Ceramic powder for thermoelectric, thermoresistive and superconducting materials

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Abstract

Complexe copper, cobalt and manganese oxide to make the great potential as bulk materials or thick and thin films for the realisation of functional materials. Cuprate shows superconducting properties, cobaltites due to high thermoelectric power and manganites to be capable to thermo- and magnetoresistance.

The synthesis of powder of these compounds with good quality (purity, desired stoichiometry, narrow particle size) is still a major concern of high-temperature chemistry. Powders of the electroceramic materials were prepared using solid-state reaction methods in more step processes. The raw materials were a mixed in solid state or in liquid state, a calcined at 750-800 °C, and a presintered at 800-850 °C. Raw powder were compacted by dies or isostatically pressing. The densification of the compacts was carried by sintering at high temperatures. Important aspect to consider is the grain size and growth, the densification rate inhomogeneities and second phase distribution. For all electroceramic materials play chemistry and physic of grain boundary significant role. The relation between microstructure and functionally properties is crucial.

Samples of cuprates ($YBa_2Cu_3O_{7-\delta}$ and $Bi_2SrCa_2Cu_2O_{8+\delta}$), cobaltites ($Na_xCoO_2$, $Ca_2Co_2O_5$), manganites ($(Cu,Co,Ni,Mn)_3O_4$ and $(Ca,La)MnO_3$) were prepared and characterised [1-4]. Microstructure was examined for non polished surface of sample after compacting and sintered of powders by use of optical and scanning electron microscopes. The sintered pellets were measurement on an electrically properties. The characteristic curves resistivity vs. temperature for these materials is shows.

Introduction

Thermoelectric materials are attractive for many electrical energy generation and cooling applications.

Conventionally thermoelectric materials (e.g. Bi_2Te_3, PbSe, Si-Ge, $FeSi_2$, skutterudites) have been shown to have relatively high thermoelectric efficiences ($S \approx 0,2$ mV/K), these materials must be protected from oxidation because of their low chemical stability in air. In this sense, the promising and the best candidate thermoelectric materials are oxide materials.

The renewed interest in doped oxide materials with perovskite-like and layred structures has been propelled by two developments: the ability to synthesize high quality ceramics, and the discovery of some phenomenons as giant magnetoresistance, thermoelectric and termoresistive effect, and superconductivity in cuprates, cobaltites and manganites.

The doped manganite perovskites are refered to as GMR materials, layerd cobaltites to as thermoelectric materials, spinel-structured manganites or nickelates to as thermistor and perovskite-like cuprates to as superconductors.

Tab.1 Oxide materials for electroceramic applications

compounds	formula	mixed valence	properties	application
alkaline-earth doped perovskite-type oxide with mixed valence				
cobaltite	$(La,A)CoO_{3-\delta}$ A=Sr, Ca	Co^{3+}/Co^{4+}	ferromagnetic	magnetoabsorption
manganite	$(La,A)MnO_{3-\delta}$ A=Sr, Ca, Ba	Mn^{3+}/Mn^{4+}	GMR	magnetoresistance
manganite	$CaMn_{1-x}Ru_xO_{3-\delta}$	Mn^{3+}/Mn^{4+} Ru^{5+}	semiconductiv	thermoelectric (+)
plumbate	$(Ba,Sr)PbO_3$	Pb^{2+}/Pb^{4+}	semiconductiv	thermoelectric (+)
rare-earth perovskite-type oxides with mixed valence				
cuprate	$YBa_2Cu_3O_{7-\delta}$ $Bi_2Sr_2CaCu_2O_{8+\delta}$	Cu^{2+}/Cu^{3+} Cu^{+}/Cu^{2+} Bi^{3+}/Bi^{5+}	conductiv	superconductor
doped cuprate, oxygen-poor	$(Y,K)Ba_2Cu_3O_{7-\delta}$ $YBa_2(Cu,Mn)_3O_{7-\delta}$ $Bi_2Sr_2CaCu_2O_{8+\delta}$ - glas	Cu^{+}/Cu^{2+}	semiconductiv	thermoelectric (-)
layered type cobaltites with mixed valence				
cobaltite	Na_xCoO_2 $Bi_{2,2-x}Pb_xSr_2CoO_y$ $Ca_{3-x}Bi_xCo_4O_9$ $Bi_{1,5}Pb_{0,5}Ca_{2-x}M_xCo_2O_{8-\delta}$	Co^{3+}/Co^{4+}	metallic or semiconductiv	thermoelectric (+)
intercalated cobaltite	$Na_xCoO_2*1,5H_2O$	Co^{3+}/Co^{4+}	metallic	superconductor
spinel-structured oxides with mixed valence				
cobaltite	$NiCo_2O_4$	Co^{2+}/Co^{3+} Ni^{2+}/Ni^{3+}	resistiv	thermistor
cobaltite	$Ni_xMn_{1-x}Co_{2-2x}O_4$	Co^{2+}/Co^{3+}	semiconductiv	thermoelectric (-)
manganite	$(Cu,Ni,Co)Mn_2O_4$	Mn^{2+}/Mn^{3+}	resistiv	thermistor
manganite	$Li_{1+x}Mn_{2-x}O_4$	Mn^{3+}/Mn^{4+}	semiconductiv	thermoelectric (-)

(+) good, (-) small

Ceramic oxide materials has been considering with regard to thermoelectric application. These materials shows high crystallographic anisotropy and different electrical and thermal properties with crystallographic directions. These structure to be constructed by two-dimensional layers with the edge-linked metal-oxide octahedra

Layers of metal-ions between metal and oxide ions forms an triangular or pyramidal lattice
Electronically and structurally two-dimenssional materials can be good thermoelectrics
Four groups of ceramic materials to come into consideration

1. perovsikte-like structure as Manganate $(La,Ca)MnO_3$, Cobaltite $(La,Sr)CoO_3$, Cuprate $(La,Sr)_2CuO_4$, Ferrate $(La,Nd,Sr)FeO_3$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$, $(Y,Me)Ba_2Cu_3O_{7-\delta}$, $YBa_2(Cu,Mn)_3O_{7-\delta}$, (oxegen-poor)
2. spinel structure as Manganate-Cobaltite-Nickelate $(Mn,Ni,Co)_3O_4$, Ferrite $Ni(Cr,Fe)_2O_4$,
3. delafossite-type structure as Cobaltate Na_xCoO_2 and other Cobaltate with layered-structure $Ca_2Co_2O_5$, $Ca_3Co_4O_9$, $Ca_3Co_2O_6$, $Bi_{2,2-x}Pb_xSr_2Co_2O_y$

Some doped oxide as Cuprate, Cobaltite show fairly high Seebeck coefficient and were expected to have unique thermoelectric properties. The electrical properties of oxide semiconductors are governed by their defect structure.

Praxis of preparation
The large efforts in HTS materials science have thus paved the way for the improved preparation of oxide materials in general, e.g. thermoelectric, ferroelectric and magnetoelectric oxide.
The optimization of these materials (metallic-like ceramic oxide) with respect to their thermoelectric properties seems to be in accord with the efforts to improve their stability in technical applications. The ceramics were prepared in three steps by means of mixing, calcination and densityfication.

Tab.2 Examples for preparation of ceramic materials

Oxide ceramics	Powder preparation with ceramic method	Ceramic fabrication with Moulding
Cuprate $YBa_2Cu_3O_{7-\delta}$ $\delta>0,5$	$Y_2O_3+4BaCO_3+6CuO$ mixing, calcination at 850 °C, 24 h milling, sintering at 950 °C, 24 h	Melt-texturing from 1000-1050 °C with cooling rate of 1-5 °C/h
$Bi_2Sr_2CaCu_2O_{8+\delta}$ $\delta<-0,1$	$Bi_2O_3+ 2SrCO_3+CaCO_3+2CuO$ mixing, calcination at 750 °C, 24 h milling, sintering at 850 °C, 48 h	Sintering at 868 °C, 72 h
Spinels $(Mn,Co,Ni,Cu)_3O_4$	$aMnCO_3+bCoCO_3+cNiCO_3+dCuCO_3$ $a+b+c+d=3$ mixing, pre-firing at 700 °C, 4h milling, firing at 800 °C, 4 h	Sintering at 1000-1250 °C, 2 h
Cobaltite Na_xCoO_2	$6xNa_2CO_3+Co_3O_4$, $x>0,8$ mixing, calcination at 750 °C, 12 h milling, sintering at 850 °C, 12 h	Sintering at 900 °C, 48-72 h
$Ca_2Co_2O_5$ $Ca_3Co_4O_9$	$3CaCO_3+Co_3O_4$ or $3CaCO_3+1,6Co_3O_4$ mixing, calcination at 750 °C, 12 h milling, sintering at 800 °C, 24 h	Sintering at 950-1050 °C, 20 h

Microstructure of electroceramics materials
SEM micrograph shows typical morphology of oxide bulk materials - fig.1

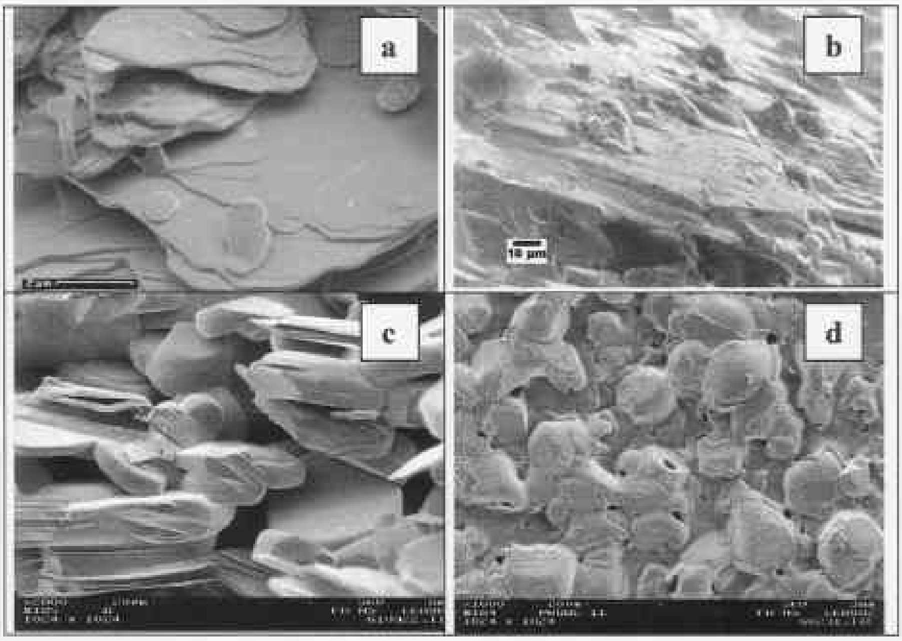

Fig.1. Microstructure of the oxide ceramic materials: $Bi_2Sr_2CaCu_2O_8$ a, $YBa_2Cu_3O_7$ b, Na_xCoO_2 c and $(Cu,Ni,Co)Mn_2O_4$ d.

The large plate-like ceramic grains of cuprate and cobaltites were produced as a result of significant grain growth with duration time at high temperature.
The spinel material are formed in granulary form with more porosity.

Functionally properties
As high temperature thermoelectric material are included numerous manganites, ferrites, chromites, plumbates, cuprates and cobaltites with different structures (perovskite-, spinel- and layered structures). These ceramic materials shows electronic conductivity. It is generally accepted that a hopping process of large and/or small polarons governs electronic transport in most of these oxides [8].
The electrical transport properties of these phases exhibits significant anisotropy due to its crystal structure, and are governed by their defects.
In cuprate the oxygen content is directly related with the carrier concentration of sample and valency of copper [9]. The conductivity of mixed Mn-Ni perovskite (NTC thermistor material) are a function of Mn^{3+}/Mn^{4+} ratio, e.g. oxidation state [10]. The electronic conduction mechanism in spinel is an electron transfer between +2 and +3 cations [11] or between +3 nad +4 cations in inverse spinels [12]. Charge carrier in layered cobaltites is thought to br restricted mainly to these CoO_2 planes, as in the case of the CuO_2 planes for the high-Tc cuprates. The oxygen partial pressure affects the defect concentration in Na_xCoO_2 and sodium concentration involving oxidation state of cobalt ions (Co^{3+}/Co^{4+}).
In spinels $(Ni,Co)_3O_4$ Co is present as Co^{2+} and Co^{3+} and with presence of Ni^{2+} and Ni^{3+}.

The electrical resistivity (fig.2) was measured through a four-probe method from 25 to 600 °C [13].

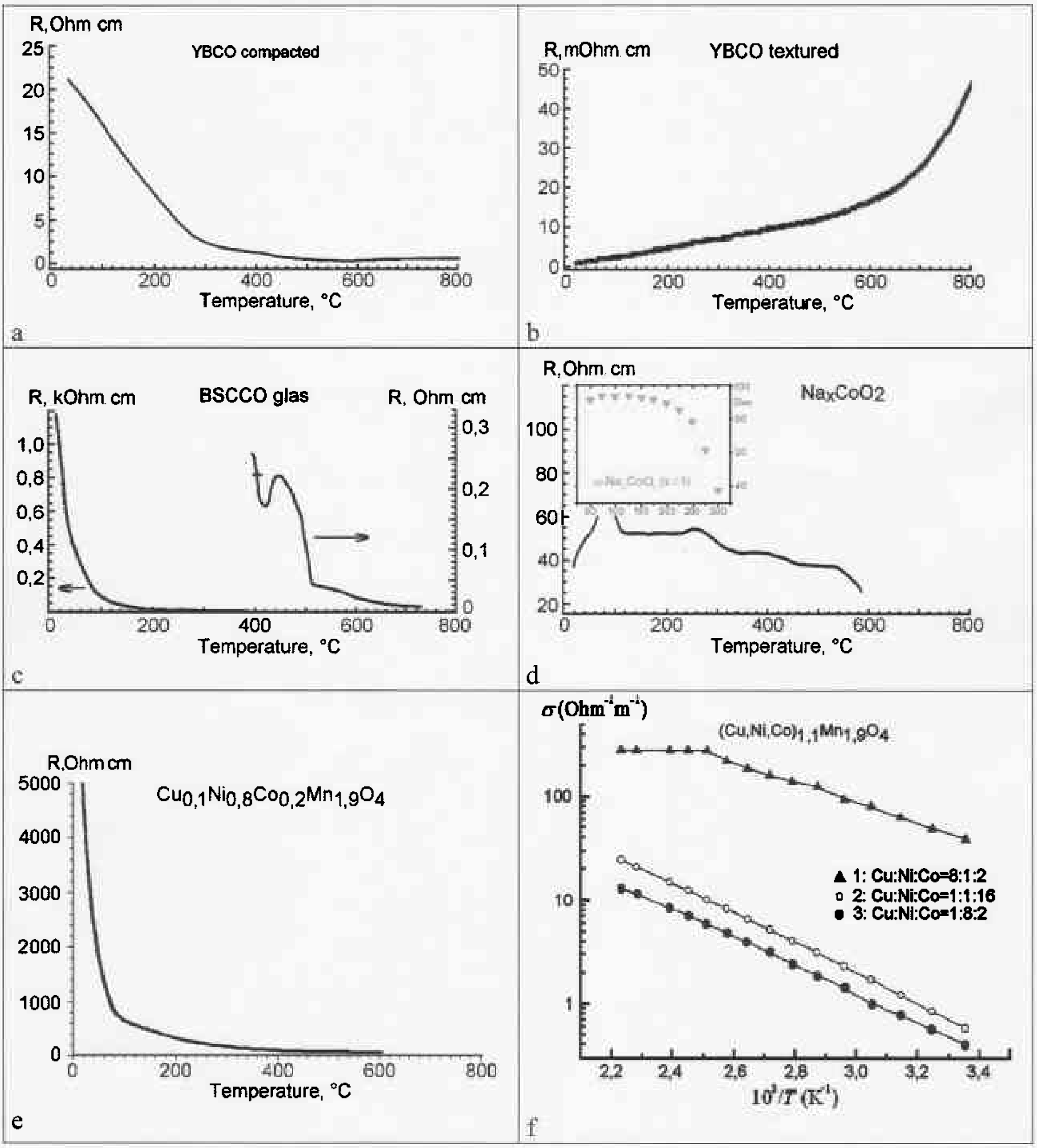

Fig.2. Examples of resistivity-teperature curves for YBCO-superconductors a and b, BSCCO precursor c, NCO thermoelectric d, NTCR thermistor e and f (conductivity curve [14])

The full oxygened superconducting cuprate YBCO show non-metallic (powder with weak-links) and metallic behavior (melt-textured sample). The electrical resistivity of glassy precursor for superconducting BSCCO with deficient oxygen decreases with increasing temperature indicating a semiconducting properties. Similary behavior show sodium cobaltite ceramic. The magnitude of the resistivity is as large, because the sample content much amount of sodium (fig.3).

The electrical conductivity of sodium-cobalt oxide materials is more sensitiv parameter and are dependent on oxygen partial pressure, element and phase composition and sample biography. The electrical conductivity of Na_xCoO_2 with big grains to attain 300 S/cm

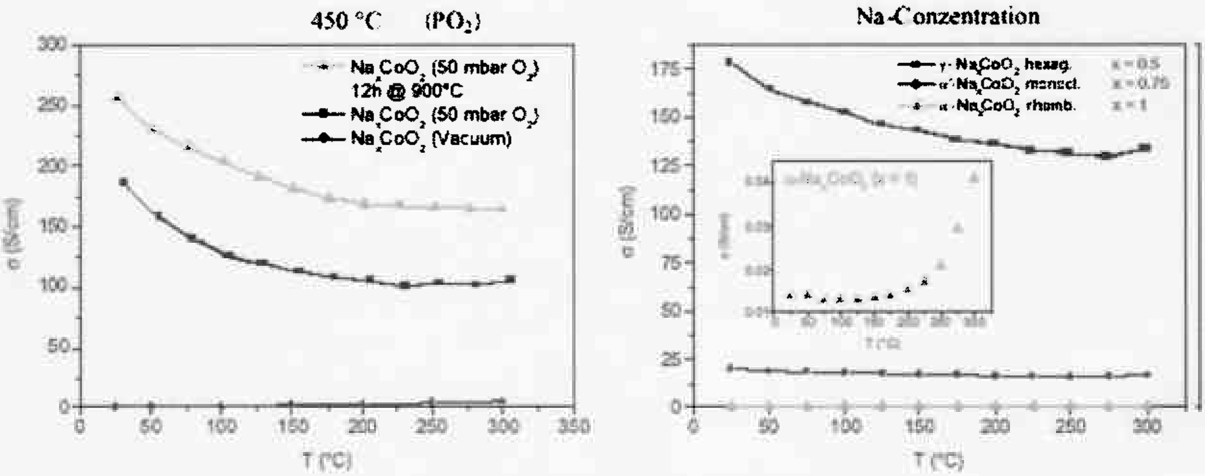

Fig.3. Electrical conductivity of Na_xCoO_2 samples [3].

For all electroceramic materials chemistry and physics of the grain boundaries play a significant role. The relation between microstructure and functional properties is crucial.
The factor governing the electrical conductivity of these materials are depend in therms of microstructural parameters as grain size, distribution and chemistry of grain-boundary phases and crystal defects in grains. This are changed during aging processes [7].

Conclusion

Electroceramic materials are the candidate for more application as superconductor, thermistor and thermoelectric, because shows high-temperature stability, layered structure, anisotropy of properties and possibly metallic or semiconducting behavior. These properties can be caused by controlling change of composition, e.g. oxygen content for cuprate, sodium content for cobaltites and metal-ration for spinels.
The development of electrical resistivity - sensitive parameter of the electroceramic materials may affect the selection for possible application.
Preparation techniques for a number of electroceramic material species are available which provide a first materials basis for application. As a stroke of god fortune, the optimization of these materials with respect to their thermoelectric properties seems to stability in technical environments in spite of the only metastable chemical nature of these substances under such conditions.

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