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Contribution of the Microwave Sintering for Getting Nanosized ZnO Based Ceramics for Varistors

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Abstract

Zinc oxide is a well-known material, used especially as varistors. The electrical properties of the zinc oxide varistor are strongly correlated to the final microstructure. The breakdown voltage is particularly grains size dependent. In this paper, a wet chemical route was used to get nano-sized ZnO based powder, with a very narrow granulometric distribution centred at roughly 20 nm. The used synthesis method is based on the direct precipitation of the zinc oxalate solution. The conventional sintering of this nano-sized powder leads to a slight decrease of the grain size (around 2 μm), compared to the grain size observed in a material originated from the powder conventionally synthesized and sintered (> 4 μm). Despite this slight grain size modification, a strong increase of the breakdown voltage is evidenced in the samples obtained through the liquid route. When the microwave sintering process is used to sinter nano-sized ZnO powder, nano-sized grains bulk ceramics are obtained owing to the very short thermal cycle (less than 5 minutes). It is undoubtedly clear that the microwave sintering allows both maintaining the grain size at the nanometric scale and achieving very high density. In that case, a high resistivity increasing below the breakdown voltage is observed and the breakdown voltage is becoming too high (> value) to be measured. Otherwise, it is clearly indicated that the very short time of the heating process induces a modification of the secondary phases composition, which are mainly localized at the grain boundaries.
Keywords: ZnO, Microwave sintering, Varistors, Nanoceramics

WKŁAD SPIEKANIA MIKROFALOWEGO W OTRZYMYWANIE NANOMETRYCZNEJ CERAMIKI ZnO Z PRZEZNACZENIEM NA WARYSTORY

Tlenek cynku jest dobrze znanym materiałem, wykorzystywanym szczególnie do wytwarzania warystorów. Właściwości elektryczne warystora z tlenku cynku związane są mocno z końcową mikrostrukturą tworzywa. Napięcie przebicia jest w sposób szczególny zależne od wielkości ziarna. W niniejszym artykule, wykorzystano mokrą metodę chemiczną do uzyskania nanometrycznego proszku opartego na ZnO, mającego bardzo wąski skład granulometryczny z centrum umiejscowionym mniej więcej przy 20 nm. Wykorzystana metoda syntezy opiera się na wytrącaniu szczawianu cynku bezpośrednio z roztworu. Konwencjonalne spiekanie tego nanoproszku prowadzi do nieznacznego zmniejszenia rozmiaru ziarna (około 2 μm), w porównaniu z rozmiarem ziarna w materiale otrzymanym z proszku syntezowanego i spiekanego konwencjonalnie (> 4 μm). Pomimo tej małej modyfikacji rozmiaru ziarna, udokumentowano mocny wzrost napięcia przebicia w próbkach otrzymanych metodą mokrą. Wtedy gdy wykorzystuje się proces spiekania mikrofalowego do spieczenia nanometrycznego proszku ZnO uzyskuje się masywną ceramikę o nanometrycznym ziarnie, dzięki bardzo krótkiemu cyklowi termicznemu (poniżej 5 min). Jest niewątpliwie oczywiste, że spiekanie mikrofalowe umożliwia zarówno utrzymanie rozmiaru ziarna w skali nanometrycznej, jak i osiągnięcie bardzo dużej gęstości. W takim przypadku, obserwuje się wysokie zwiększenie rezystywności poniżej napięcia przebicia, a napięcie przebicia staje się zbyt duże, aby mogło być zmierzone. Poza tym jasno wykazano, że bardzo krótki czas procesu ogrzewania wywołuje modyfikację składu faz drugorzędnych, które zlokalizowane są głównie w granicach międzyziarnowych.
Słowa kluczowe: ZnO, spiekanie mikrofalowe, warystory, nanoceramika

1. Introduction

Zinc oxide is a well-known functional material due to its numerous applications in various fields [1]. In the field of electrical engineering, ZnO is also widely used as varistors, thanks to its highly nonlinear current-voltage characteristic. Its main role is to protect equipments connected to it as surge absorbers. Nowadays, due to the considerable development of PC equipment and telecommunication networks, there is a need to develop highly nonlinear current-voltage characteristic varistors whose production can be implemented at a large scale. A typical composition of a varistor consists of minor additions of several metal oxides, such as Bi_2O_3, Pr_6O_{11}, CoO and Cr_2O_3, to the ZnO powder in order to generate a non-ohmic behavior [2]. Some dopants react with the matrix while others stay in the vicinity of the grain boundaries, forming inter-granular phases. The non linearity of the I(V) response comes from the grain boundaries which act at low voltage as barriers for the current flow.

A lot of processing parameters have been tailored in order to achieve the most appropriate ZnO microstructure from the point of view of the electrical response. Among them, one can mention the influence of vibratory milling [3], sintering temperature [4, 5] and annealing temperature [6].

Different synthesis methods have been also investigated, such as precipitation [7-8], solution-coating [9], sol-gel [10], combustion [11] and self-propagating high-temperature [12] methods. However, the critical point is that during conventional sintering, the grain growth occurs and it is a real challenge to keep the nano-sized grains on the sintered specimen. Nahm indeed studied the ZnO-based varistors sintering doped with various oxides (such as Pr_6O_{11}, CoO, Cr_2O_3 and La_2O_3). He reported that the electrical properties are strongly dependent of the microstructure, in particular, he showed that the non-linearity coefficient is as high as the grain size low [2]. Experimentally, Nahm have synthesized ZnO by a conventional route which is based on the solid state reaction between the precursors. It is expected that a liquid route could allow a finer microstructure to be obtained and hence an improvement of the electrical properties. In our study, we propose to investigate the influence of the grains size on ZnO properties as varistors, starting from Nahm's composition. ZnO based powders were elaborated by the direct precipitation method which was already reported by Takehana [13] in order to obtain nano-sized powder. Microwave sintering is well-known as a very fast sintering method to avoid grain growth and therefore this method has been selected for the sintering stage. The electric response of samples sintered by the conventional process and microwaves was measured and the results discussed and compared as a function of the microstructure.

2. Experimental

2.1. Liquid route synthesis

Fig. 1 shows a flow sheet describing the precipitation method. Zinc acetate (Chempur 99.5 %) was dissolved in absolute ethanol. Oxide dopant powders were then added to the solution in proportion of 97.0 mol% ZnO, 0.5 mol% Pr_6O_{11}, 1.0 mol% CoO, 0.5 mol% Cr_2O_3, and 1.0 mol% La_2O_3. After mixing for one hour at 70°C the dihydrate oxalic acid was poured into the solution provoking the precipitation of zinc oxalate. After filtration and drying under infrared lamps, the zinc oxalate based powder was calcined in air at 400°C for one hour to get the ZnO based powder. The oxalate decomposition was studied by a thermo gravimetric measurement (Setaram TGA92).

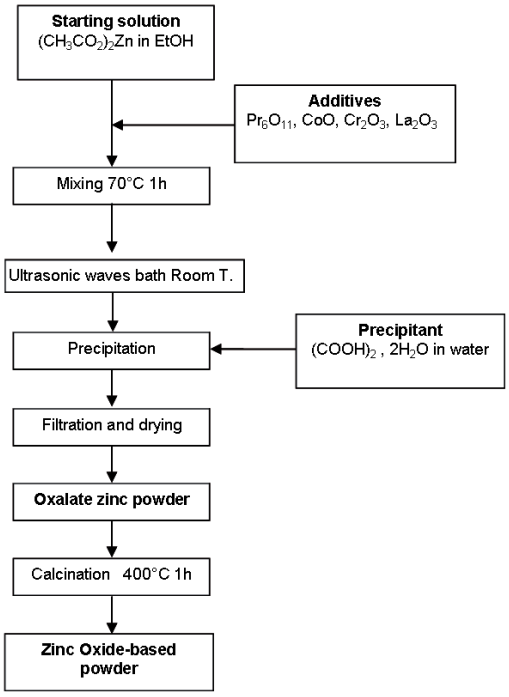

Fig. 1. Flowsheet of the synthesis of ZnO based powder by the liquid route.

2.2. Powder characterization, shaping and conventional sintering

The crystalline phases were identified by XRD using the CuKα radiation (Philips X'Pert diffractometer). The microstructures were observed by SEM (Zeiss Supra 55), whereas the nano-sized powder was characterized by TEM. The specific surface area was determined by the BET method based on the nitrogen adsorption. For the shaping, an organic binder (Rhodoviol 4 %, Prolabo) was manually added to the powder and disks (6.4 mm in diameter, 1.3 mm in thickness) were shaped using a 30.6 kN uniaxial load. A thermo mechanical analysis (TMA Setaram) was performed in air in order to study the behaviour of this powder when it is subjected to a thermal cycle and to determine the optimal sintering temperature. A dwelling time of 30 minutes at 1450°C was applied with a heating/cooling ramp of 150°C/h. The sample density was measured by He-pycnometer (Micromeritics AccuPyc 1330).

2.3. Microwave sintering

The microwave furnace consists of a microwave generator (2.45 GHz Sairem GMP20KSM) which delivers a variable power up to 2000 W. Rectangular waveguide (WR340) allows the transport of microwaves from the source to the TE10p cavity. This cavity was excited in TE102 mode by tuning the

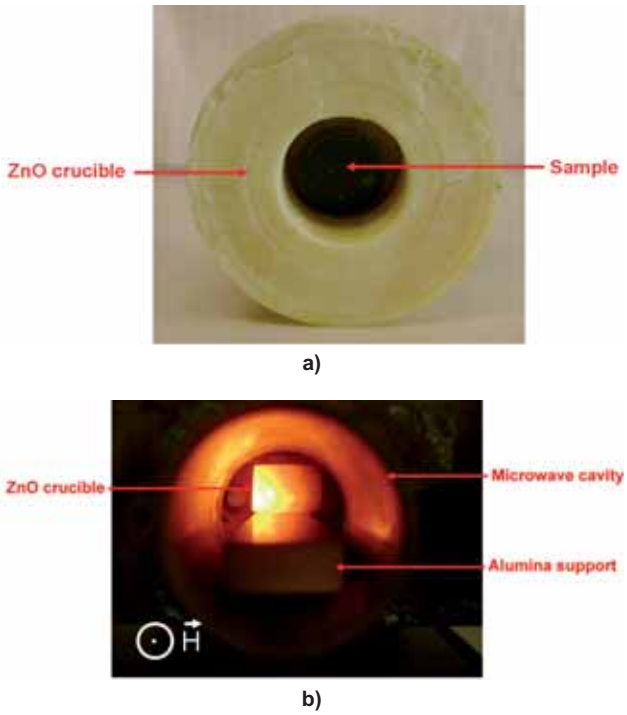

Fig. 2. a) Photograph of the ZnO crucible susceptor for microwave heating; b) The susceptor in the microwave cavity.

length between the coupling iris and the short circuit piston (iris and piston delimit the cavity). A zinc oxide susceptor, with a cylindrical crucible shape, was positioned in the centre of the cavity with its axis parallel to the electric field (Figs. 2a and 2b). Using this configuration, one fraction of the microwaves radiation is absorbed by the sample while the other fraction is absorbed by the crucible. Owing to the susceptor, the sample is located in a warm environment (warm wall phenomena) which allows the thermal radiation from the sample surface to be significantly reduced. Therefore, the temperature field inside the sample is quite homogeneously distributed. ZnO was chosen as a material for the crucible in order to avoid any contamination of the sample by the susceptor. Before microwave sintering, the first heating treatment was implemented in a conventional furnace at 400°C for one hour to remove the organic binder.

2.4. Electrical measurements

Silver paste was coated on both faces of samples and ohmic contacts were formed by heating at 900°C for one hour. Electric field-current density (*E-J*) response was measured at room temperature using an *I-V* source/measure unit (Keithley 237). Different parameters of the varistors were calculated from the *E-J* curves when these curves enabled us to do it. Thus, the breakdown voltage, E_b, was measured at a current density of 1 mA/cm^2. The non-linearity coefficient, α, was estimated for the current density range from 0.1 mA/cm^2 to 1 mA/cm^2 and the leakage current density, J_L, was defined as the current density at 0.5 E_b.

3. Results and discussion

3.1. Liquid route

XRD pattern of the powder obtained by the oxalate method shows that zinc oxide has been synthesized (Fig. 3). Pr_6O_{11} phase is also evidenced. Furthermore, the XRD peaks width is broad which suggests a small grain size.

This assumption was confirmed by the specific surface area, whose value is 48.9 m²/g. From this value, the particle diameter is estimated at roughly 20 nm. This calculation is based on the following relation, suitable for the spherical and mono-dispersed powder:

$$d = \frac{6000}{\rho \cdot S},$$

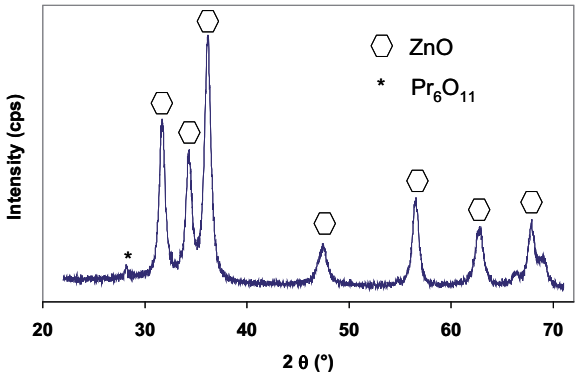

Fig. 3. XRD pattern of the zinc oxide based powder synthesized by liquid route.

where *d* is the grain size (nm), r is the theoretical density (g/cm^3) and *S,* the specific surface area. This calculated diameter of 20 nm is in good agreement with the high resolution TEM image (Fig. 4a), which shows nearly spherical grains with a very narrow granulometric distribution. On the HRTEM image, the characteristic contrasts of a well crystallized phase are also evidenced. For comparison, the SEM micrograph of the powder synthesized by the solid state reaction was also plotted (Fig. 4b). The grains size is much higher and its distribution as well.

3.2. Conventional and microwaves sintering

In order to get a reference, conventional sintering of samples synthesized by solid state reaction has been implemented. The sintering temperature was 1250°C with a dwelling time of one hour (heating ramp +/- 150°C/hour). After sintering, the sample density was measured at 5.71 g/cm^3. One can see in Fig. 5a that the grain size is around 4 µm, a value comparable to that obtained by Nahm [2]. The spatial distribution of the dopants is shown in Fig. 5b . One can see in it that inter-granular phases are not well dispersed in the matrix and are more or less agglomerated.

The samples obtained by the liquid way were sintered in the same conditions. A higher density (5.89 g/cm^3) was measured on it and a lower grain size was observed as shown on the SEM micrograph (Fig. 5c). A better dispersion of the dopants, localized at grain boundaries, is also evidenced (Fig. 5d).

Microwave sintering of the samples synthesized by liquid way was implemented. The appropriate incident power cycle shown in Fig. 6 was determined by a trial/error method. The total time cycle was 180 seconds with 3 steps of 60 seconds each at 100, 150 and 175 W respectively. The density achieves 5.57 g/cm^3. One can see on the SEM micrographs (Fig. 5e and Fig. 5f) that the grain size was drastically decreased as compared to the one observed after the conventional heating treatment. The average grain size is about 200 nm, thanks to the short time of the heating process.

All the sintered samples were crushed in an agate mortar and XRD patterns were recorded on it (Fig. 7). First of all, ZnO is well crystallized whatever the processing route. In the same manner, $LaCrO_3$ and La_2O_3 are found as secondary phases in each sample. Praseodymium oxides, with different oxidation states, were found in the samples being synthesized by the liquid route, whereas these phases are not observed on the conventional synthesized sample. Nevertheless, the most notable difference among those three XRD patterns is that the peaks intensities of the secondary phases are lower for the samples sintered by the microwaves compared to the others. The very short sintering cycle (less than 5 minutes) in microwave heating does not allow a complete reaction between the dopants. In any case, the different behaviors which have been stressed must be kept in mind when electrical characterizations will be performed.

3.3. Electrical measurements

Fig. 8 shows the *J*(*E*) characteristics of different varistors. For the varistors elaborated by the solid state reaction and sintered by the conventional process, all the usual param-

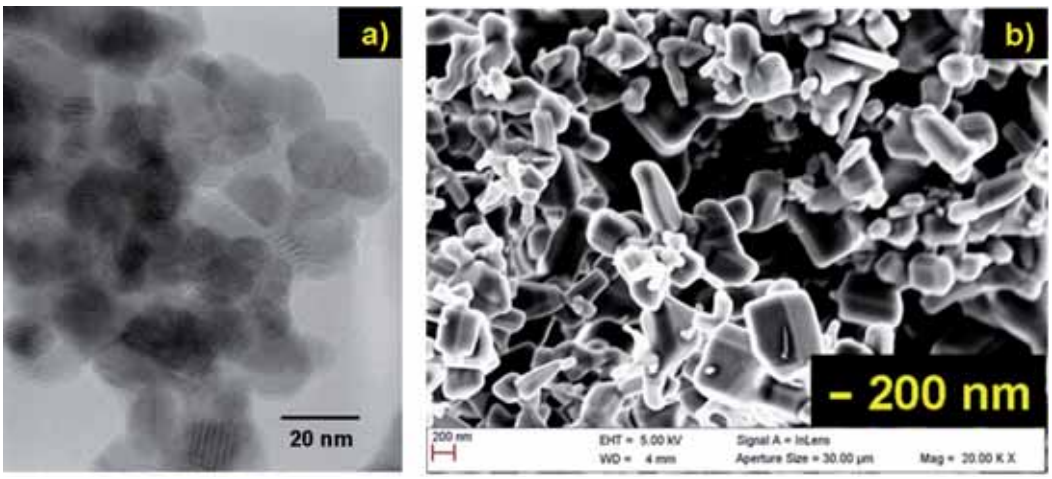

Fig. 4. a) HREM image of the powder synthesized by liquid route; b) SEM micrograph of the powder synthesized by conventional route.

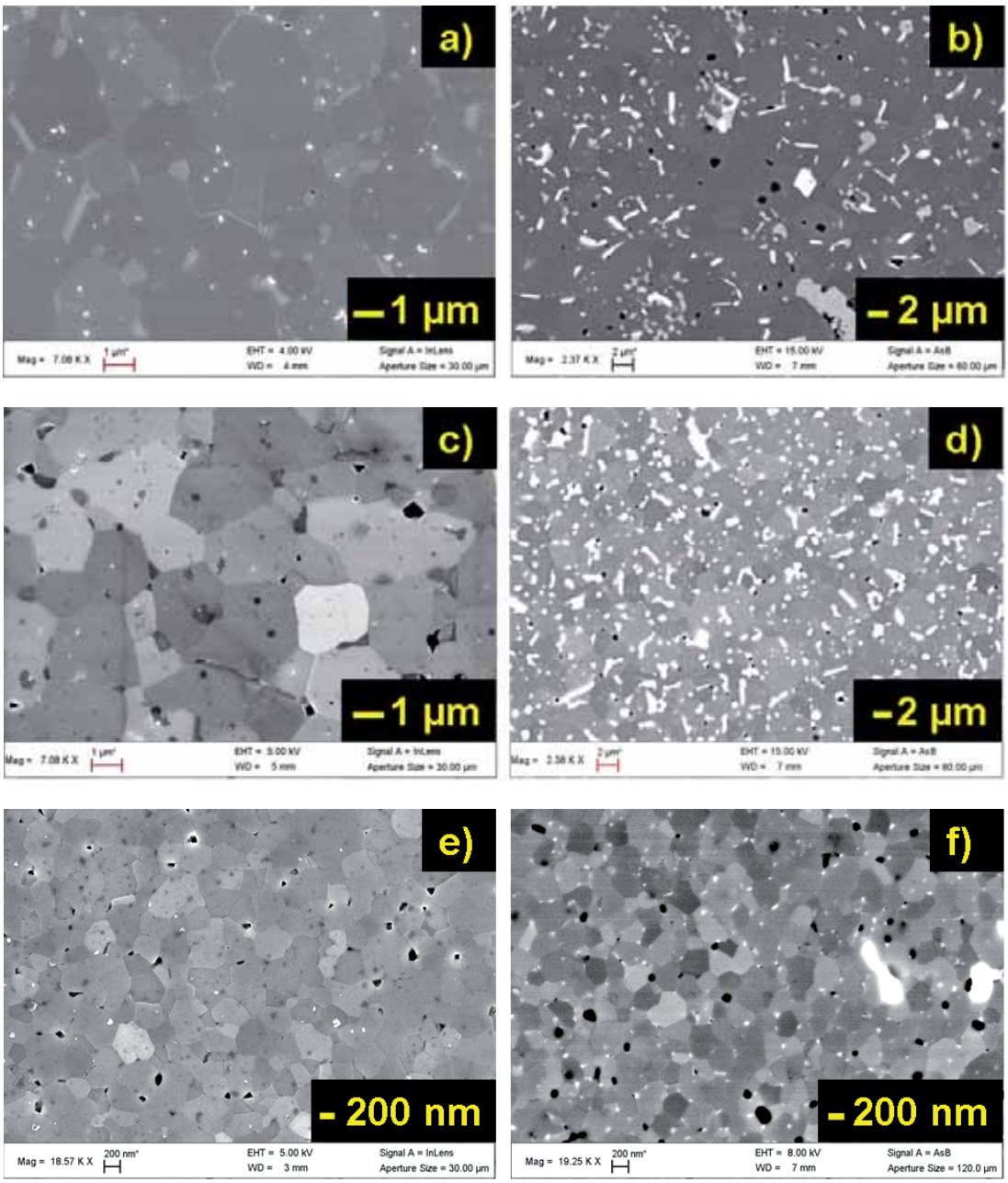

Fig. 5. SEM micrographs of the samples a) and b) synthesized by solid route, c) and d) synthesized by liquid route and sintered in conventional furnace, e) and f) synthesized by liquid route and sintered by microwaves.

eters have been calculated (Table 1). The values of breakdown voltage (938 V/mm), non-linearity coefficient (12) and leakage current density (84 μA/cm²) for varistors are in good agreement with those reported in the literature [2]. For the samples synthesized by the liquid route and sintered either conventionally or by microwave, it was not possible to reach a current density of 1 mA/cm², and consequently no varistor parameters were determined in these cases.

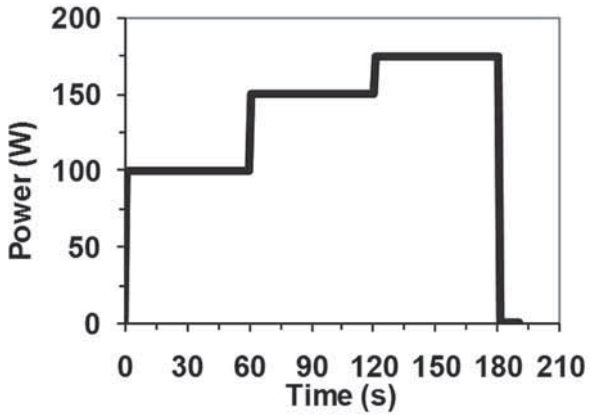

Fig. 6. Incident power versus time cycle for microwave sintering.

Table 1. Microstructure and electrical parameters of the varistors

Synthesis and sintering conditions	ρ [g/cm³]	*d* [μm]	E_b [V/mm]	α	J_L [μA/cm²]
Solid statesynthesis – conventional sintering	5.71	5	938	12	84.5
Liquid synthesis – conventional sintering	5.89	2	>1380	-	-
Liquid synthesis – microwave sintering	5.57	0.2	>1470	-	-

Nevertheless, it is clearly shown that the breakdown voltage strongly increases for the samples made of powder synthesized by the liquid route (Fig. 8). Its value is higher than 1380 V/mm and 1470 V/mm for, respectively, the nano-sized powder conventionally and microwave sintered. One of the reasons for this increase is that the grain size has strongly decreased, especially for the sample sintered by microwave. Otherwise, it is important to mention that the nature of the secondary phases is different, depending on the sintering method used (Fig. 7). As a consequence, the characteristics of the Schottky barrier formed by these secondary phases are undoubtedly modified and hence, that it also contributes to the differences which are observed on the *J*(*E*) curves.

4. Conclusion

A nano-sized zinc oxide based powder was synthesized by a wet chemical method. A powder with grains having a nearly spherical shape with a diameter around 20 nm was obtained. The conventional sintering of this nano-sized powder does not allow keeping the nano size, whereas microwave sintering enables a dense and very fine microstructure to be obtained. In that latter case, the dense sample having an average grains size around 200 nm, has been success-

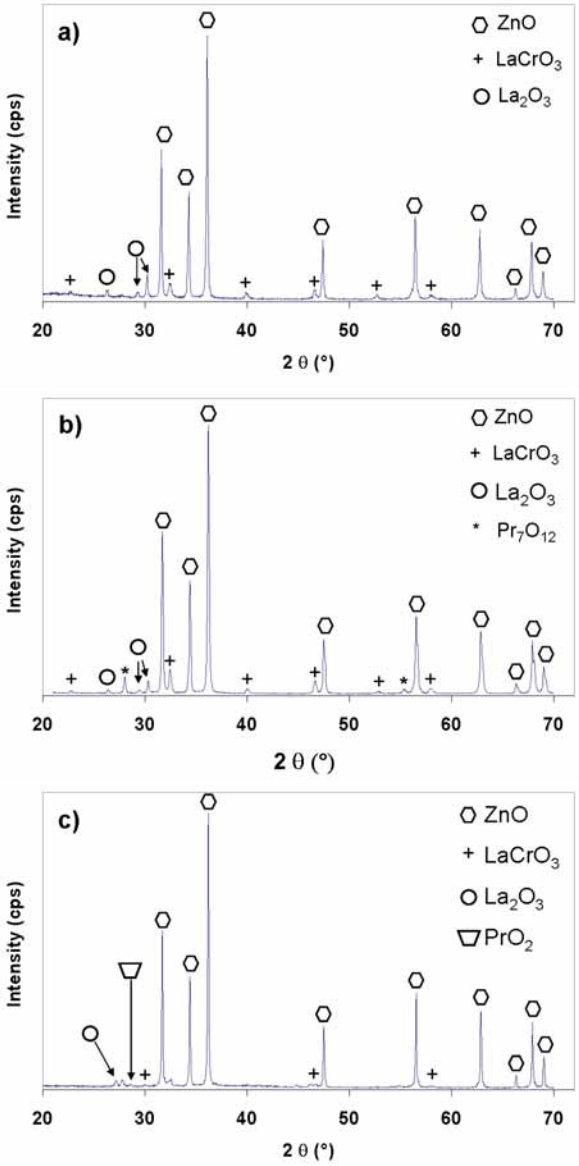

Fig. 7. XRD pattern of powder coming from: a) sample synthesized by solid route, b) sample synthesized by liquid route and sintered in conventional furnace, c) sample synthesized by liquid route and sintered by microwaves.

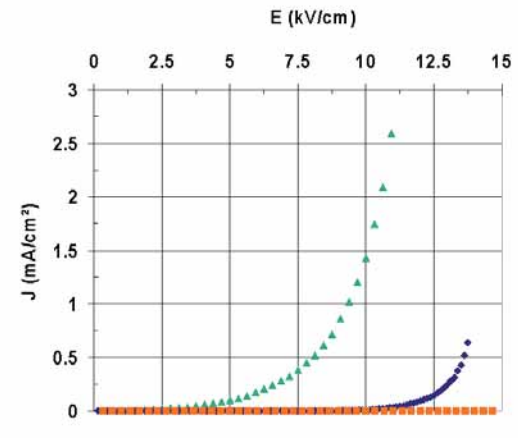

Fig. 8. E-J characteristics of the varistors synthesized by solid route (△), synthesized by liquid route and sintered conventionally (◇) and synthesized by liquid route and sintered by microwaves (□).

fully sintered. Otherwise, due to the very short thermal cycle in microwave, the chemical composition of the secondary phases is modified – the time being too short to complete the reactions between the dopants. The changes in the microstructure lead to a drastic modificatio of the electrical response of the material; in particular, the breakdown voltage highly increases. The next step of this work is to perform different annealings on microwave sintered materials in a view of keeping fine microstructure while modifying the secondary phases composition. The feasibility to tailor both the grains size and the nature of the inter-granular phases would open interesting routes for varistors.

Acknowledgements

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