Preface - Final publication of COST 539 Action "Electroceramics from nanopowders produced by innovative methods-ELENA"

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This issue of the journal *Processing and Application of Ceramics* is prepared as the *Final Publication* of COST 539 Action "Electroceramics from nanopowders produced by innovative methods-ELENA". It contains a selection of 14 refereed papers addressed to the activities in COST 539 Action summarised on the scientific context and objectives:

- Nanopowder metrology
- Assessment of the different nanosized synthesis methods for their applicability in the production of nanosized powders, films, nanotubes, nanowires for electroceramics applications
- Confinement and interface-related effects, core-shell and graded structures in electro-ceramics
- Modelling and size effects in nanostructured ceramics and films
- Local studies of properties (domains, dielectric mapping, piezoelectric, etc) in particles of nanopowders, nanocomposites, films and ferroelectric nanostructures

The improvement on that scientific context is of strong importance for European Communities and the research of this field obviously touches issues of economic, environmental, social, organizational, politic, networking and funding interest.

The COST 539 Action aimed to be a platform for presenting state of the new developments in the broad area of fabrications, properties and applications of nanostructured electroceramics produced by innovative methods from nanopowders. The Action also aimed to be a forum for strengthening the networking in the research cooperation, particularly in the Thematic Call of EU Research Programmes.

In recent period the scientists participating in COST 539 Action put strong effort to increase the knowledge of tailored innovative procedures for the synthesis of electroceramics powders and materials, to improve their quality for specific electronic sector application, as well to nanometrology. COST 539 Action gives strong opportunity for groups focused on nanopowders and nanostructured electroceramic materials prepared by advanced methods and techniques to work together, to exchange the knowledge and experience joining together and exploring matters of common multidisciplinary interest, especially from public and government research and technological sectors, or representatives of funding agencies for research and technology.

Generally, the main objective of COST Action ELENA was to improve the physical and electronic properties of advanced electroceramics and films produced by chemical, physical and mechanical synthesis techniques focusing on the polymeric precursors, sol-gel, spray pyrolysis, microemulsion, ultrasonic, vapor-phase and freeze-drying methods. Knowledge on the precursor chemistry, physical and chemical mechanisms, as well as knowledge on the mechanically activated processes, sintering, co-strain and co-fired sintering, microstructure and nanostructure should increase and tailor to the requirements of industries. The outcomes were the promotion of an integrated approach towards novel technologies and special analysis and equipments for the characterization required for multifunctional applications in order to improve the industrial exploitation of nanostructured electroceramic materials in Europe.

ELENA COST Action tried to bridge the gap between the fundamental research in the field of electroceramics and their final technological application in electronics and electronic systems. The involvement of industrial participants was the essential to pinpoint innovative applications of advanced electroceramics. Bringing together the specialists in the innovative methods for the synthesis, processing and characterisation of advanced electroceramic material led to possibility to gain a significantly better understanding of these materials and their manufacture. Action COST 539 with participation of more than 60 institutions from Universities,

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Institutes, Academies of Sciences, public and private industry sectors from 22 European countries and 6 non European countries provided an ideal opportunity to form an international network and regular forum for experimental scientists, engineers and policy and decision makers in public and private research sector. Working together to improve their most recent research findings in nanopowders synthesis and nanosructured materials to highlight technique developments and issues that are limiting their progress, COST 539 expressed the good practice how to disseminate throughout the EU community previously obtained results by national and international networking activities.

It was shown that the synthesis of nanomaterials with uniform and sharp particle size distribution is the subject of intensive research in the recent time because of their fundamental scientific interest as well as for the technological importance. Many methods have been developed to produce nanoparticles. The generic themes of chemistry, physical-chemistry and mechanochemistry processing, micro- and nano-structure and finally the physics of the nanopowders and characterisation of their properties and modelling were investigated. To a large extent, processing is responsible for the structures of the ceramics and films, and these micro- and nanostructures have strong effects on their physical properties and characteristics and on the device performance in witch they are incorporated. Precursor chemistry and relation between precursor chemistry and processing (sol-gel and organometallic complex based at Pechini process), micro- and nano-structure of powders is subject of special interest. Hydrothermal synthesis is sometimes called a "soft solution chemical processing" because the middle reaction conditions under which the products are achieved (low temperature and short reaction times), leads to controlled particle size and morphology. These characteristics decrease the sintering temperatures and, consequently, low price products can be obtained.

In situ synthesis of functional nanocrystalline powders and nanocomposites using chemical reactions in aerosols (spray pyrolysis) is based on single-step high temperature aerosol decomposition ultrasonically generated from various precursor solutions. Since the stages of solid-phase precipitation, decomposition and sintering occur in a dispersion phase at the level of several micrometer sized droplets; the advantages of this process relate to the careful control over the particle size, morphology, chemical and phase composition by adjusting the solution and process parameters. An outstanding result of new synthesis techniques is that the calcination and sintering temperature may be lower, the porosity lower and the homogeneity higher if during the overall thermochemical treatment of powders a careful control is taken to avoid any local change of the composition.

Solid-state reactions that normally require high temperatures will occur at lower temperatures during mechanochemical synthesis without any externally applied heat. In addition, the high defect densities induced by intensive milling in high-energy mills accelerate the diffusion process. Alternatively, the particle refinement and consequent reduction in diffusion distances (due to microstructural refinement) can at least reduce the reaction temperatures significantly, even if they do not occur at room temperature. Mechanical treatment of ceramic powders can reduce particle size and enables obtaining of nano-structured powders, which are of the main interest in current trend of miniaturisation and integration of electronic components.

There are 23 groups from 16 countries contributing to research and development within the theme. The various groups were working on topics that fall within the 3 sub-project groups set out in the memorandum of collaboration for the COST Action 539 - ELENA addressed to *Chemical methods, Physical methods and Mechanical methods for nanopowders synthesis and their characterization* with main topics: *Soft Chemistry* (Sol-Gel, precipitation, polymeric precursor), *Vapour Phase Methods* (CVS, CVD, Spray-drying, spray pyrolysis), *Mechanical Activation and Mechanochemical Synthesis and Powder Characterization* (PSD, SSA, XRD, SEM, TEM). Overall around 20 different powders or compositions have been synthesised using different methods: sol-gel, polymeric precursors method (Pechini process), hydrothermal synthesis, microemeulsion, mechano-chemical synthesis, vapor-phase and solid-state synthesis: Al_2O_3, ZnO, TiO_2, $LiFe_2PO_4$, $La_{2/3}TiO_3$, $Pb_{1-x}Ca_xTiO_3$, $BaTiO_3$, $BaBi_2Ta_2O_9$, $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Bi_4Ti_3O_{12}$, $BaBi_4Ti_4O_{15}$, $SrTiO_3$, $PbTiO_3$, $Pb(Zr,Ti)O_3$, ZrO_2, $ZnFe_2O_4$, $Mg_xZn_{1-x}Fe_2O_4$, $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$, $La_{1-x}Sr_xCoO_3$, La_2O_3-CoO_3-SiO_2(Pr,Ca)CoO_3, $H_2Ti_3O_7$, $Pr_{1-x}Bi_xCoO_3$, $SiO_2/CoFe_2O_4$, $Ti_{24}Al_{11}Nb$, $SnO_{2/7}Ag$, $(K_{0.5}Na_{0.5})NbO_3$, $NaNbO_3$, (1-x)$NaNbO_3$-x$SrTiO_3$, 0.92$PbZn_{1/3}Nb_{2/3}O_3$-0.08$PbTiO_3$, (1-x)$BiScO_3$-x$PbTiO_3$ and $SnO_{2/7}Ag$. Synthesis and characterization of different types of nanowires and nanotubes were successfully realized.

It is well known that many properties of polycrystalline electroceramics fall far below the figures of merit for single crystals. One way of approaching these hugely promising properties is by introducing texture and crystallographic orientation into polycrystalline ceramics. Both the chemical and mechanical methods to synthesis powders are possible routes where anisotropic particles can be produced. The addition of dopants can also strongly influence to the grain shape and microstructure anisotropy during the sintering stage, even sintering with applied loads could be envisaged to modify ceramic microstructure texture. All these possibilities linked with the fine control of grain boundary composition and at the nanoscale level should enhance

electroceramic properties. To obtain the needful quality of materials, the further processing of nanopowders is of strong importance. Experimental and theoretical approach to thermal treatment (calcinations, firing of functional phase of thick films, reactive or liquid phase sintering of electroceramics or annealing of films) is of fundamental significance.

There are 18 groups from 14 countries contributing to research and development within the theme. The various groups were working on topics that fall within the sub-project groups set out in the memorandum of collaboration for the COST Action 539 – ELENA. Confinement and interface-related effects, core-shell and graded structures in electro-ceramics were investigated. The coating of fine particles with a different perovskite and the subsequent consolidation to dense ceramics retaining a radial composition gradient within the single grains represents a new approach for the preparation of ceramic materials with tailored dielectric properties. Dense ceramics with locally graded structure can be only obtained by a careful choice of the sintering conditions controlling the inter-diffusion between core and shell. The final materials show strongly modified dielectric properties in comparison to both the parent compounds and the homogeneous solid solutions. The proposed approach is generic and suggests a new avenue to create functional and structural polycrystalline materials with locally graded structure by the controlled sintering of core-shell particles.

In particular the following materials systems and compositions have been investigated: $BiFeO_3$, $BiMnO_3$, $BiFeO_3$-$BaTiO_3$, La-Bi(Fe,Mn)O_3, $BaTiO_3$-Fe_2O_3, $EuTiO_3$, (Na,K)NbO_3, including $KNbO_3$, $NaNbO_3$, $K_{0.5}Na_{0.5}NbO_3$ and K_2O-Nb_2O_5-SiO_2,-Pb(Zr,Ti)O_3 and more specifically $Pb(Zr_{0.52}Ti_{0.48})O_3$,(Pb,La)(Zr,Ti)$O_3$,$BaTiO_3$,Ba(Zr,Ti)$O_3$, $SrTiO_3$,(Ba,Sr)TiO_3,$BaTiO_3$-Ag,$BaTiO_3$-Ni,$BaTiO_3$-Cu, $Bi_4Ti_3O_{12}$,$BaBi_4Ti_4O_{15}$,ZrO_2,$La_2Zr_2O_7$,$Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$-$Pb(Fe_{1/2}Nb_{1/2})O_3$-$PbTiO_3$, Pb(Mg,Nb)O_3-Pb(Fe,Nb)O_3, $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$, MgO-ZnO-Fe_2O_3, $La_{0.2}Sr_{0.8}Fe_{1-x}Ti_xO_{3-\delta}$, $(Na,H)_2Ti_3O_7$, HfO_2 and Si_3N_4-SiC, etc.

Main contribution could be summarised relevant to research topic: i) Size and grain boundary effects in ceramic systems (nanostructured ceramics, thick and thin films) prepared from nanopowders obtained by different innovative methods; thickness effects in films; interfaces effects in porous and composite ceramics), ii) Study of piezoelectric systems with anisotropic particles (nano-wires) and of their properties in free standing and in self-organised form, iii) Developing new electroceramics for dielectric, electrostrictive and piezoelectric applications with superior properties and iv) Advanced ceramic nanocomposites with high hardness and wear resistance, high strength and weight/strength ratio, high creep and oxidation resistance.

Micro- and nano-structures strongly influence physical properties. To develop a more comprehensive understanding of the influence of microstructure and nanostructure on the physical, chemical and mechanical properties one should begins with comprehending its nanostructure. As for most materials of technological interest, the microstructure and nanostructure of electroceramic materials are keys for understanding their physical and chemical properties. The essential importance is to predict the performance and develop methods to engineer electroceramics with desired and controllable properties. In order to transfer the developed technology into industrial applications with a view to develop industrial scale synthesis, characterisation of the microstructure/nanostructure of electroceramics is the key issue.

There are 15 groups from 12 countries contributing to research and development within the theme "*Functional characterisation of electroceramic materials and films*". The various groups are working on topics that fall within the sub-project groups set out in the memorandum of collaboration for the COST Action 539 – ELENA. Standing on the knowledge developed in ELENA action concerning novel fabrication methods of nanopowders and their compositional, microstructural and morphological characterization and control, the progress in both advanced aspects of nanofabrication and understanding, mainly on polar materials, but also on multiferroic materials, was shown. Main contribution could be summarised as follows: i) Local studies of electrical properties (domains, dielectric mapping, piezoelectric, etc) in particles of nanopowders, nanocomposites films and ferroelectric nanostructures, ii) Macroscopic electrical characterization (ferroelectric, piezoelectric, piroelectric, ionic conduction) as a function of the temperature, frequency, field and iii)Modeling and size effects in nanostructured ceramics and thin films.

The *Final Publication* has intention to present the selection of papers addressed to main scientific topics and objectives of COST 539 Action.

Topic *Nanometrology* is represented in paper "Nanopowder metrology and nanoparticle size measurement - Towards the development and testing of protocols" (A. Aimable, P. Bowen).

Topic *Assessment of the different nanosized synthesis methods for their applicability to the production of nanosized powders, films, nanotubes, nanowires for electroceramic applications* is represened in papers: "Ferroelectric perovskite nanopowders obtained by mechanochemical synthesis" (I. Szafraniak-Wiza, B. Hilczer, E. Talik, A. Pietraszko, B. Malic), "Comparison of two innovative precipitation systems for ZnO and Al-doped ZnO nanoparticle synthesis" (A. Aimable, T. Strachowski, E. Wolska, W. Lojkowski, P. Bowen), "Direct synthesis of nanocrystalline oxide powders by wet-chemical techniques" (V.V. Srdić, R. Djenadić, M.

Milanović, N. Pavlović, I. Stijepović, L.M. Nikolić, E. Moshopoulus, K. Giannnakopoulos, J. Dusza, K. Maca), "Aerosol route in processing of nanostructured phosphor material" (K. Marinković, L.S. Gomez, M.E. Rabanal, L. Mančić, O. Milošević), "Solution based approaches for the morphology control of $BaTiO_3$ particulates" (F. Maxim, P. Ferreira, P.M. Vilarinho, I. Reaney, A. Aimable, P. Bowen), "Perovskite type nanopowders and thin films obtained by chemical methods" (V. Fruth, M. Popa, J. Calderon-Moreno, O.E. Tenea, M. Anastasescu, P. Osiceanu, E. Anghel, L. Predoana, B. Malic, M. Zaharascu) and "Organic crystals - More than simple additives toward better electroceramic materials" (M. Senna, C. Ando, M. Vijatović Petrović, J. Bobić, B. Stojanović).

Topic related to *Confinement and interface-related effects, core-shell and graded structures in electroceramics* is standing with "Nanoferroelectric perovskite oxides with unusual morphology produced by different synthesis procedures" (A. Bassano, V. Kalazani, L.P. Curecheriu, M.T. Buscaglia,V. Buscaglia, L. Mitoseriu, P. Nanni).

Topic *Modelling and size effects in nanostructured ceramics and films* is standing with "Mechanically clamped PZT ceramics investigated by First-order reversal curves diagram" (L. Stoleriu, C. Ciomaga, F. Fochi, P. Ochoa, J.F. Fernandez, C. Galassi, V. Buscaglia, P. Nanni, L. Mitoseriu).

Topic addressed to *Local studies of properties (domains, dielectric mapping, piezoelectric, etc) in particles of nanopowders, nanocomposites, films and ferroelectric nanostructures* is represented through papers: "Dielectric investigations of La-doped barium titanate" (T. Ramoška, J. Banys, R. Sobiestinskas, M. Vijatovic Petrović, J. Bobić, B. Stojanović), "Piezoelectric characterization of lead-free ferroelectric ceramics" (L. Pardo, A. Garcia, K. Brebol, L.P. Curesheriu, L. Mitoseriu, E. Mercadelli, C. Galassi), "Properties of $BaTiO_3$ confined in nanoporous Vycor and artificial opal silica" (D. Nuzhnyy, P. Vanek, J. Petzelt, V. Bovtun, M. Kempa, I. Gregora, M. Savinov, R. Krupkova, V. Stutunička, J. Buršik, M.I. Samozlovich, W. Schranz) and "Thickness dependent magnetic transitions in pristine MgO and ZnO sputtered thin films" (M. Kapilashrami, J. Xu, K.V. Rao, L. Belova).

The scientific level of the presenting papers was evidenced. On this point, it is worth to remark that the *Final Publication* looks very stimulated fulfilling one of the main COST target, i.e. to create closer networking among the different European scientific groups. The high number of authors gives a significant contribution to COST 539 Action. They mostly reported the results obtained by the different groups of the ELENA Action in the field of the synthesis and processing of nanostructures and in their properties. A few contributions were also presented for films preparation, characterisation and nanometrology. On that way, the significance of the *Final Publication* COST 539 is much more discernible and can be interesting for the wide scientific community.

Finally, we are greatly grateful to the colleagues that helped to prepare this Special Issue of the journal *Processing and Application of Ceramics*. In addition, we would like to thank to all manuscript referees who devoted their time and enthusiasm to improve the quality of the Special Issue.