

## ZnCr<sub>2</sub>O<sub>4</sub> 'in NEM ALGILAMA DAVRANIŞININ K<sub>2</sub>CrO<sub>4</sub> EKLENEREK GELİŞTİRİLMESİ

N. KAVASOĞLU<sup>1</sup>, M. BAYHAN<sup>2</sup>, S. KAVASOĞLU<sup>1</sup>

<sup>1</sup> Hacettepe Univ., Müh. Fak., Fizik Müh. Bölümü, Beytepe, Ankara

<sup>2</sup> Muğla Üniv., Fen Edeb., Fak., Fizik Bölümü, Kötekli, Muğla, Tel: 252 2111592, E-mail:mbayhan@mu.edu.tr

### ÖZET

Spinel ZnCr<sub>2</sub>O<sub>4</sub> seramiğine çeşitli yüzdesel oranlarda potasyum kromatla yapılan katkılandırmanın neme karşı davranışı ile ilgili etkileri çalışılmıştır. Nümuneler arasında sadece %20 K<sub>2</sub>CrO<sub>4</sub> içeren ZnCr<sub>2</sub>O<sub>4</sub> seramik sensörün %25 ile 90 arasında değişen göreceli nem (*RH*) aralığındaki *d.c.* direnci, üç merteye değişim gösteren üstel bir davranış sergilemiştir. Yük iletiminin esasen protonik olduğu ve iletimin tane yüzeylerinde soğurulan ince su tabakaları arasından metal kontaklara doğru yapılan yük transferi ile kontrol edildiği sonucuna varılmıştır. *a.c.* empedans ölçüm sonuçları ışığında RC paralel devresine seri bağlı sabit faz elemanlarından oluşan bir devre sensör eşdeğer devresi olarak önerilmektedir.

**Anahtar kelimeler** - Nem sensörü, ZnCr<sub>2</sub>O<sub>4</sub>-K<sub>2</sub>CrO<sub>4</sub>, Empedans spektroskopisi

## IMPROVEMENT OF THE HUMIDITY-SENSING BEHAVIOUR OF ZnCr<sub>2</sub>O<sub>4</sub> BY ADDITION OF K<sub>2</sub>CrO<sub>4</sub>.

### ABSTRACT

The effects of the addition of various percentages of potassium chromate as a sintering aid on the response to air moisture of ZnCr<sub>2</sub>O<sub>4</sub> spinel ceramic body were studied. Only the material containing 20% K<sub>2</sub>CrO<sub>4</sub> in ZnCr<sub>2</sub>O<sub>4</sub> exhibited an exponential behaviour to humidity, which shows about three orders change in the *d.c.* resistance over the relative humidity (*RH*) range between 25 and 90%. It was concluded that conduction is due mainly to protonic motion and is controlled through the thin layers of water, adsorbed on the surface of the grains, with charge transfer to the metallic electrodes. Based on *a.c.* impedance measurements, an equivalent circuit associated with a network of RC parallel circuit in series with constant phase elements (CPEs) has been suggested.

**Keywords** - Humidity sensors, ZnCr<sub>2</sub>O<sub>4</sub>-K<sub>2</sub>CrO<sub>4</sub>, Impedance spectroscopy



## 1. INTRODUCTION

The growing demand for the measurement and control of humidity in an industrial or household environment has led to considerable interest in the research devoted to the development of new materials for humidity sensors [1,2]. The relative humidity (*RH*), which is the ratio of actual vapour pressure at a particular temperature, is commonly used to measure humidity. Commercially developed sensor materials are either polymeric or porous ceramic, each of which have its own merits and provide a direct electric signal as a function of humidity in the atmosphere. Ceramic type of humidity sensors based on sintered oxides via solid state reactions are in general superior in performance to polymeric types, due to their high thermal stability and mechanical strength towards a wide range of operating temperatures, fast response to the changes of humidity, resistance to contaminants and irradiation and the ease with which it may be produced in thin film form [3]. However, they are to a certain extent not fully satisfactory in terms of the need for periodic thermal cycling to recover their humidity-sensitive properties. In recent years, nanostructured ceramic films have been identified as a optimal candidates for humidity sensing due to the high surface area exposed for adsorption of water molecules [4].

The principle of humidity measurement is the variations in the electrical conduction and capacitance due to water chemisorptions and/or capillary water conduction within the pores [5,6]. When adsorption starts on the clean oxide surface, a layer of hydroxyl groups is formed. The water vapour molecules are chemisorbed through a dissociative mechanism by which two surface hydroxyls per water molecule are formed. This layer, once formed is not further affected by exposure to humidity. Once the first layer is formed, subsequent layers of water molecules are physically adsorbed. Many more physisorbed layers will be joined as humidity gets higher. These physisorbed layers are easily and reversibly removed by decreasing the humidity. Physisorbed water molecules dissociate, because of the high electric fields in the chemisorbed water layer. The charge transport occurs when hydronium ions release a proton to neighbouring water molecules, which accepts it while releasing another proton and so on (Grotthuss's chain reaction). This proton moves freely along the water layer and thus determines the sensor conductivity [7]. Finally, at high humidity, liquid water condenses in the capillary pores, according to Kelvin's law, and electrolytic conduction occurs simultaneously with protonic transport.

Materials based on zinc chromite, as an example of a ternary metal oxide spinel have long been identified as a candidate for an active material in chemical sensing applications [8,9]. However, air moisture sensitive

ceramic sensors based on pure zinc chromite are rather poor in performance and as a result composites with TiO<sub>2</sub> or LiZnVO<sub>4</sub> have been studied instead [10]. Additionally, ceramic composites containing K<sub>2</sub>CrO<sub>4</sub> or ZnO in zinc chromite have been suggested as candidate materials for humidity sensing [11,12]. In this article, the response to relative humidity (*RH*) of porous ceramics with composition ZnCr<sub>2</sub>O<sub>4</sub>-K<sub>2</sub>CrO<sub>4</sub> prepared by solid state reaction at elevated temperatures, was studied.

## 2. EXPERIMENTAL PROCEDURE

Highest purity commercially available powders of ZnO and Cr<sub>2</sub>O<sub>3</sub> were used as precursors. Intimate mixture of ZnO:Cr<sub>2</sub>O<sub>3</sub> with a molar ratio of 1:1 was crushed in an agate pestle and mortar for 30 min. followed by calcination at temperatures ranging between 800 and 1100°C with a heating rate of 500°C h<sup>-1</sup> in a muffle furnace (Carbolite RWF12/5). The composition and the phase were assessed by X-ray diffraction patterns (Shimadzu XRD-600 diffractometer employing a Cu target with iron-filtered radiation of wavelength 1.5418Å).

The sensor materials were fabricated by adding in various percentages (by weight) of potassium chromate (K<sub>2</sub>CrO<sub>4</sub>) to the ZnCr<sub>2</sub>O<sub>4</sub>. The mixture was ground for 30 min and compacted into pellets (with a 13 mm in diameter and 1-3 mm in thick) at a pressure of 1-2 tons cm<sup>-2</sup>, which were then fired at a temperate of 1100°C for about 12 hours. The surface and fractured morphologies of the pellets were observed by scanning electron microscopy (Jeol JSM IC848). Elemental species present in the pellets were also analysed using energy dispersive analysis by X-rays (EDX).

The *d.c.* resistance as a function of relative humidity measurements were carried out using two point probe technique. To this purpose, a Keithley-236 source and measure unit was used. The samples were initially mounted in a custom built chamber, where the humidity was controlled by passing a carrier gas through water at predetermined rates. The relative humidity in the chamber was monitored using a Testo 625 reference humidity meter. Metallic contacts were made from gallium which was found to give Ohmic behaviour. The *a.c.* impedance measurements were performed using a Hewlett Packard HP 4192A impedance analyser over the



frequency range between 5Hz–13MHz, using an excitation signal of <50 mV amplitude.

### 3. RESULTS AND DISCUSSION

Although the diffraction peaks at  $2\theta_B$  ( $\theta_B$ : Bragg angle) angles of  $30.5^\circ$ ,  $35.9^\circ$ ,  $37.5^\circ$ ,  $43.5^\circ$ ,  $54.0^\circ$ ,  $57.5^\circ$ , and  $63.2^\circ$  obtained from the powder of  $2\text{ZnO}:\text{Cr}_2\text{O}_3$  after firing at temperatures between  $800\text{--}1100^\circ\text{C}$  for about 12 hours are associated with corresponding planes of  $\text{ZnCr}_2\text{O}_4$ , the peaks at  $2\theta_B$  angles of  $34.5^\circ$ ,  $47.7^\circ$ ,  $56.8^\circ$ ,  $68.1^\circ$ ,  $69.2^\circ$  are associated with ZnO and the peak at  $2\theta_B$  angle of  $31.9^\circ$  with  $\text{Cr}_2\text{O}_3$ . These results indicated that despite the stoichiometric ratio chosen to produce a single compound of  $\text{ZnCr}_2\text{O}_4$ , the formation of  $\text{ZnCr}_2\text{O}_4$  did not go to completion the residuals of both ZnO and  $\text{Cr}_2\text{O}_3$  which are evident in the X-ray patterns.

Conversely, the Bragg peaks in the X-ray diffractometer patterns from the powder of  $1\text{ZnO}:\text{Cr}_2\text{O}_3$  fired at  $800\text{--}1100^\circ\text{C}$  at  $2\theta_B$  angles of  $18.43^\circ$ ,  $30.33^\circ$ ,  $35.74^\circ$ ,  $37.38^\circ$ ,  $47.74^\circ$ ,  $53.91^\circ$ ,  $57.47^\circ$ ,  $63.12^\circ$ ,  $71.63^\circ$  and  $74.70^\circ$  all correspond to planes of  $\text{ZnCr}_2\text{O}_4$  implying the formation of a monophasic cubic body (see Figure 1). The Miller indices and the Bragg peak ratios estimated are in detail reported elsewhere [13]. The lattice constant,  $a_0$ , derived from each diffraction peak was plotted against  $2\theta / \sin \theta$  (not shown here) and the extrapolation of the data to  $\theta = \pi/2$  yielded the lattice constant as  $3.728\text{\AA}$  [14].

Figure 2 shows typical secondary electron micrograph of the as-fired surface of  $\text{ZnCr}_2\text{O}_4\text{--K}_2\text{CrO}_4$  (20%) sample fired at  $1000^\circ\text{C}$  for about 12 hours. The ceramic body was porous in nature with a grain size about  $1\text{--}2\text{ }\mu\text{m}$  and a great number of pores, indicative of volatilization of one or more of the components (probably, potassium) at high temperatures. Moreover, EDX scans over the regions of grain and grain boundaries revealed that potassium content of grain boundaries was significantly higher as compared to that of the grains as is shown in the Figure 3.

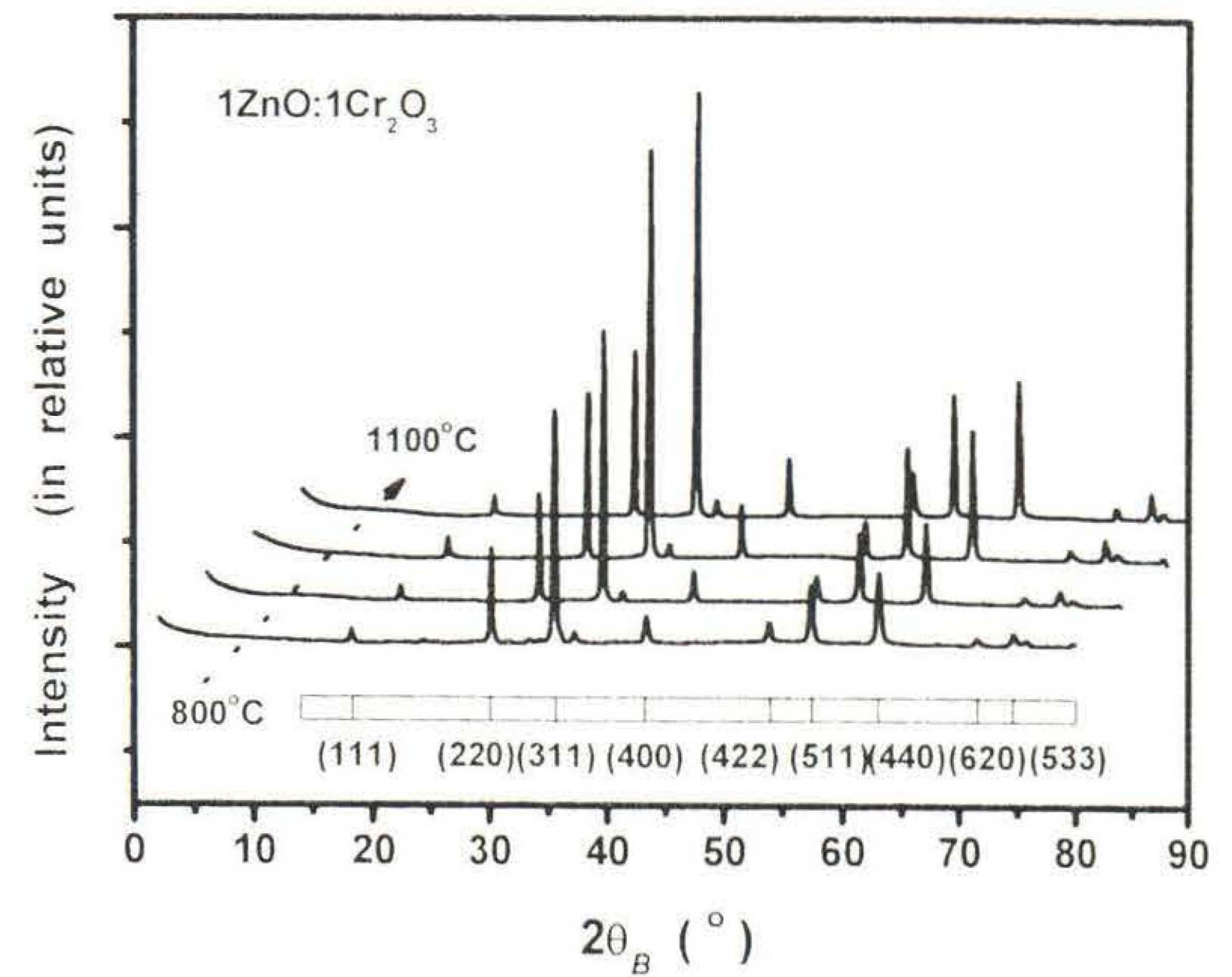


Figure 1. X-ray diffraction patterns of  $1\text{ZnO}\text{--}1\text{Cr}_2\text{O}_3$  powder obtained after firing in the range  $800\text{--}1100^\circ\text{C}$  for about 12 hours in air.

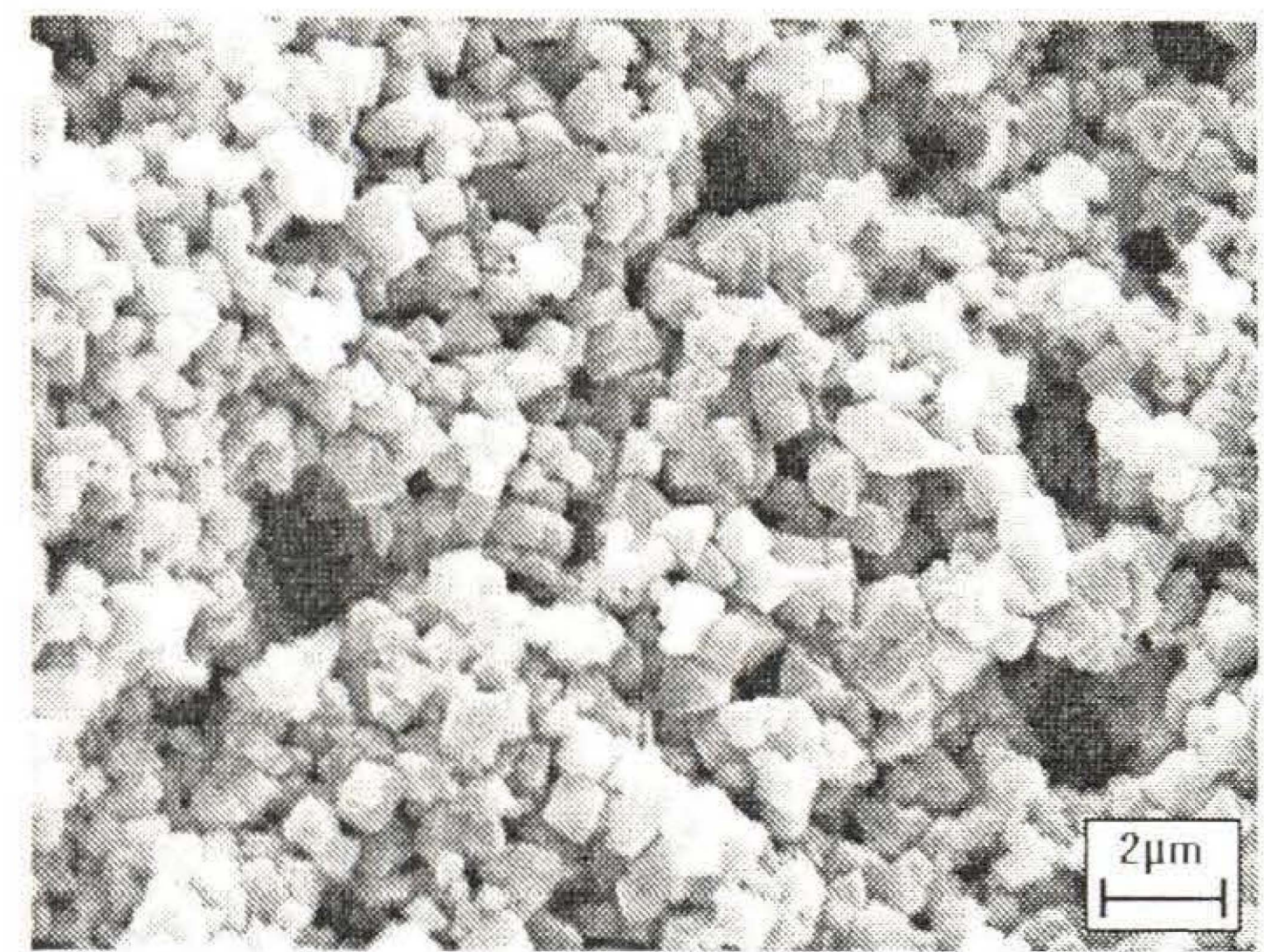


Figure 2. The as-fired surface secondary electron micrograph of  $\text{ZnCr}_2\text{O}_4\text{--K}_2\text{CrO}_4$  (20%) sample sintered at  $1000^\circ\text{C}$  for about 12 hours.

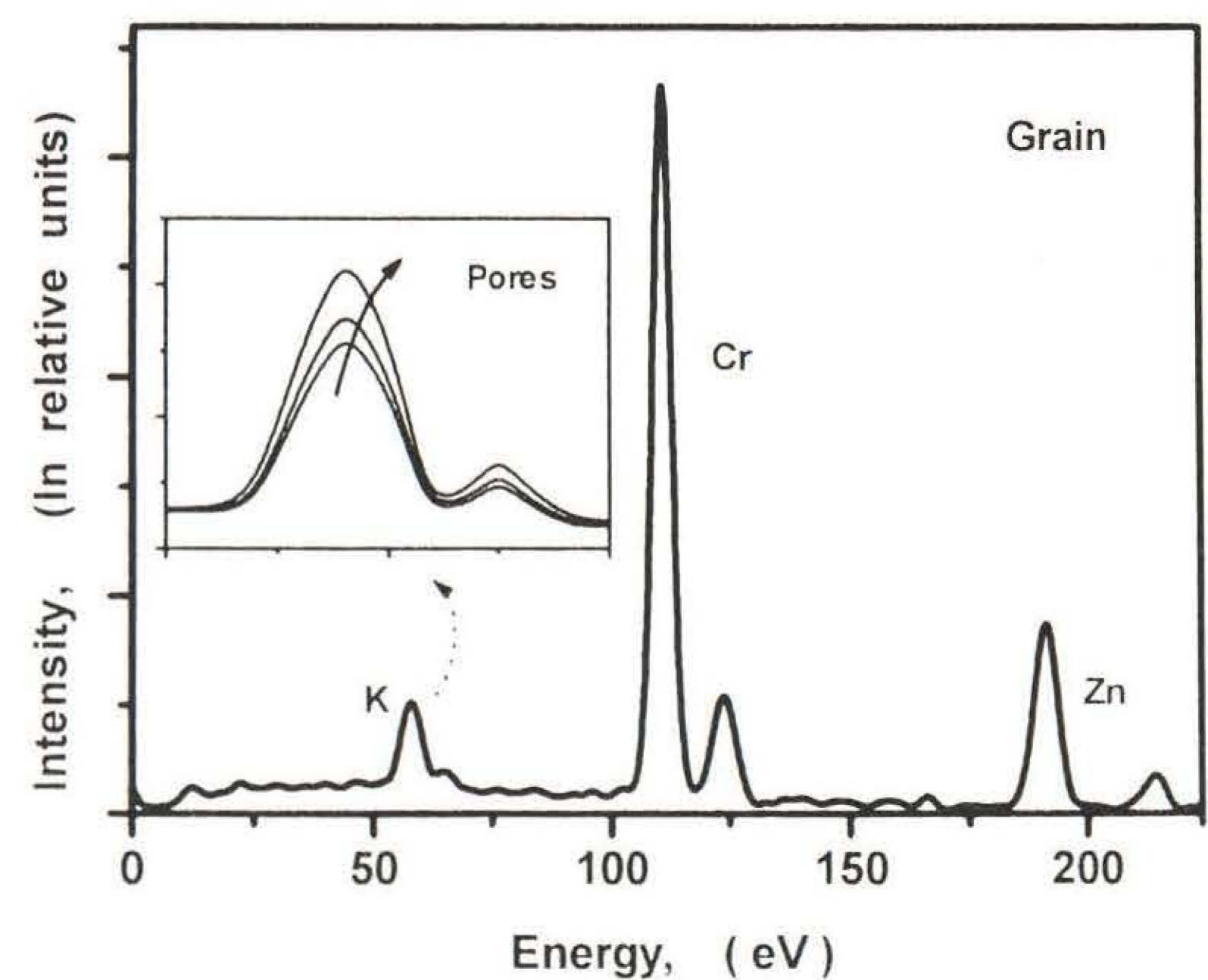
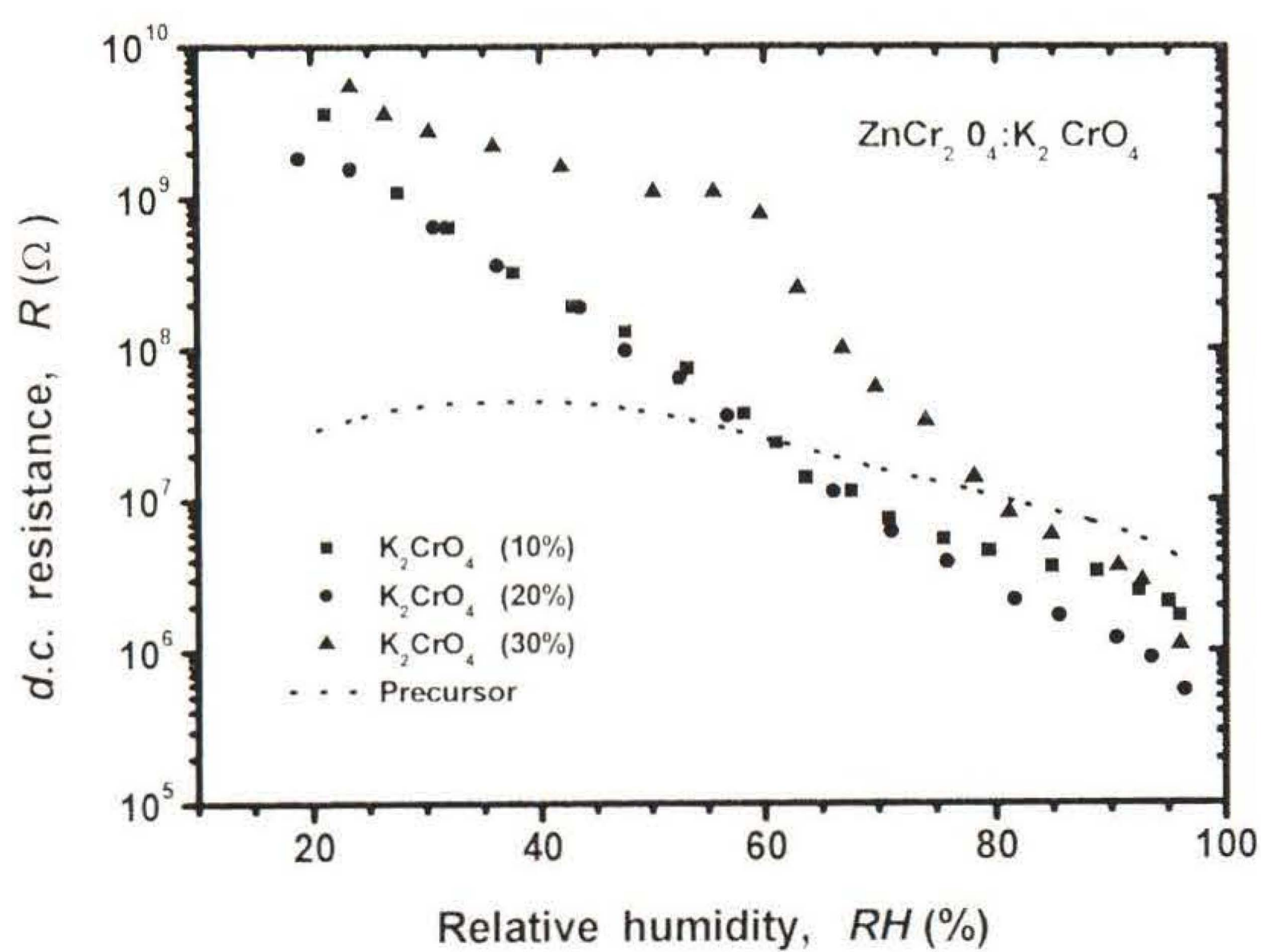


Figure 3. Typical EDX spectra recorded from the pellet containing 20%  $\text{K}_2\text{CrO}_4$ . In the inset the potassium peak is replotted with respect to increasing percentages of  $\text{K}_2\text{CrO}_4$ .



Figure 4 shows *d.c.* resistance as a function of relative humidity for ZnCr<sub>2</sub>O<sub>4</sub>-K<sub>2</sub>CrO<sub>4</sub> ceramic system at various percentages of potassium chromate. The *d.c.* resistance was a strong function of the humidity for all compositions, decreasing by several orders of magnitude upon increasing humidity, although only material containing 20% K<sub>2</sub>CrO<sub>4</sub> displayed an exponential behaviour as function of *RH*. This is broadly consistent with what is normally reported and is generally understood in terms of through an adsorbed water phase [15,16]. The conduction mechanism concluded from the evidence given above is ionic and that protons are probably the dominant charge carriers [17]. A least-squares best fit to the values of *d.c.* resistance versus relative humidity for the sample containing 20% K<sub>2</sub>CrO<sub>4</sub> yielded  $\log(R) = 10.22 - 0.05(RH)$ , (for *R* in ohms and *RH* in %).

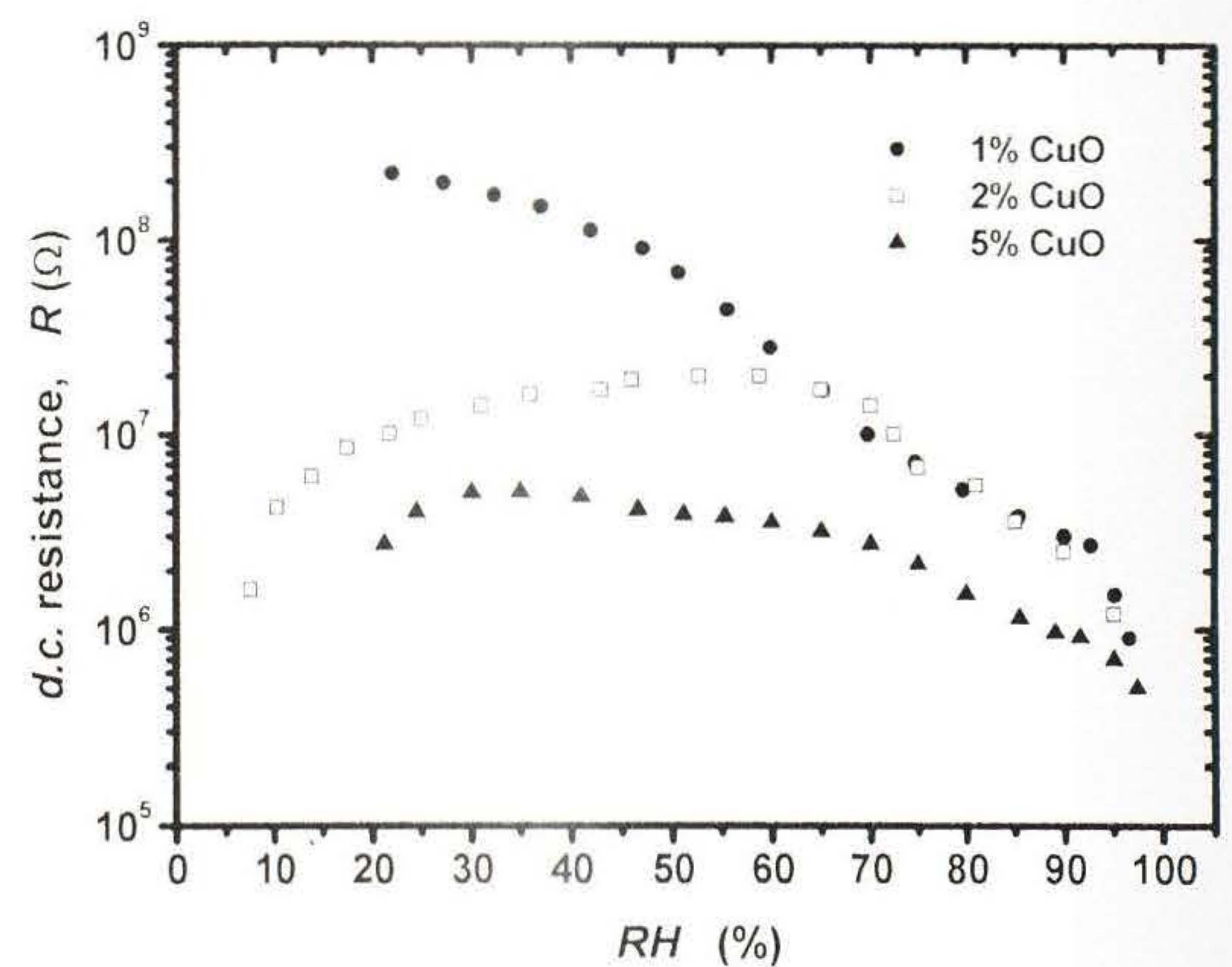


**Figure 4.** *d.c.* resistance versus relative humidity characteristic of ZnCr<sub>2</sub>O<sub>4</sub>-K<sub>2</sub>CrO<sub>4</sub> ceramic system at various percentages of potassium chromate.

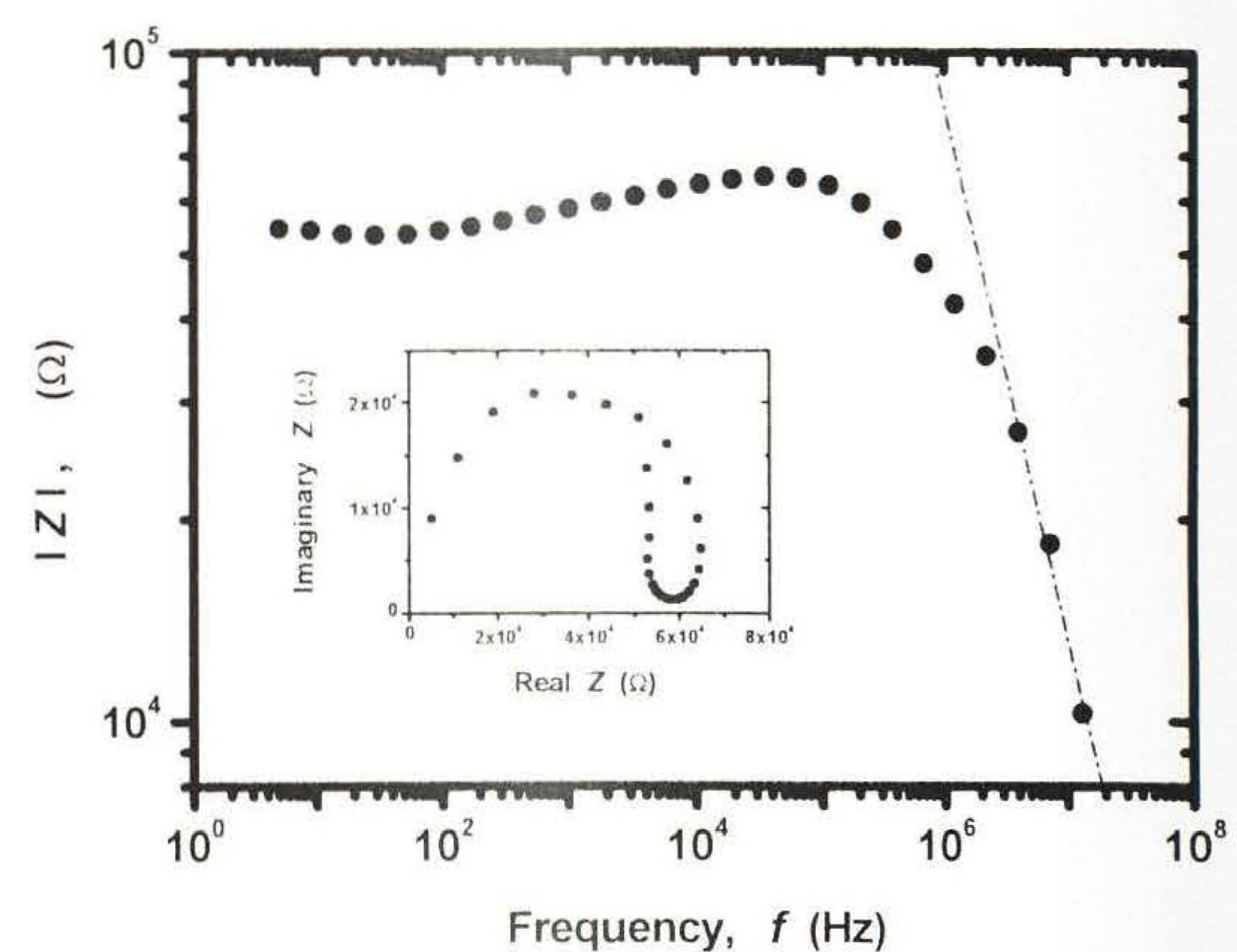
In an attempt to increase conductivity, CuO was added to some samples containing 20% potassium chromate. The corresponding *d.c.* resistance versus relative humidity characteristics are given in Figure 5 and reveal that the addition of CuO had a dramatic effect on the humidity dependence. The addition of only 1% CuO reduced the resistance at low humidity (*RH* < 40%) by approximately an order of magnitude, while at higher humidity it appeared to have no effect. Increasing the level of CuO doping not only reduced the low humidity resistance even more, it reversed the slope of the characteristic, so that for *RH* < 40% resistance increased with increasing humidity. The reasons for this reversal of slope are not at present clear.

The variation of the magnitude of impedance ( $|Z|$ ) versus frequency (*f*) for the sample containing 20% K<sub>2</sub>CrO<sub>4</sub> (see Figure 6) under a dry humid ambient shows a high frequency fall-off of  $|Z|$  as  $f^{-0.8}$ , which is due

mainly to capacitive effects within the system from cables, the equipment input capacitance and physical geometry of the contacts. At frequencies below 10<sup>5</sup> Hz, magnitude of impedance varies very slowly with *f*, indicating that resistive-type behavior is more dominant. This type of behavior is reported widely in similar ceramic systems [18,19]. The Cole-Cole plot of complex impedance (i.e.,  $Z''$  versus  $Z'$  where  $Z''$  and  $Z'$  correspond to complex and real part of the impedance) is also displayed in the inset of Figure 6. It consists of a depressed semicircle corresponding to a parallel combination of a *d.c.* conductance and a slightly dispersive capacitance together with a so-called pseudo-inductance loop [20].



**Figure 5.** *d.c.* resistance versus relative humidity characteristic of the ZnCr<sub>2</sub>O<sub>4</sub>-K<sub>2</sub>CrO<sub>4</sub> (20%) ceramic system at various percentages of CuO.



**Figure 6.** A plot of  $|Z|$  versus frequency for the sample containing 20% K<sub>2</sub>CrO<sub>4</sub> under 22% *RH*. In the inset Cole-Cole plot of the impedance measured for this sample is also shown.



A home-made ZnCr<sub>2</sub>O<sub>4</sub>-K<sub>2</sub>CrO<sub>4</sub> (20%) ceramic humidity sensor was also satisfactorily calibrated using a reference humidity sensor SHT75, obtained from Sensirion. To that aim, a novel circuitry consisting of a 12 bit A/D, SHT75 interface circuit and I to V bridge amplifier was developed. The typical sampling rate of developed A/D circuit is about 10 kHz and it works 0-5 V range with an approximately 1.25 mV resolution. The circuit is controlled by a Qbasic routine on the PC which allows to acquire one hundred data per second. The SHT75 is a single chip multi sensor module including a capacitive polymer humidity sensing element and a band gap temperature sensor.

#### 4. CONCLUSION

Air-moisture sensitive ZnCr<sub>2</sub>O<sub>4</sub> ceramic body produced from the solid state reaction between zinc oxide and chromite oxide at elevated temperatures displayed a rather poor sensing performance to humidity. However, the resistance as a function of relative humidity showed a strong dependence, decreasing over several orders of magnitude with increasing humidity being a smooth exponential in the case of the sample prepared using K<sub>2</sub>CrO<sub>4</sub> (20%) in ZnCr<sub>2</sub>O<sub>4</sub>. The addition of CuO resulted in an increase in the conductivity but had a deleterious effect on the humidity. These results indicate that ZnCr<sub>2</sub>O<sub>4</sub>-K<sub>2</sub>CrO<sub>4</sub> system once calcined, compacted and sintered under proper conditions has potential use as an active material for the humidity sensors.

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