist conditions represents the sensing mechanism as a diffusion process.

I. Introduction

In response to the increasing demands for automatic control systems, humidity-sensing elements using materials such as electrolytes, organic polymers and metal oxides have been investigated and placed on the market [1–10]. Among them, those which utilize the conductivity change of metal-oxide ceramics have been investigated the most actively [1–9]. These sensors can detect humidity on the basis of the enhancement of the surface electrical conductivity of oxides by water adsorption, and they have a greater durability probably because they are both physically and thermally stabilized, and thus fulfil the requirements for the widest range of applications, such as good sensitivity, quick response, reproducibility and no hysteresis. They can be classified into two types, i.e. ionic and electronic. In the former type, porous ceramic elements made with insulating materials exhibit ionic conductivity in humid ambient due to capillary condensation of water vapour [1–3]. The latter type utilizes the sensitivity of the semiconducting materials to the water vapour which acts as an electron-donating gas such that their chemisorption increases or decreases the electronic conductivity depending on the n- or p-type nature of the semiconductors [4–7].

Ternary oxide ceramics have been shown to exhibit interesting properties with regard to their electrical conductivities [8–11] and to the ways in which their conductivity changes with environmental humidity [12]. Zinc chromite is an example of a ternary metal oxide spinel, which has been suggested would be a good candidate for chemical sensing applications [13, 14]. Moreover, materials fabricated using an excess of either zinc or chromite have been reported to be promising for oxygen sensors and catalytically active in the hydrogenation of carbon monoxide [15–18]. Humidity sensors based on pure zinc chromite ceramics are rather poor in performance. The sensor's performance could, however, be greatly enhanced by the addition of certain ceramic compounds. This paper reports on the effects that adding varying amounts of potassium compounds to the zinc chromite has on the humidity sensing properties of the material.

2. Experimental details

The compound was prepared using powders of the highest commercially available purity. Intimate mixtures of 2ZnO:1Cr$_2$O$_3$ and 1ZnO:1Cr$_2$O$_3$ were crushed in a pestle and mortar, followed by calcination at varying temperatures ranging from 800 to 1300 °C. All the samples were cooled down to room temperature at the natural cooling rate of the furance. At each stage in the fabrication, X-ray diffraction patterns (Philips PW1130 diffractometer employing a Cu target with iron-filtered radiation of wavelength 0.15418 nm) were obtained to monitor the reaction progress and eventually to identify the optimum sintering temperature.

The fine-powdered ZnCr$_2$O$_4$ was pressed at 1.5–2 tons cm^{-2} into 13 mm diameter pellets, which were then fired in a muffle furance at temperatures between 1325 and 1350 °C. Then the pellets were examined by scanning electron microscopy (JEOL JSM IC848) to establish the surface morphology, grain growth and

porosity. The presence of additional phases was also determined using energy dispersive X-ray analysis (EDX). The d.c. resistance of the sample as a function of relative humidity was measured by a two-point probe technique using a current source and digital electrometer; ohmic contacts were made from a gallium indium mixture.

Measurements were made in a purpose-built chamber in which the relative humidity was controlled by admitting appropriate mixtures of water, saturated and dry air. The relative humidity in the chamber was monitored using a Thermal Systems Model THP-338 humidity meter. The a.c. impedance measurements were carried out using a Hewlett Packard HP 4192A LS impedance analyser operating over a range of frequencies from 5 Hz to 13 MHz. All a.c. measurements were corrected using an identical arrangement with and without sensor samples.

3. Results and discussions

Fig. 1a–g shows the X-ray diffraction patterns using CuK_α radiation with a wavelength of $\lambda = 0.15418$ nm from the precursor (a), and the powder of $2ZnO:1Cr_2O_3$ that has been fired at elevated temperatures ranging between 800–1300 °C with a heating rate of 500 °C h^{-1} (b–f). Although the diffraction peaks at $2\theta_B$ angles of 30.5, 35.9, 37.5, 43.5, 54.0, 57.5, and 63.2° are associated with corresponding planes in $ZnCr_2O_4$, the peaks at $2\theta_B$ angles of 34.5, 47.7, 56.8, 68.1 and 69.2° are associated with ZnO and the peak at $2\theta_B$ angle of 31.9° with Cr_2O_5. These results indicated that despite the stoichiometric ratio chosen to produce a final chromite compound of $ZnCrO_4$ no evidence for the formation of $ZnCrO_4$ was found at any of the stated firing temperatures. Consequently, some residuals of both ZnO and Cr_2O_5 could be found in chromite X-ray patterns.

In order to produce a monophase body the stoichiometric ratio was adjusted to correspond directly to the final composition of $ZnCr_2O_4$. Fig. 2 shows the X-ray diffraction patterns of the precursor and the powder of $1ZnO:1Cr_2O_3$ that has been fired at 1100 °C. Unlike the former spectra, it contained only the principal peaks at $2\theta_B$ angles which corresponded to the diffraction from the planes of $ZnCr_2O_4$ only. No other diffraction peaks which could be associated with either zinc or chromium oxides were observed, suggesting production of a monophase body.

Fig. 3a and b shows SE micrographs from the as-fired surface (a), and fracture surface (b) of a $ZnCr_2O_4$ sample fired at 1350 °C. The grain sizes were between 2–6 μm, while the pore sizes were from 1–6 μm. It is obvious that the pellets fired at both 1325 and 1350 °C did not display much difference in their grain sizes, and in fact they were quite powdery in nature, supporting the findings of SEM for an incomplete sintering process. No significant differences were recorded in the grain and grain-boundary regions by EDX suggesting that no liquid phase formation took place. It became obvious, therefore, that a sintering aid was necessary in order to produce a ceramic body with reasonable mechanical strength. The main re-
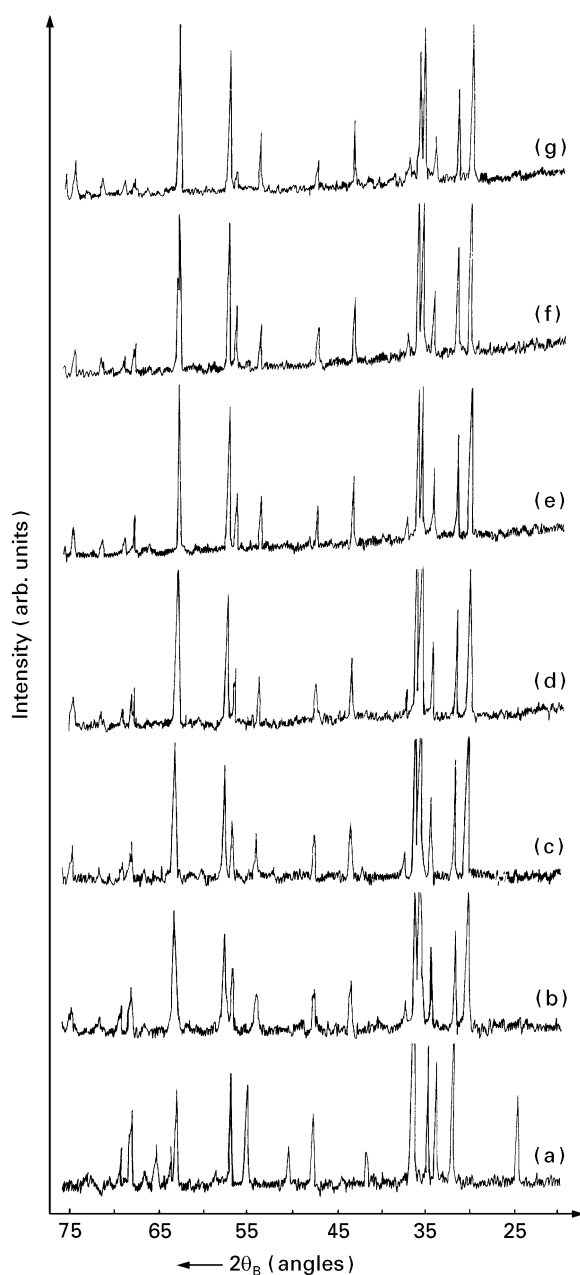

Figure 1 X-ray diffraction patterns of $2ZnO:1Cr_2O_3$ at different stages of firing; (a) precursor material, (b) fired at 800 °C, (c) fired at 900 °C, (d) fired at 1000 °C, (e) fired at 1100 °C, (f) fired at 1200 °C, and (g) fired at 1300 °C.

quirement for this new phase was that it should not interfere with the reaction of the main body to the environmental humidity. In the following discussion, the effect of the addition of various percentages of potassium chromate and/or cupric oxide as sintering aids and their effect on the humidity-sensitive nature of the body as well as the overall conductivity is considered.

Fig. 4 shows EDX spectra for the pellets that had been prepared using $ZnCr_2O_4(90\%)$–$K_2CrO_4(10\%)$ mixture before and after firing at 1200 °C for 20 h. No significant evidence of potassium presence in the pellets was found, as is the case indicated in Fig. 4 (dashed line), or was detected by EDX for samples fired at 1200 °C (solid line). This could be attributed to the evaporation of potassium compound during the firing process at elevated temperatures. SEM micro-
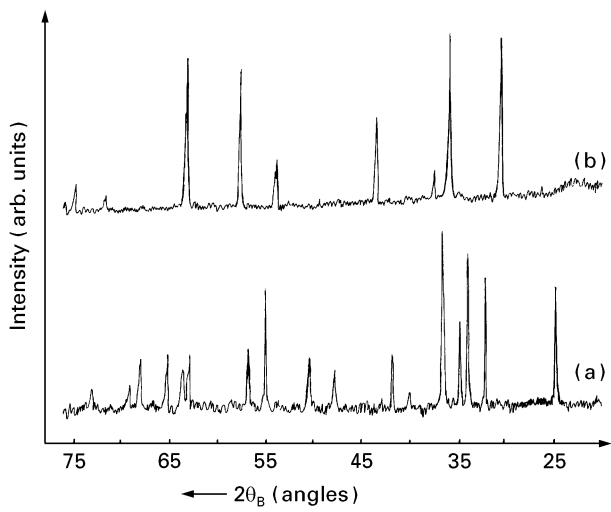
Figure 2 X-ray diffraction patterns of $1ZnO:1Cr_2O_3$ at different stages of firing; (a) precursor material and (b) fired at 1100 °C.
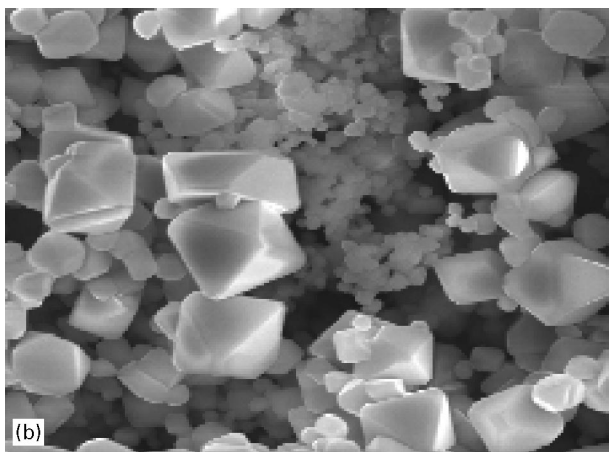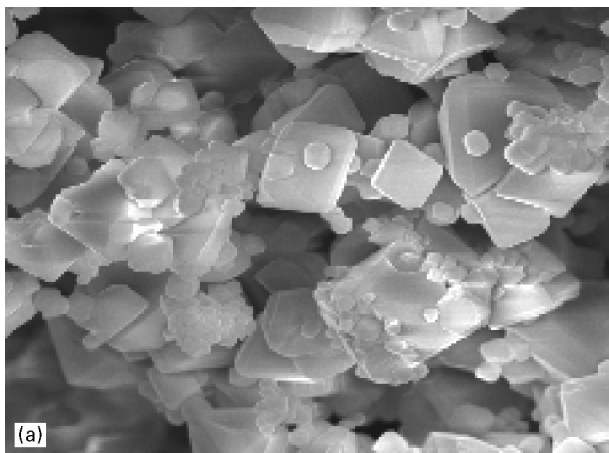

Figure 4 Typical EDX spectra for the pellets that had been prepared using $ZnCr_2O_4(90\%)$–$K_2CrO_4(10\%)$ mixture before (dashed line) and after (solid line) firing at 1200 °C for 20 h.

Figure 3 Typical electron micrographs of samples fired at 1350 °C; (a) surface area, and (b) cross-sectional.

Figure 5 Typical electron micrograph of as-fired surfaces; (a) the sample prepared using $ZnCr_2O_4$–K_2CrO_4 (10%) followed by a firing at 1200 °C and (b) the sample prepared by incorporation of 20% potassium carbonate as sintering aid to $ZnCr_2O_4$–K_2CrO_4 mixture fired at 920 °C for 1 h.

graphs of these samples (Fig. 5a) showed a great number of pin holes which are normally associated with volatilization and escape of one or more of the components (potassium in the present case) at high temperature. No improvement was observed with regard to the mechanical properties of these pellets.

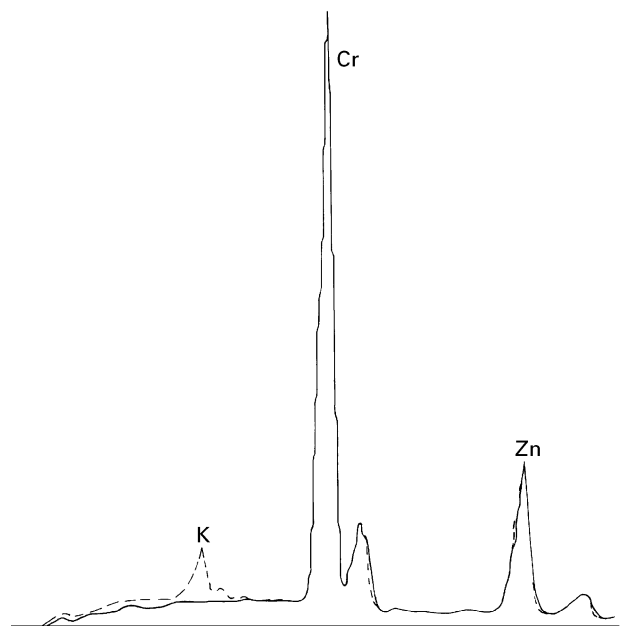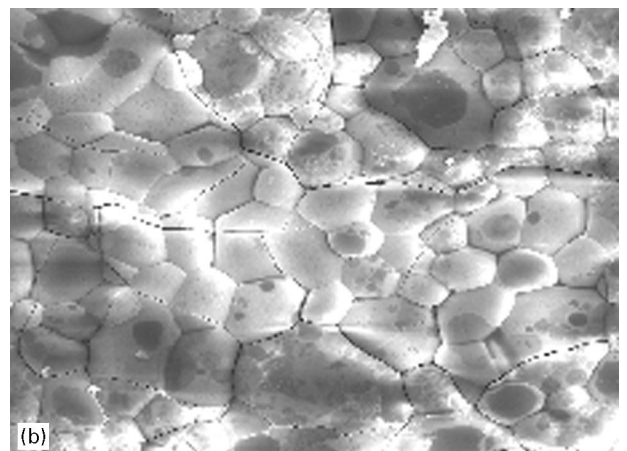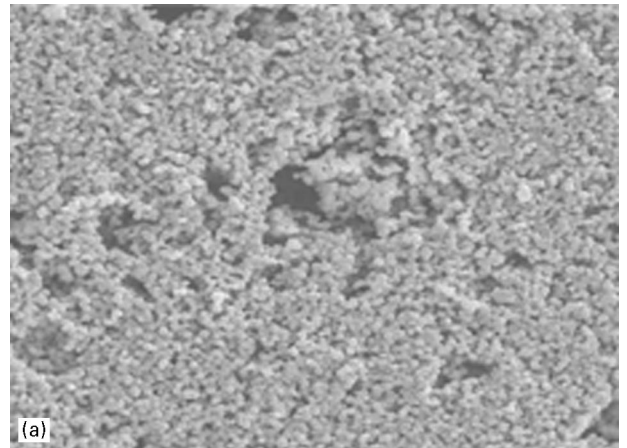Samples prepared by a mixture of $ZnCr_2O_4$–K_2CrO_4 (20%) and fired at a lower temperature (about 1000 °C) contained potassium (revealed by EDX) at both grain (solid line) and grain-boundary (dashed line) regions. Comparing typical EDX spectra

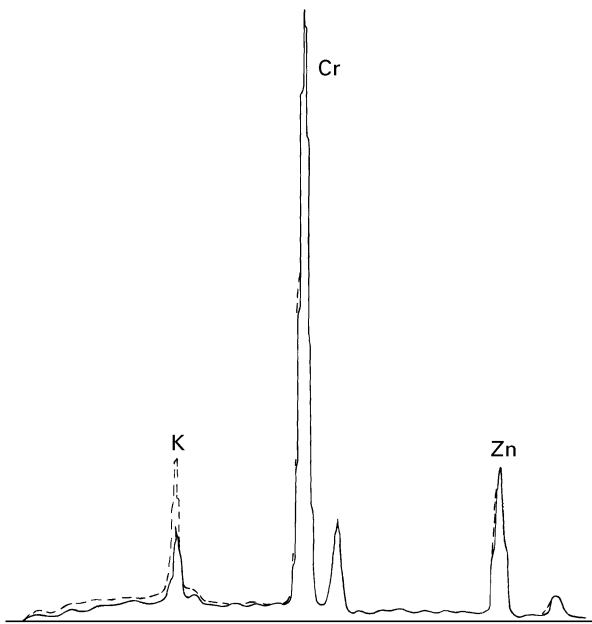*Figure 6* Typical EDX spectra taken from a sample prepared using $ZnCr_2O_4$–K_2CrO_4 (20%) followed by a firing at 1000 °C for (a) grain (solid line) and (b) grain boundary (dashed line).

Figure 7 Resistance-humidity characteristics of the sample produced using the starting material of $ZnCr_2O_4$–K_2CrO_4 (20%).

for grains and grain boundaries as is shown in Fig. 6 revealed that the potassium content of grain boundaries was typically almost twice as much as that of the grains.

These results suggest the incorporation of potassium atoms in the lattice and the formation of a potassium-rich phase as a liquid phase to assist the binding of
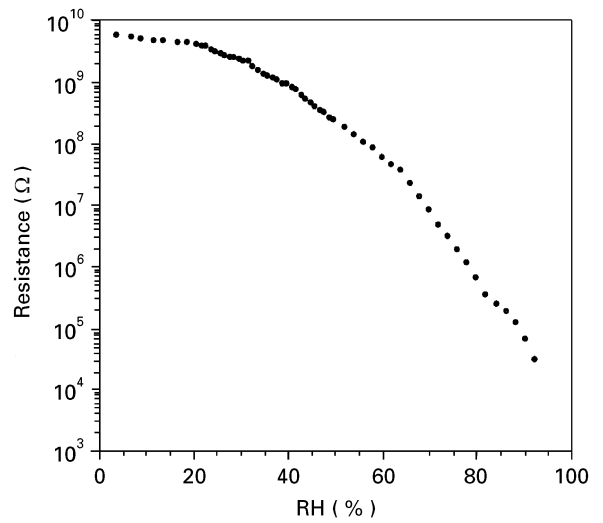
the grains together, which results in higher mechanical strength of the ceramic bodies. The conclusion, therefore, is that potassium compounds afford a binding action and act as a good sintering aid. A well developed microstructure with enhanced grain growth was achieved by incorporating 20% potassium carbonate as a sintering aid to $ZnCr_2O_4$–K_2CrO_4 mixture fired at 920 °C for 1 h, Fig. 5b. Some indication of twinning processes was observed for larger grains.

Fig. 7 shows the typical humidity characteristics of the sample at 22.5 °C obtained from $ZnCr_2O_4$–

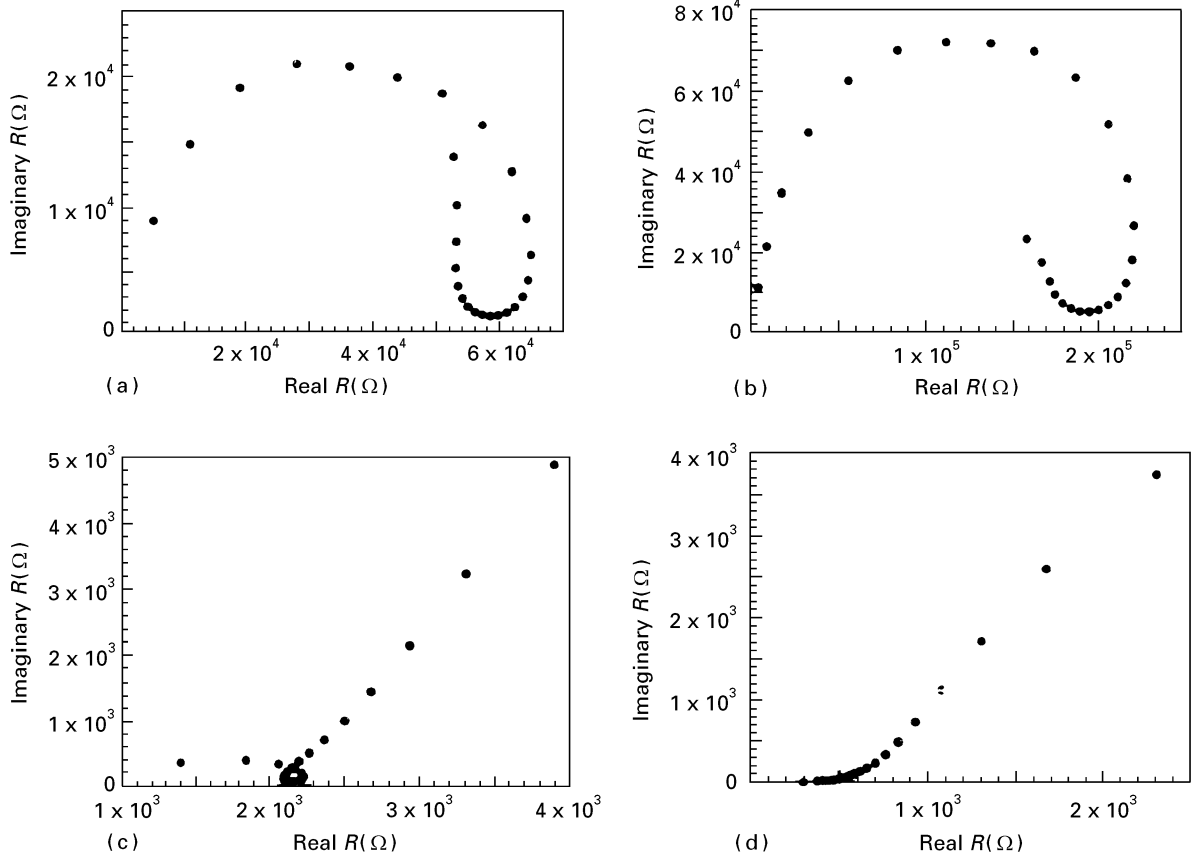*Figure 8* The complex a.c. impedance spectra of $ZnCr_2O_4$–K_2CrO_4 (20%) sample for different relative humidities; (a) 10%, (b) 22%, (c) 33%, and (d) 93%.

K$_2$CrO$_4$ (20%) starting material. The resistance has changed as a logarithmic function with increasing humidity. However, the samples prepared using K$_2$CrO$_4$ (30%) in ZnCr$_2$O$_4$ did not show any significant differences in the resistance versus humidity characteristics. Hence, it may be concluded that increasing the molar percentage of K$_2$CrO$_4$ in the starting material does not result in a higher sensitivity to humidity.

In order to increase the conductivity, CuO was introduced as a low percentage additive. The values of the resistance changed by about one order of magnitude at low humidities. However, the resistance values at higher humidity values remained almost the same as those of the undoped ceramics.

Complex a.c. impedance measurements of ceramic bodies at room temperature were performed under various relative humidities. Fig. 8 shows the results for a typical ceramic sample at 10, 22, 33 and 93% relative humidities. A semicircle characteristic of an *RC* equivalent circuit is present on all spectra, together with a so-called pseudo-inductance loop at lower humidity levels which has been previously associated with the formation of adsorbed species on the surface [18]. It was found, however, that this was strongly dependent on the formation of oxide layers at terminal electrodes. Apart from this problem, these kinds of complex impedance plots may be well modelled by an equivalent circuit associated with a network of resistors together with series capacitors, which was first proposed by Jonscher [19]. It can be assumed that such an equivalent circuit model of the sensor under these moist conditions may represent physical significance of the model to a diffusion process.

4. Conclusion

The ZnCr$_2$O$_4$–K$_2$CrO$_4$–CuO system once calcined, compacted and sintered under proper conditions can be used as a ceramic humidity sensor. Solid state reaction between zinc oxide and chromite oxide at elevated temperatures proved to be capable of producing monophase ZnCr$_2$O$_4$–K$_2$CrO$_4$ with or without CuO being added as a sintering aid, and the beneficial effect of potassium carbonate both as sintering aid and the enhancing humidity response agent was proved. The fired ceramic bodies, which proved to be mainly constructed from ZnCr$_2$O$_4$ spinel grains, were porous. The humidity characteristics of the sensor showed that the resistance decreased as a logarithmic function with increasing humidity. A network of resistors together with series capacitors is suggested for an equivalent circuit. Such an equivalent circuit model of the sensor under these moist conditions indicates a diffusion process.

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