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Complex semiconducting ceramic

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Abstract

Complex semiconducting ceramic compositions were prepared. Structure, crystallite morphology, hardness and electrical conduction were investigated. After annealing at 150 °C a distinct crystalline phase was obtained and the ceramic became compact, hard, of higher resistivity, while preserving the basic semiconducting properties

Keywords: Electrical conductivity; Mixed oxides; Hardness

1. Introduction

A continuously growing interest was paid in the last years to oxide ceramics and especially to the novel and enhanced properties of nanostructured ceramics.[1] Interest has been focused on a variety of synthetic nanostructured materials with the anticipation that their properties will be different from, and often superior to those of conventional materials that have phase or grain structures on a coarser size scale.[2]

Another idea in the field of oxide ceramics is to design ceramic bodies by using a number of atomic species in order to control the growth of crystallites and to determine the extent of the grain boundaries in the material.

This paper describes the preparation and properties of new complex ceramic body exhibiting a distinct phase from the crystallographic point of view, although the presence of a high number of species prevents the ordered arrangements of the cations in a simple basic unit cell.

2. Experimental

A complex ceramic body was prepared by the standard ceramic method starting from a mixture of powders of several types of compounds in a pre-established cation proportion. High purity (p.a.) raw materials were used in the preparations. The aim was to introduce glass network former materials (such as silicon and boron oxides) for improving the sintering and mechanical properties and a mixture of cations for getting good electrical properties for various applications.

Twenty-five different compounds of elements with various cation radii (see Fig. 1) have been mixed with methyl alcohol and thoroughly ground in a planetary mill for 2 h. The cation composition is: B, Mg, Al, Si, Ca, Ti, V. Cr, Mn, Fe, Co. Ni, Cu, Zn, Sr, Zr, Nb, Sn, Ba, La, Ce, Nd, Ta, Pb and Bi in equal cationic proportion. Calcium, strontium, barium and manganese were introduced under the form of carbonates; copper, nickel and cobalt were introduced as hydrocarbonates and iron as FeOOH. Boron was introduced as boric acid, H_3BO_3. The other elements were introduced in the form of oxides.

All the cation species in the mixture were in rigorously equal amount (4 at.%). The slurry containing the mixture was gently dried in an oven at 150 °C. The fine, yellow powder thus obtained was pre-fired at 850 °C for 1 h and then the powder was again ground for 2 h. Disc shaped pellets were pressed in a steel dye at 77.6 MPa. Finally, pellets of 1 cm in diameter and 3 mm in thickness were put on ZrO_2 plates and rapidly fired at various temperatures: 1000°C, 1100, 1300, 1400 and 1500 °Cfor a half h in air. The highest temperature is situated in the vicinity of the melting point for this ceramic. The resulting samples have been polished and

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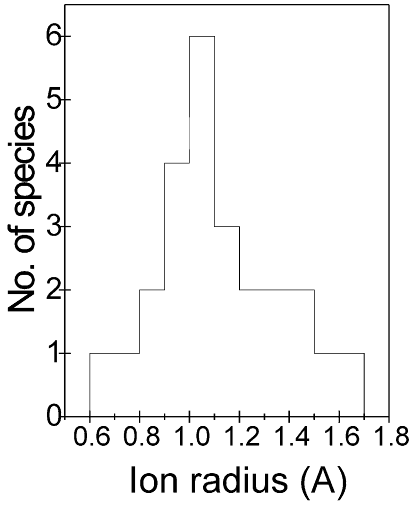


Fig. 1. The distribution of the ionic radii of the cations which build the complex ceramics (the radii were estimated after Chua).[3]

investigated by X-ray diffraction, density and hardness measurements, electrical conduction in a large temperature range, thermoelectric effect and magnetoresistance.

3. Results

The pellets fired at high temperatures exhibit a black colour. X-ray diffraction diagrams show the formation of only two crystalline phases. The main phase is a cubic (fcc) phase. The mean size of the crystallites, as determined from the (111) peak profile is around 200 nm, near to the upper limit of sensitivity of the X-ray method. This size, determined on the sample fired at 1100 °C is enlarged for higher temperatures of treatment. The minor phase is a srinel-type phase. In the sample fired at 1000 °C the amount of the minor phase estimated from the X-ray diffraction peaks is under 10 at.% and in the sample fired at 1300 °C is of ~4–5 at.%. Only traces of spinel phase have been detected on the X-ray diagram of the pellets fired at 1500 °C. Table 1 shows the values of the lattice parameters for the crystalline phases observed in this complex ceramics.

In order to show the crystallite morphology and size, thermal etching was made on polished ceramic samples. The samples were rapidly fired for 5 min at 1200 °C. The optical microscopy pictures (Fig. 2 a–c) show the morphology and size of the crystallites after firing the samples at 1100, 1300 and 1400 °C, respectively. After the firing (at 1100 °C) a uniform distribution of small size crystallites can be observed (Fig. 2a). Two type of sizes were evidenced by electron microscopy: 0.5–0.6 μm and 1 μm, corresponding to two cubical phases, as evidenced, also, by SAED (selected area electron diffraction). After firing at 1300 °C large size crystallites with (~20 μm average size), of cubical symmetry, dominate the ceramic sample (see Fig. 2b). SAED measurements show a structure with the unit cell parameter approaching that determined by X-ray diffraction. Fig. 2c shows what happens with the crystallites when the ceramics is fired at 1400 °C. Large size crystallites with size ~30–50 μm are evidenced. The crystallites exhibit black colour and represent the crystallite cubic phase observed by X-ray diffraction. Superlattice formation with the doubling and tripling of the unit cell has been observed by SAED in the ceramics fired at 1500 °C.

Table 1
Lattice parameters of the crystalline phases

Firing temperature (°C)	Lattice parameter a(Å)	
	Main phase (fcc)	Spinel phase
1100	5.346	8.452
1300	5.278	8.363
1500	5.240	–

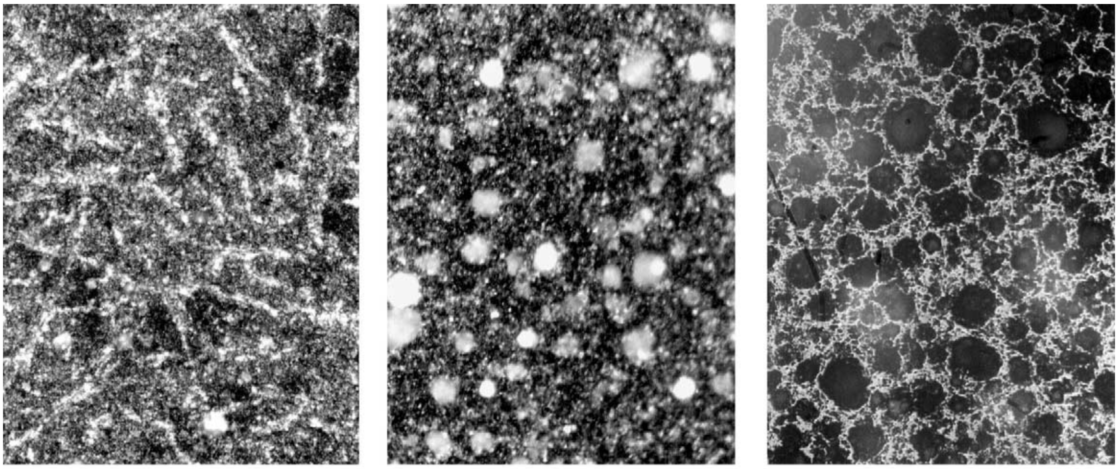
The density of the ceramics after firing was determined by the Archimedes method. While the density of the ceramics fired at 1100 °C is 5.83 g/cm^3 (the ceramic look dense when investigated by optical microscopy), the densities of the samples fired at 1300 and 1400 °C are 5.63, 5.41 g/cm^3, respectively. The ceramics prepared at 1400 °C presents a shining surface when the pellet in the form of a disk is polished.

The microhardness (Vickers hardness) has been determined by a PMT-3 apparatus provided diamond indentation prism. The hardness increases with the firing temperature. For 1100 °C the hardness of the ceramics is 600 HV, for 1300 °C is 700 HV and for 1500 °C the hardness reaches 850 HV.

The ceramics are semiconducting. The electrical conduction plots $\log(\sigma)\sim f(1/T)$ show three linear domains of different activation energy (Fig. 3). Table 2 shows the electrical data for the measured samples.

The calculation of the thermal coefficient of the resistivity for the temperature region around 200–250 °C gives the following results: for 1100 °C firing temperature is 1%/K, for 1400 °C is 1.2%/K and for the highest firing temperature is 1 .4%/K. These values suggest to use such material for thermistors. The thermoelectric effect is quite high in this complex ceramics. Seebeck coefficient for the temperature range 200–300 K is as = 100 μV/K for the sample fired at 1100 °C.

An important feature of this ceramics is the magnetoresistive effect. The sample resistivity exhibits a nearly linear dependence on the magnetic induction, B, in the range of magnetic induction (0– 0.8 T) used in the measurement, in contrast with the common behaviour of semiconducting samples magnetoresistivity. The magnetoresistance coefficient measured on the polished discs made from the ceramics fired at 1500 °C is $(\triangle\rho/\rho)/\triangle B\sim 10$.



(a) (b) (c)

Fig. 2. SEM micrographs on ceramic powder fired at various temperatures for 2 h: (a) 1100 °C, (b) 1300 °C and (c) 1400 °C. Magnitude:—20μm.

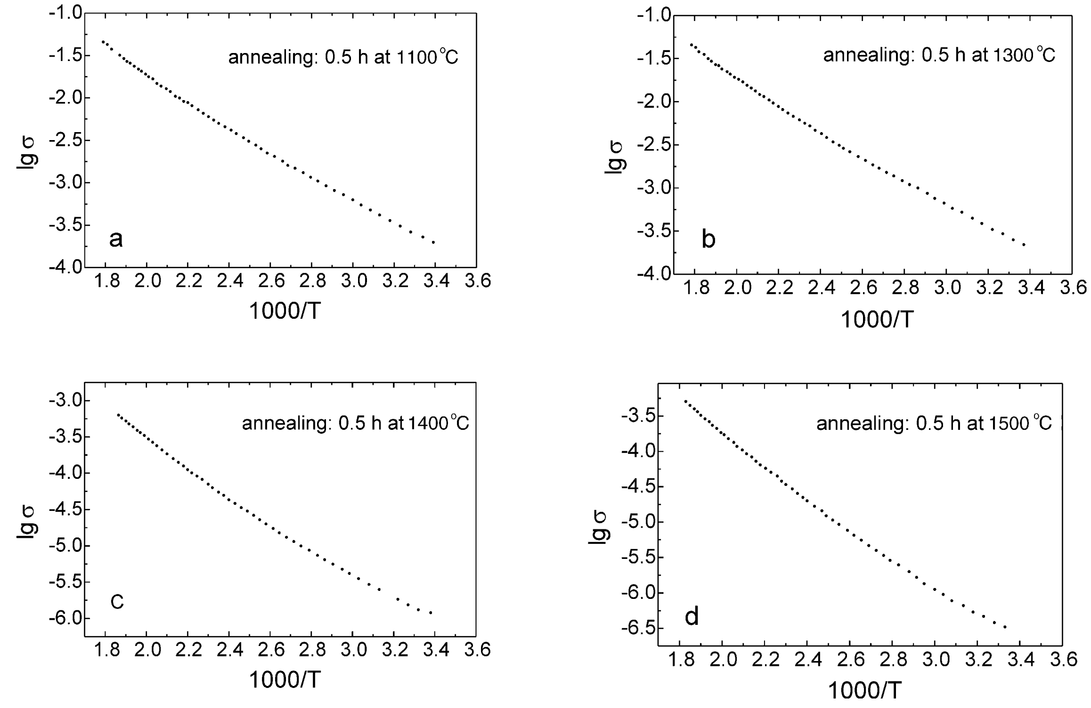


Fig. 3. Arrhenius plots of the electrical conductivity for complex semiconducting ceramics.

Table 2
Electrical data for complex semiconducting ceramics

Firing temperature(°C)	Activation energy (eV)			Resistivity (Ω.cm)
	20–120 °C	120–200 °C	200–300 °C	
1100	0.26	0.30	0.35	6.9×10^{5}
1300	0.26	0.31	0.33	6.2×10^{5}
1400	0.30	0.39	0.39	1.2×10^{8}
1500	0.30	0.45	0.45	4.2×10^{6}

4. Discussion

The complex semiconducting ceramics prepared by us exhibits interesting structural and physical properties, which deserve a possible use in applications. Although a high number of cations of a large radius distribution take place in the formation of the crystalline lattice, nevertheless the overall lattice is cubical. Only traces of a second spinelic phase are observed in the sample fired near to the melting temperature. This means that the lattice of the ceramics is chemically disordered. This disorder accommodates well various types of cations. After our knowledge no such structure has been reported till now.

The density of the sintered ceramics decreases slowly when the firing temperature is raised from 1100 to 1400 °C. The maximum density is reached at 1500 °C when melting of the composition occurs (the Fig. 2c). The unusual decreasing of the density up to firing temperature of 1400 °C may be due to the profound change in the ratio of the crystalline phases in the ceramics, because in all the cases no pores have been detected in the samples.

The ceramics is hard and semiconducting. The sinterability is similar to the best quality commercial PLZT ceramics.[4] Clustering of some magnetic ions in the lattice is possible. The possibility to have giant magnetoresistance in nanochemical materials is of considerable interest both at a fundamental level and in applications to magnetic recording technology.[5] Detailed ultramicroscopic investigation will be also of interest. Spin dependent tunneling or tunnel magnetoresistance is an other important effect in ferromagnetic-insulator structure.[6] Such effect appears when the ferromagnetic aggregates are embedded in an insulating matrix. The clustering in the material is, therefore, important and further investigations by grazing incidence small-angle X-ray scattering will be without any doubts rewarding.

5. Conclusions

A disordered lattice of cubical symmetry (fcc) characterizes the new complex composition prepared by standard ceramic technology. This special structure exhibits interesting properties. The material is hard, semiconducting and exhibits a large magnetoresistive effect. Superlattice formation in this type of ceramics seems to be an outstanding feature of this ceramics. Rapid firing and the presence of glass forming elements as silicon and boron ensure an excellent sinterabiity of the material.

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