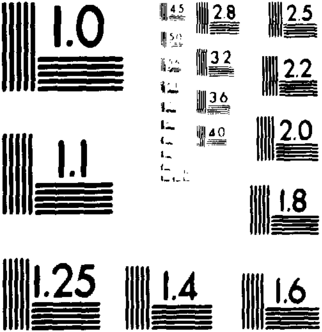

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DELL'ENERGIA NUCLEARE E DELLE ENERGIE ALTERNATIVE

SUPERCONDUCTIVE CERAMICS OBTAINED WITH SOL-GEL METHODS

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ABSTRACT

Several sol gel routes have been considered, studied and developed to produce large quantities of granulates which can be processed to obtain ceramics having good superconducting characteristics.

In the considered process a mixture of commercial nitrates is atomized, at room temperature, in a solution 1:1 of Primene JMT and Benzene and a pale blue gel of the starting elements is suddenly formed.

The granulates obtained are free flowing, very reactive and well suited for pressing.

For their intrinsic characteristics they could be very good precursors for the production of large quantities of superconductive ceramics in different forms.

The precipitated gel is dried, calcined, pressed in the form of cylindrical pellets which are sintered up to 960 degrees C. No grinding or different thermal treatments are needed.

The sintered material has low electric resistance, shows a clear Meissner effect and has a transition temperature of between 91 and 95 K.

INTRODUCTION

Within the framework of an R & D program on SYNROC and Special Ceramics [1] we have studied and developed two different sol-gel methods for the production of large quantities of precursor granulates of different sizes and shapes suitable for the fabrication of YBCO ceramic superconductors having good superconductive properties.

Up to now the laboratory-scale system allows the production of 100 gr. of sintered material every 36 hours.

The sol-gel granulates are free-flowing, they have good specific surfaces, they are very reactive, they can be fabricated in a spheric shape and the final product has better processability and superconductive properties than the material obtained with other methods.

For their intrinsic characteristics and the advantages these granulates offer if compared with other materials they could be valid precursors for the preparation of large quantities of superconductive ceramics, in different shapes and sizes, having good reproducible properties and good suitability for commercial applications like sputtering on hot sol-gel oxides substrata or thin film tape or bars to be used as current adductors for big magnets.

EXPERIMENTAL PROCEDURES

On the basis of our early work on the sol-gel ceramic superconductors, preliminary results of which have been presented at the " First European Workshop on high Tc Superconductors and potential applications " held in Genova (Italy) last July, [2] we developed and set up two different sol-gel processes to yield large, significative and reproducible amounts of granulates to be used as precursors for the fabrication of superconductive ceramics [3],[4].

M.S.G. PROCESS

In Fig. 1 the flow-sheets of the MSG (modified sol-gel) and ALCOX processes are shown.
Taking the MSG method, an intimate aqueous solution of commercial nitrates of the considered elements is atomized, at room temperature, in an organic mixture composed of 50% Primene JMT, a primary amine, and 50% benzene, as diluent.
A consistent pale blue gel is instantly formed. The long chain amine is used in order to extract the counter-ions, from an acidic solution of the starting elements, in to the organic phase.
Through the extraction of the acid ions the pH of the aqueous phase increases and the hydrouos oxides of the cations precipitate forming an amorphous gel.
The gel formed is then separated from the liquid phase and dried at 180°C in an oven where it turns to a brown black colour. A subsequent calcination treatment is carried out in the air at 700-800 °C, in order to form the oxides and to get rid of the organics.
The calcined black material is then pressed with a hysostatic hydraulic device in the form of cylindrical pelletts and/or bars.
The pressed material undergoes a sintering treatment up to 950°C with a climbing rate of 100°C/h, a dwell at 950°C of three hours and a cooling rate of 100°C/h in flowing oxygen atmosphere.
Due to the elasticity of the process this procedure can be easily adapted to the other rare earths and other elements of the 3° and 4° group and superconductors of different final composition can be easily made.
Specimens containing Eu and Sr in the place of Y and Ba respectively have been prepared by our group; they present the same characteristics and behaviour as YBCO compounds.

ALCOX PROCESS

The flow-sheet of this second preparation method, chosen in order to obtain granulates of smaller dimensions to improve the reactivity of the powders during thermal treatments and to control the rate of degradation due to moisture conditions, is similar to the above MSG flow-sheet, although the starting nitrate salts are first dispersed in an ethylen-glicol solution and then sprayed in a tertiary amine.

RESULTS

The precursors obtained with sol-gel methods present large specific surface [2], quite good tap-density, pressing behaviour and reactivity.
Five batches of 100 gr. each have been fabricated; we have characterized 20 pellets (Φ = 12 mm, height= 2 mm) from each batch.
The characterization concerned:

- transition temperature;
- fracture surfaces;
- x-ray diffraction patterns;
- scanning electron microscopy;
- thermogravimetry;
- Meissner effect.

Transition Temperature Measurements

Tc was measured by a classic four-points d.c. system which measures the electrical resistance of a specimen as a function of temperature.
The results show the linear decrease of the resistance from 300 K down to 94 K where the superconducting transition occurs.
The resistance drop in the transition field is very sharp with a width of about 1 K.
During the warming up of the sample the phenomenon is perfectly reversible without any hysteresis effect (Figg. 2,3).

Some samples showed a Tc of 95 K (Fig. 4).
The average resistance of the considered samples, measured with the four points method at room temperature , is ca. 3.7 E-3 ohm for the MSG samples and ca.45 E-3 ohm for the ALCOX samples.(fig. 5)

Fracture Surfaces

Preliminary results of surface fracture analysis by Auger Electron Spectroscopy (SAM PHI Mod. 600) are reported.
MSG sample has been fractured in the analysis chamber under ultra high vacuum conditions (p= 2E-10 torr.) in order to avoid contamination of the sample. A qualitative analysis was carried out in order to obtain information about chemical compositions and homogeneity.
In fig. 9 an Auger spectra, carried out with a surface scanning, is reported.
The presence of a small quantity of carbon is probably due to the shortened calcination time of the granulate.
In pictures 1-5 Auger Electron spectroscopy images and the Auger maps of Y, Ba, Cu and O are shown; one can see a good chemical homogeneity on the whole surface.
The darker zones are due to topographic phenomena. (CF. picture 1)
In picture 6 a SEM image (5000X) of the grain boundaries surface (marked with a black arrow on picture 1) is reported while in pictures 7-9 Auger maps for Y, Ba, and Cu are reported. In this case also a good chemical homogeneity can be observed.

X-Rays Diffraction

The x-ray diffraction patterns, reported in fig.6 show a polycristalline structure typical of an orthorombic oxygen deficient perovskite phase with a small amount of CuO phase.

The significative peaks have been identified according to literature. [5]

Scanning Electron Microscopy

The free parallel surfaces of the sintered specimens (M.S.G. and ALCOX) have been examined by Scanning Electron Microscopy (SEM) using a Cambridge 250 MK III instrument equipped with La ß 6 emitter and LNK 860 II X-ray analysis system.

From the morphological point of view the MSG samples appear to be monophase as shown in pictures 10-12

In the reported areas one can notice well distributed rod, disk and globular shaped particles. The observed material is the best produced up to now, it has a very remarkable Meissner effect and a Tc of 95 K. The ALCOX samples appear to be dual phase as shown in picture 13 .In the area reported in picture 14 rod shaped particles are observed while in picture 15 globular particles of the same material are shown.

It has to be noticed that, owing to the specimen surface roughness, the quantification procedure of x-ray intensities can result in higher errors that the statistical ones and thus concentration data are not reported.

The SEM analysis has been carried out on samples after an average "aging" time of 40 days.

Thermogravimetry

The powders fabricated with the MSG method were pressed into small pellets to be analysed with a thermal balance system NETZSCH 6500.

Fig. 7 shows the effect of heating a sample up to 1000°C (7°C/min) in oxygen and then cooling it down to room temperature.

The initial weight loss (at ca. 200°C) is probably due to the water and the organic compounds.

On further heating the sample looses considerable amounts of oxygen, but the reaction is partially compensated during cooling, until finally the weight becomes constant., according to the formula $YBa_2Cu_3O_{6.94}$

Results of thermogravimetry analysis are in accordance with the data reported in the available literature [6].

Meissner Effect

The Meissner effect has been pointed out through the use of a " home built " system. The pellet, at liquid nitrogen temperature, is placed on a magnetic tape (6 feet in length) where it runs for several lengths of the tape, until it warms up, levitating at 1 - 2 mm above the tape surface (pictures 16 and 17).

CONCLUSIONS

We believe that, to improve the production of large quantities of ceramic superconductors having valid and reproducible characteristics, the control of the physical-chemical properties of the starting precursors and the microstructure of the green body are very important.

The sol-gel process provides a sufficient and significant control of the particle morphology and permits to obtain specimens with rather good final densities (from 81.2 to 86.2 % of the T.D.) which are reached at a lower sintering temperature, since the particulate is more reactive, and with a unique sintering cycle not requiring any intermediate step during the entire treatment.

We believe that the final theoretical density of the samples can be raised through the use of a longer dwelling period during the calcination of the granulates and the sintering of the pressed material. Presently, tests aiming at the achievement of more than 90% of the T.D. are in progress and the change in density will be related with Critical Current measurements.

On the other hand the large homogeneity, obtained at molecular level since the mixing of the starting elements is carried out in a liquid phase, gives a well defined and reproducible stoichiometry at the end of the preparation route.

Furthermore, despite the degradation effect reported by other researchers [7] - degradation due to an instability of the 1-2-3 phase even for short exposure to moisture - we noticed that MSG sol-gel specimens, left in open air (85% rel. humidity) for 45 days, still show a noticeable Meissner effect and present a Tc of 91 K

We remarked the same behaviour for the samples prepared using the finer granulate from ALCOX process even if we noticed a lower transition temperature and the loss of the Meissner effect in a shorter period of time (25-30 days) at the same ambient conditions.(fig. 8)

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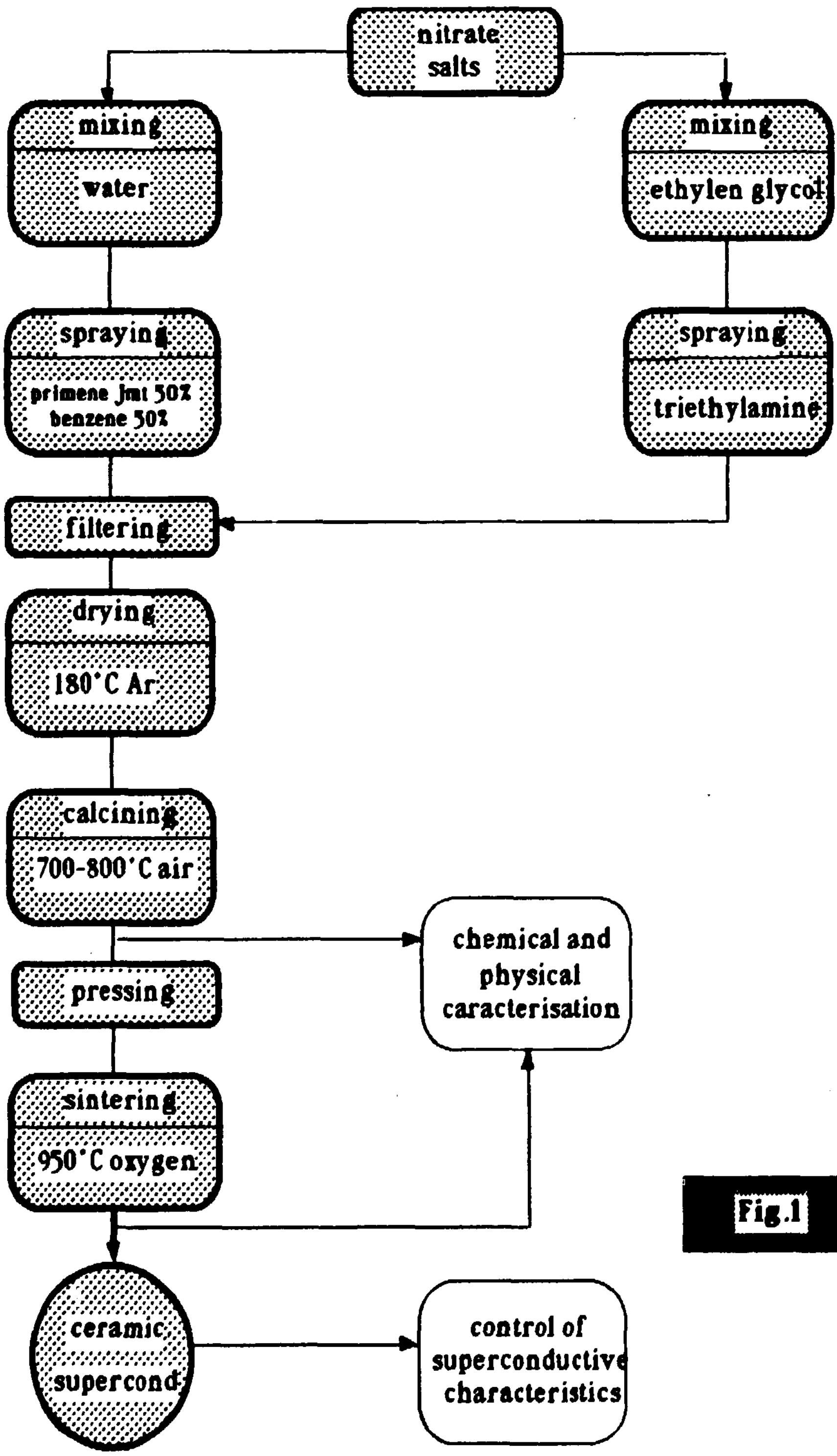

nitrate salts
mixing
water
mixing
ethylen glycol
spraying
primene Jmt 50%
benzene 50%
spraying
triethylamine
filtering
drying
180°C Ar
calcining
700-800°C air
chemical and physical caracterisation
pressing
sintering
950°C oxygen
ceramic supercond
control of superconductive characteristics

Fig.1

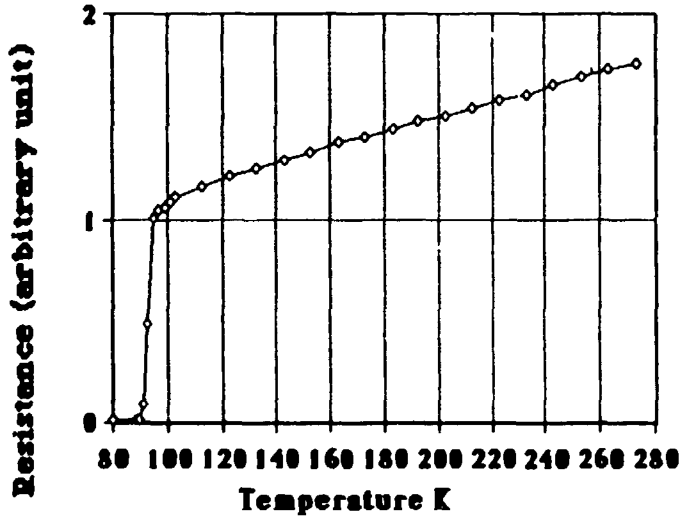


Fig. 2: Resistance vs temperature of a MSG sample (Tc= 93 K)

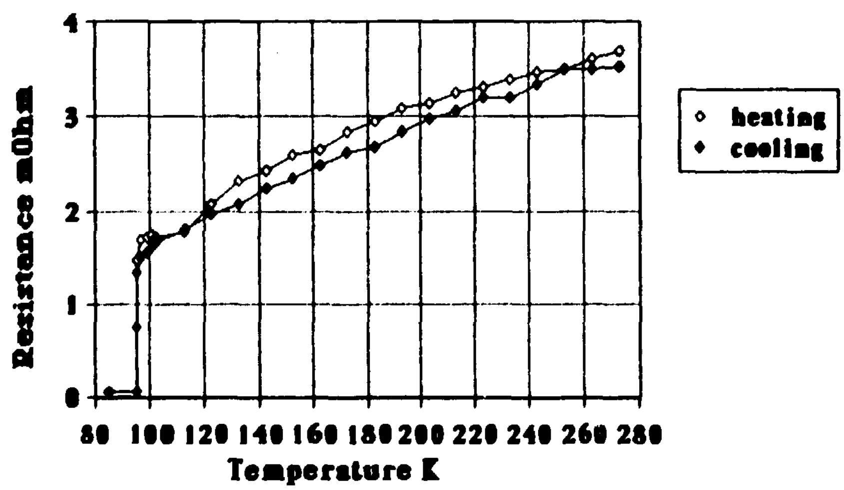


Fig. 3: Resistance vs Temperature of an MSG sample (Tc= 93 K)

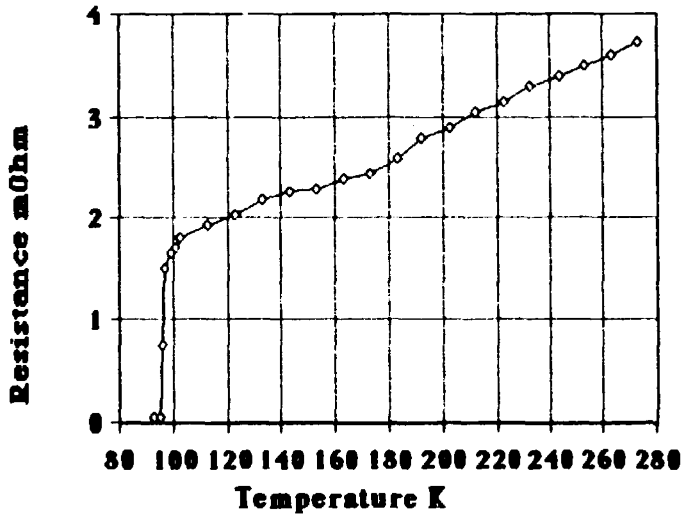


Fig. 4: Resistance vs Temperature of MSG sample (Tc= 95 K)

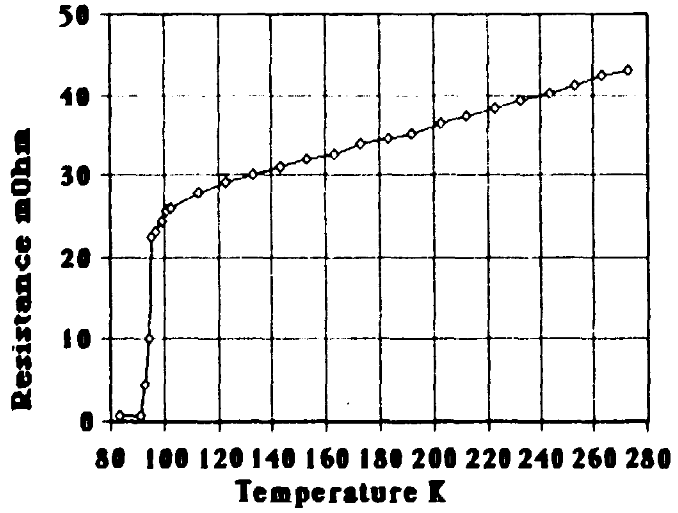
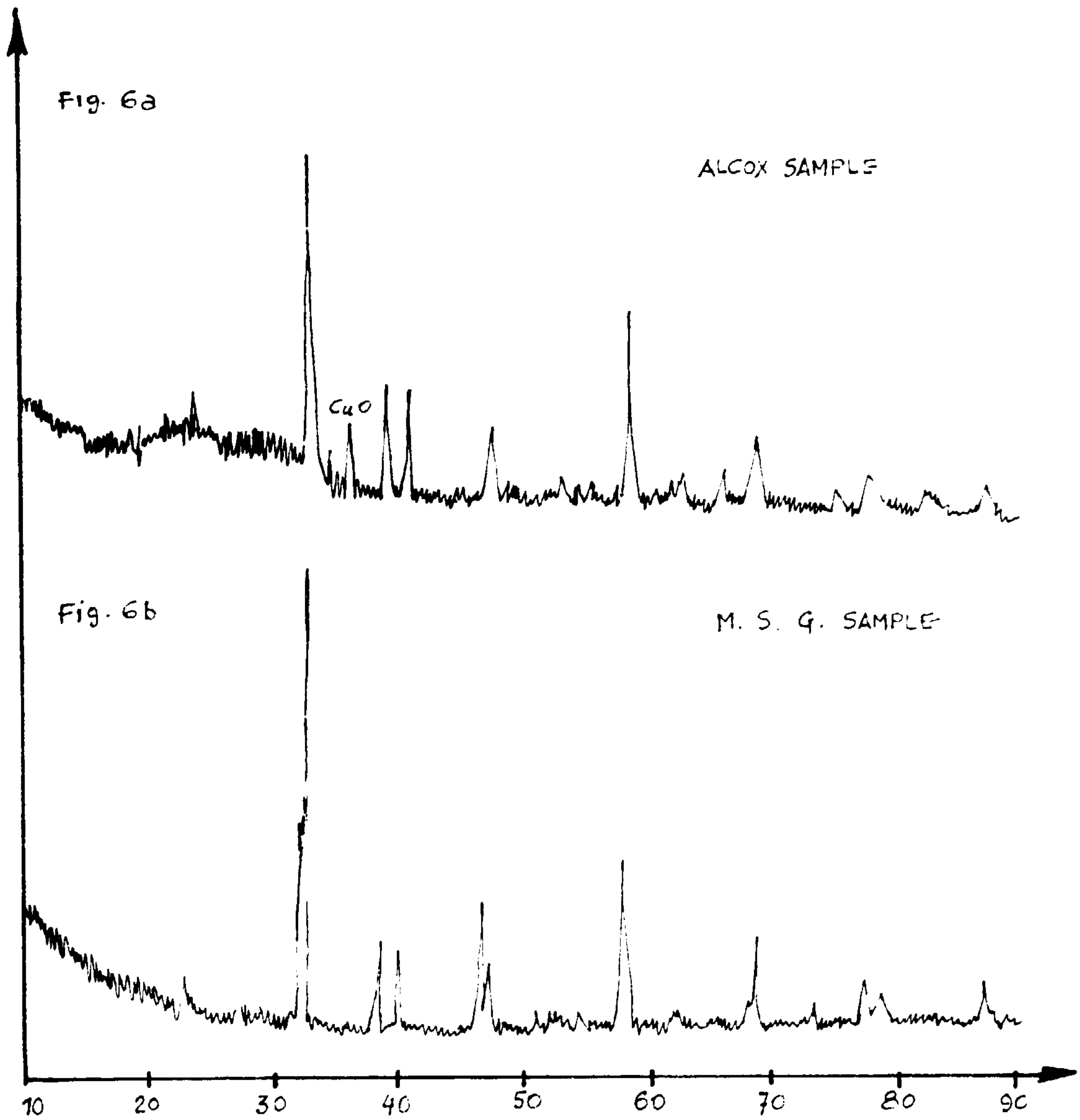


Fig. 5: Resistance vs temperature of an ALCOX sample (Tc= 93 K)



X-Ray diffraction patterns of specimens prepared with M.S.G. and ALCOX methods.

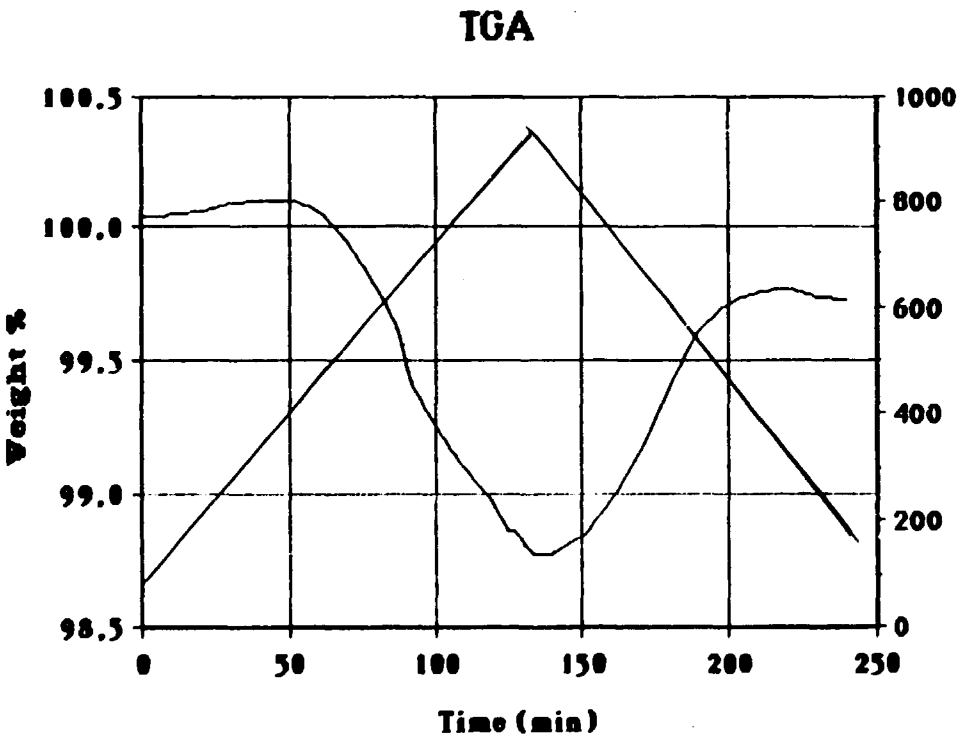


Fig. 7. TGA in oxygen of a M.S.G. sample

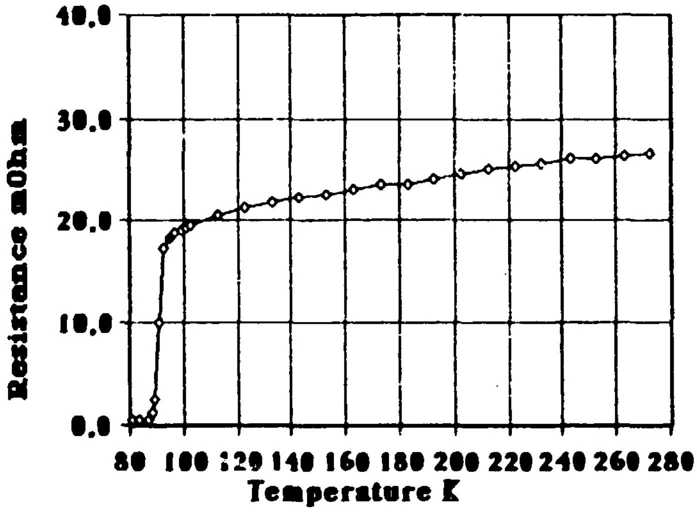


Fig. 8: Resistance vs Temperature of an ALCOX sample left in open air (85% rel. humidity) for 45 days (Tc= 91K)

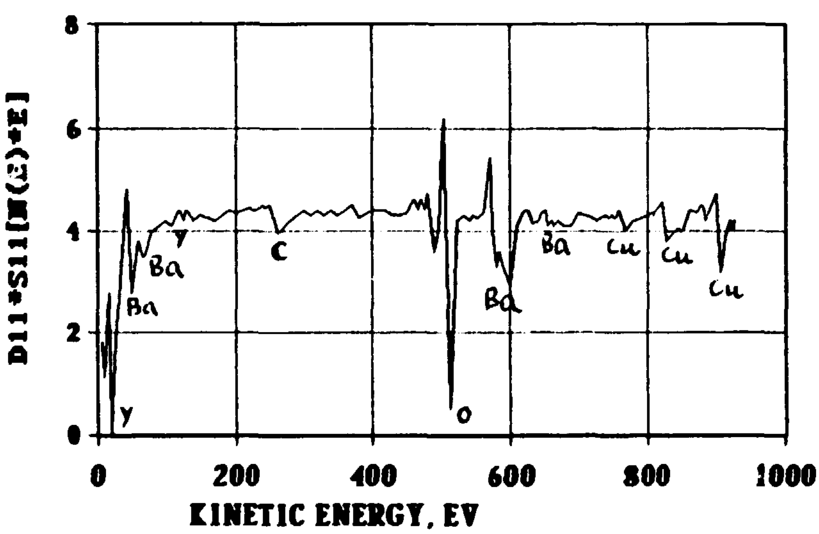
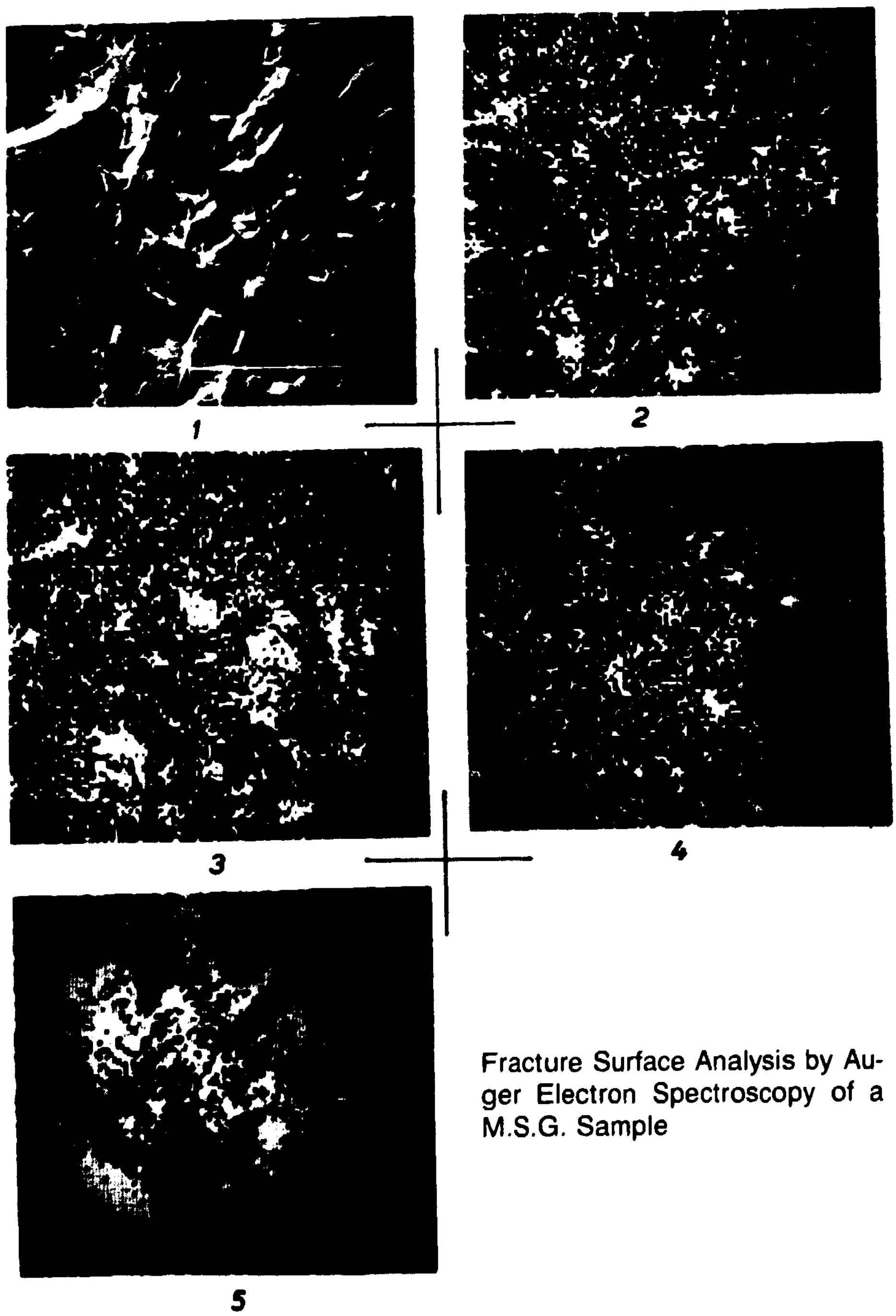
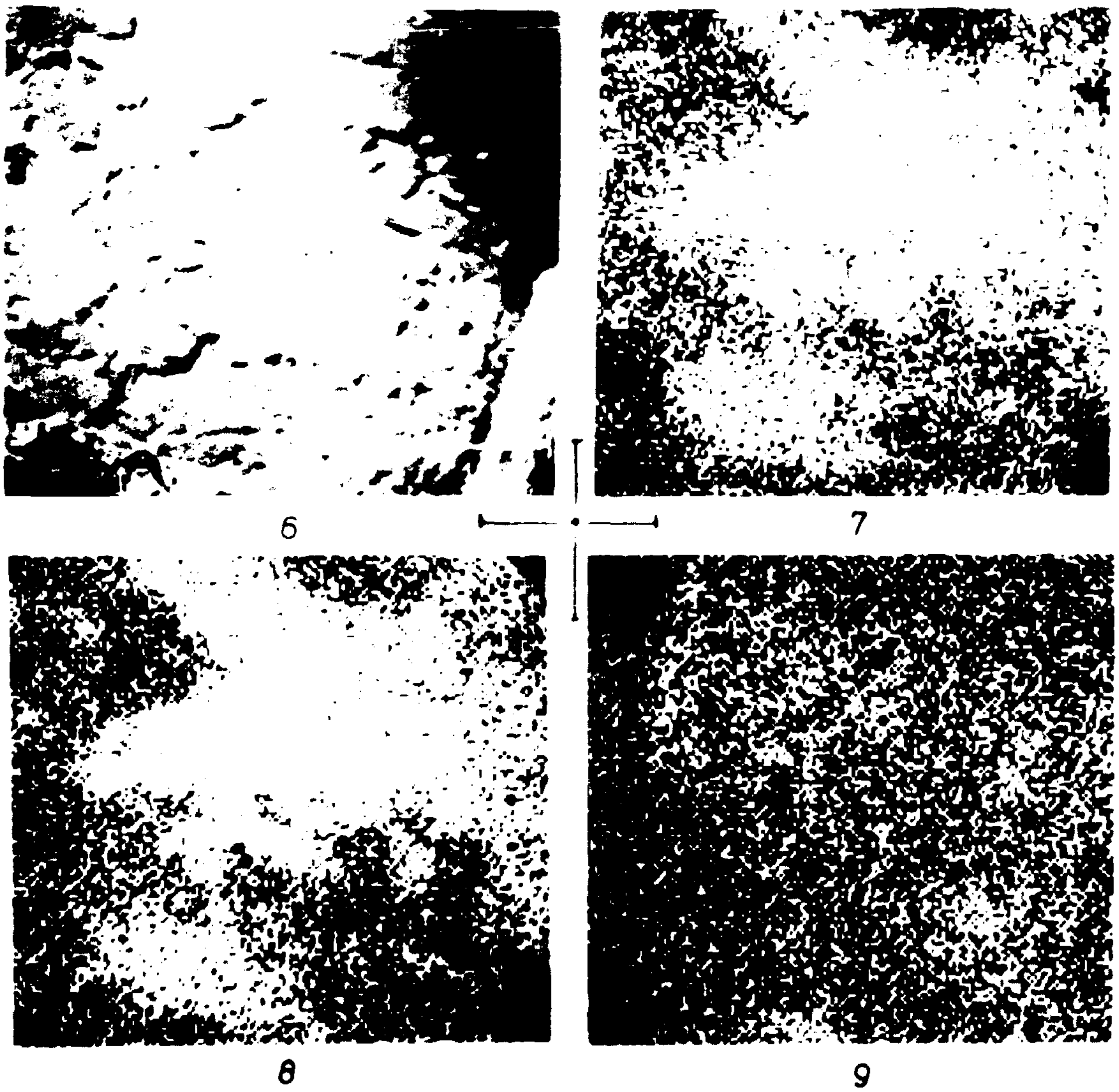


Fig. 9: Auger spectra of M.S.G. Sample



Fracture Surface Analysis by Auger Electron Spectroscopy of a M.S.G. Sample



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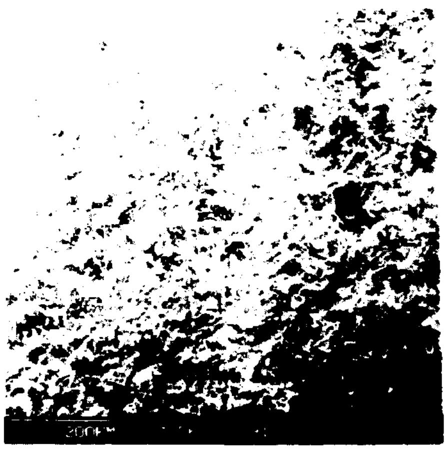

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S.E.M. Images of a M.S.G. Sample

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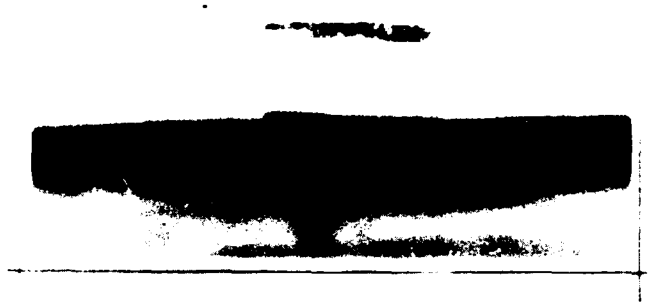
S.E.M. Images of an Alcox Sample



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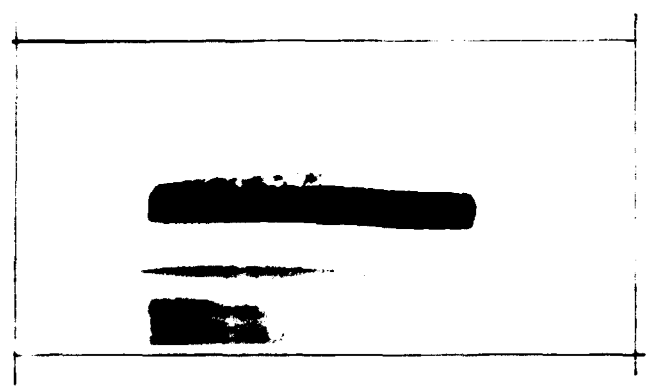

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M.S.G. Samples levitating on a plastic magnetic tape

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