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ANALYTICAL ELECTRON MICROSCOPY OF ADVANCED CERAMIC MATERIALS

Goran Dražič
J. Stefan Institute, Ljubljana, Slovenia

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Keywords: advanced ceramic materials, AEM, Analytical Electron Microscopy, PZT-PNN piezoelectric materials, PLZT ferroelectric thin films, TEM, Transmission Electron Microscopy

Abstract: Application of analytical electron microscopy (AEM) in the development of advanced ceramic materials is presented and discussed. The capabilities of different techniques which are used in analytical electron microscope are described with examples of the investigation of various materials such as PZT-PNN, Si_3N_4, NiO-ZnO solid solution, RuO_2 based thick film resistors and PLZT thin ferroelectric films. The importance of proper TEM sample preparation and selection of appropriate operating conditions for transmission electron microscope experiments is emphasized.

Analitska elektronska mikroskopija sodobnih keramičnih materialov

Ključne besede: materiali keramični zahtevnejši, AEM mikroskopija elektronska analitična, PZT-PNN materiali piezoelektrični, PLZT plasti tanke feroelektrične, TEM mikroskopija elektronska transmisijska

Povzetek: Hiter razvoj sodobnih keramičnih materialov s posebnimi mehanskimi, električnimi, optičnimi ali magnetnimi lastnostmi je pogojen z uporabo specialnih metod karakterizacije mikrostrukture. V delu so opisani primeri uporabe analitske elektronske mikroskopije (AEM) pri raziskavah in razvoju novih materialov. Metode preiskav, ki jih omogoča AEM so visokoločljivostna elektronska transmisijska mikroskopija (HRTEM), s katero direktno opazujemo kristalno mrežo, energijska spektroskopija rentgenskih žarkov (EDXS), ki nam omogoča določitev elementne kemijske sestave izredno majhnih volumnov in različne vrste elektronske difrakcije (elektronska difrakcija izbranega področja (SAED), mikrodifrakcija ter elektronska difrakcija s konvergiranim snopom (CBED)), ki nam omogočajo določitev strukture in kristalografskih odnosov med posameznimi fazami v vzorcu. Materiali, ki jih delo obravnava so feroelektrični prahovi in tanke plasti na osnovi PZT, Si_3N_4 keramika, azbesti, fulereni, ZnO-NiO trdne raztopine in debeloplastni upori na osnovi RuO_2.

1. INTRODUCTION

The development of advanced ceramic materials with special mechanical, electrical, optical or magnetic properties is related to the parallel development and use of different methods for their microstructural characterization. In many cases, a knowledge of the chemical composition and structure of various phases (precipitates, intergranular layers, corrosion products, interface layers) is important for a better understanding of the chemical and physical processes taking place during the fabrication of ceramic materials.

Methods which may be used for the characterization of the microstructure of advanced ceramic materials are limited due to the relatively small particle size of some phases. Various techniques of optical microscopy can be used for the study of particles with sizes much larger than a few µm. X-ray diffraction, normally used in routine investigations of phase composition, cannot detect the presence of amorphous or extremely fine-grained phases. For determination of the chemical composition, electron probe microanalysis (EPMA) may be used in cases where particles of interest are not smaller than a few µm. With relatively low accelerating voltages (below 10 keV) it is possible to avoid the influence of the matrix or substrate material, and to analyze particles with sizes just below 1 µm, but under such conditions large errors in the results are to be expected.

Frequently the only method allowing the examination of very small volumes is analytical electron microscopy (AEM), which combines scanning transmission electron microscopy and some microanalytical method, such as energy dispersive X-ray spectroscopy (EDXS) and/or electron energy loss spectroscopy (EELS). AEM enables simultaneous examination of the structure, structural relationships between phases, and chemical composition of the samples. /1/

The basic techniques for material investigations using the analytical electron microscopy are:
- Conventional Transmission Electron Microscopy (CTEM) which is used for the observation of the

morphology of samples, determination of different parameters related to crystal structure and identification of various defects and features in crystal lattices using bright and dark field experiments. /2/

- High Resolution Transmission Electron Microscopy (HRTEM), where direct imaging of the crystal lattice is possible. The application of this method is limited by the resolution of TEM. The technique is used for determination of very thin intergranular phases, examination of interfaces in multilayer structures, and investigation of different defects and the crystal lattice structure. /3/
- Various techniques of electron diffraction, such as Selected Area Electron Diffraction (SAED), Microdiffraction and Convergent Beam Electron Diffraction (CBED). From the diffraction patterns the structure, orientation, symmetry, crystallographic relations and thickness of the sample may be determined. /2/
- Energy Dispersive X-ray Spectroscopy (EDXS). This method allows chemical analysis of very small particles. While qualitative and semiquantitative analysis is rather routinely used, the quantitative analysis of small particles and phases containing light elements (C,N,O) is quite complicated and time consuming. /4/
- Electron Energy Loss Spectroscopy (EELS) is used for chemical analysis of light elements, determination of the valency state of elements, energy filtering, etc. /5/

In the present paper examples of the application of techniques of analytical electron microscopy in research on and development of different advanced ceramic materials are presented and discussed.

2. EXPERIMENTAL

Experimental details of the preparation of the materials used in this study were published elsewhere /14-16, 20, 21, 27, 29/. Powder samples were ground in an agate mortar in ethanol and ultrasonically dispersed on a hollow carbon coated Cu grid for TEM investigations. Plan-view specimens of bulk samples and thin films supported on substrates were prepared by mechanical thinning, dimpling and ion milling using argon ions. In the case of bulk material, samples were eroded from both sides, while in the case of thin films only from the substrate side. Cross-sections of the thin film samples were prepared using a Gatan cross-sectional TEM specimen preparation kit. Normally, samples were cooled with liquid nitrogen during the final stages of ion erosion.

Samples were examined by Jeol 2000 FX transmission electron microscope (TEM), operated at 200 kV. The chemical composition of phases was determined using a Link AN-10000 EDXS system (Energy Dispersive X-ray Spectroscopy) with an Ultra Thin Window Si(Li) detector, connected to the TEM. The Cliff-Lorimer /6/ method and absorption correction /7, 8/ were used for quantitative analysis. In most cases the concentration of oxygen was calculated from stoichiometry. Quantitative EDXS analysis with a precision (defined as the relative standard deviation) equal or below 5% was achieved, notwithstanding problems during the sample preparation, peak overlapping and absorption corrections.

3. RESULTS AND DISCUSSION

3. 1. TEM-EDXS analysis of powder and porous bulk samples

AEM techniques used in investigations of powder samples enable chemical reactions taking place during the ceramic material fabrication to be followed on a micro or even nano scale. The size (thickness) of the powder particles should not be much higher than 100 nm to enable the penetration of electrons. Thicker particles should be milled, but in such a case the interfaces and the relationships between different powder particles are usually destroyed. Various methods /9-12/ of embedment of larger powder particles were proposed using epoxy, electroless nickel and copper or amalgam. Subsequently TEM samples are prepared employing ion erosion or microtome cutting. These methods may be problematic due to excessive heating and selective ion milling, or introduce defects due to large stresses (in the case of microtomy).

A solid solution of $Pb(Zr,Ti)O_3$ - $Pb(Ni_{1/3}Nb_{2/3})O_3$ (PZT-PNN) is a promising material for piezoelectric applications. Chemical reaction mechanisms during synthesis of the material are not yet well understood because of the quite complicated composition (5 different starting oxides)/13/. Many binary and ternary compounds in this system have similar crystal structure with similar unit cell parameters, and some starting oxides have extremely small particle size, and therefore just the XRD technique alone could not be used for positive identification of all the phases present during thermal treatment of the samples. Using analytical electron microscopy we were able to answer some unsolved questions /14/. We systematically examined TEM samples of the starting mixture of oxides and powders prepared at different firing conditions. On each sample we inspected numerous particles and determined their structure by electron microdiffraction (the size of the particles was between 20 and 200 nm) and chemical composition by quantitative EDXS. In Figure 1 TEM micrographs (a), EDXS spectra (b) and microdiffraction patterns (c) of powder fragments of PZT-PNN loose powder, thermally treated at 650 °C for 60 min are shown. Most of powder the particles were small enough, not to require any particular sample preparation. Using EDXS and electron microdiffraction techniques, it was found that the three binary phases PN, PZ and PT could coexist at this temperature. NiO and partly ZrO_2 were still unreacted at this point of the sample synthesis. The ternary compound $Pb(Ti,Zr)O_3$ was also detected (not present in Fig. 1). Obviously NiO enters the solid solution at much higher temperatures.

Examination of the chemical composition of primary particles (grains) in the first stages of sintering (neck formation stage) may provide interesting and valuable results. Preparation of such samples for TEM observation represents severe problem. Usually samples are

mechanically extremely sensitive and should be handled with great care during the grinding, polishing and dimpling procedures. In the ion erosion step the structure and chemical composition of the grains could be altered due to overheating.

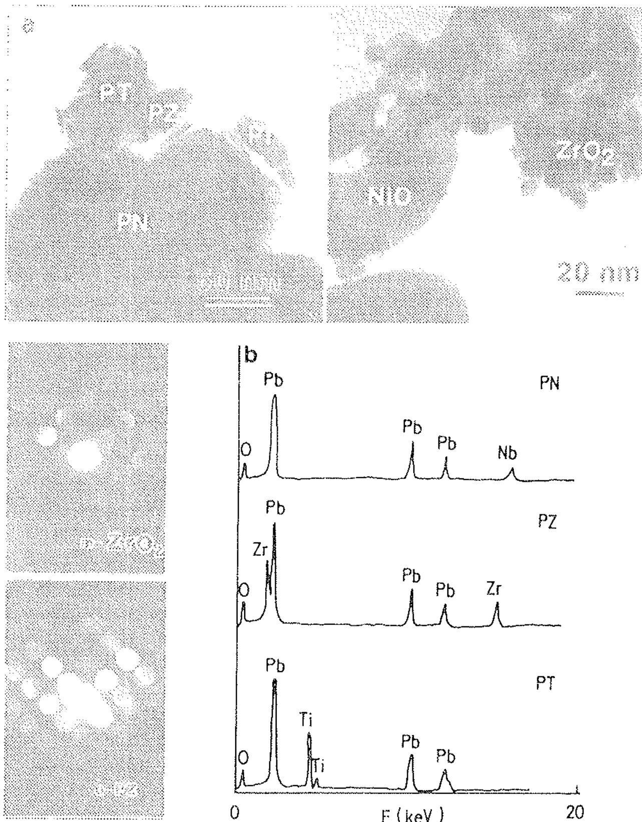

Fig. 1: (a) - TEM micrographs of fragments in a PZT-PNN loose powder sample fired at 650 °C for 60 min, (b) - EDXS spectra of $Pb_2Nb_2O_7$ (PN), $PbZrO_3$ (PZ) and $PbTiO_3$ (PT) phases, (c) - microdiffraction patterns of monoclinic ZrO_2 and orthorhombic PZ.

Particles (grains) are bound together only in the necks, so that thermal conductivity is poor. Cooling of the sample with liquid nitrogen in the final stages of ion milling could partly, but not completely overcome heating problems.

Figure 2 displays a dark field TEM micrograph of sol-gel derived PZT (50/50) grains in a sample fired at 650 °C for 5 hours and reheated at 850 °C for 1 hour. The TEM sample was prepared by ion milling (Ar ion energy of 4.0 keV) and was cooled with liquid nitrogen (LN_2) in the final stages of the erosion (last half hour). The micrograph was taken using diffuse scattered electrons, so that the bright contrast around grains and at neck areas represents an amorphous phase containing extremely small (few nm) precipitates (bright spots). Deficient cooling of the sample during ion milling could be deduced from the results. After using a lower energy of ion milling (3.8 keV) and a longer cooling period (during the whole milling time) it was found that some PbO - rich phase was still present at the neck areas. Based on other experimental results of methods such as XRD, DTA and sintering curves, it was concluded that this t PbO rich phase was not an artifact but a consequence of dehomogenization during the early stages of sintering /15/.

3. 2. Deterioration of the structure and chemical composition during TEM experiments

Beside the danger of altering the structure and chemical composition of the samples during ion milling, some samples could also deteriorate during observation in the transmission electron microscope (in-situ) due to electron beam induced heating or high energy electrons damage. The latter case is characteristic of high-energy microscopes (400 keV and higher). Most organic materials, glasses and inorganic solids with high volatility (for example lead and bismuth oxides), or with chemically bound crystalline water or (OH)- groups (talc, chrysotile asbestos, etc.) are especially sensitive to this phenomenon. Fullerene, a globular form of carbon (with chemical formula C_{60} and C_{70}) is among the materials that are very susceptible to an electron beam.

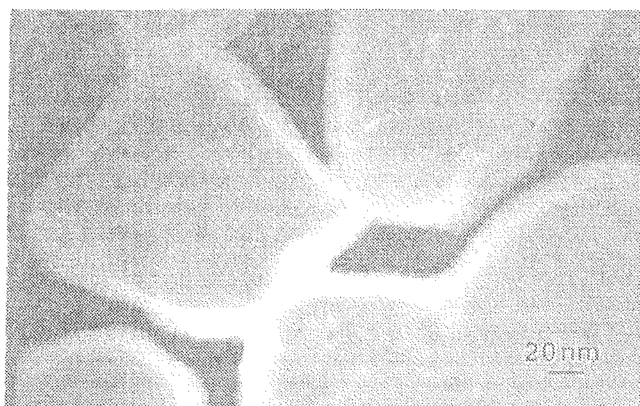

Fig. 2: Dark field TEM micrograph (using diffused scattered electrons) of neck areas in a sample of PZT (50/50) fired at 650 °C for 5 h and 850 °C for 1 hour.

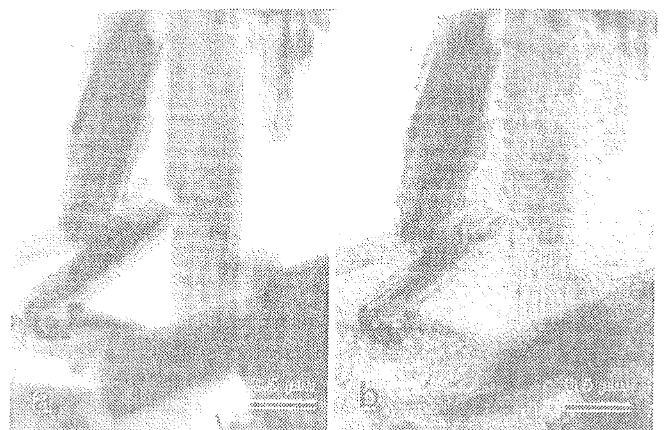

Fig. 3: (a) - TEM micrograph of fullerite crystals before and (b) - after the in-situ heating experiment

In Figure 3a a TEM micrograph of crystals of fullerite (crystals of a solid solution of C_{60} and C_{70} in f.c.c. or h.p.c. form) before degradation is shown. During the in-situ heating experiment using an intense electron beam (larger condenser aperture and smaller spot size), part of the material evaporates. The residues of the crystals (skeletons) became amorphous but still preserve their original size and shape. The evaporated material condensed in the vicinity of the amorphous residue of the crystals. In Figure 3b a TEM micrograph of the crystals after the heating experiment is displayed. Small (up to 50 nm) droplets between the skeletons of the crystals were found to consist of fullerite nanocrystals. We were able to explain the anomalous vapour pressure of fullerite at higher temperatures in terms of its tendency to become amorphous on heating /16/.

3. 3. Structural ceramics, wear and erosion

Ceramics used for applications where mechanical properties are of main importance and limit their use (strength, hardness, toughness, shock resistance, etc.) are called structural ceramics. Among other materials, light Si_3N_4 is quite promising, mainly for high temperature applications (turbine rotors etc.). During the fabrication of Si_3N_4 ceramics, a thin amorphous oxy-nitride layer is normally formed at the grain boundaries (GB) between adjacent grains, with the exception of the low angle and special grain boundaries /17/. The presence of this amorphous phase is usually determined by different techniques of transmission electron microscopy /18/. Serious problems in using these methods include the thickness of the intergranular phase (around 1 nm), the amorphous contamination layer and the grain boundary grooving produced during ion milling of the samples. The chemical composition of the secondary phase at the GB, which is believed to have a strong influence on the mechanical properties at high temperature, could not be accurately determined even using extremely narrow electron beams in dedicated TEMs with field emission guns /19, 20/. The most reliable method for determination of the presence of the amorphous intergranular phase is high resolution electron microscopy.

Figure 4 represents a high resolution transmission electron microscope (HRTEM) micrograph of a 1 nm thick intergranular layer of oxy-nitride glassy phase between two Si_3N_3 grains in Si_3N_4:Yb_2O_3 ceramic material.

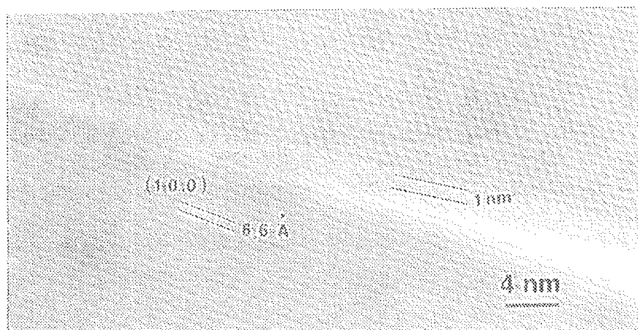

Fig. 4: HRTEM micrograph of a 1 nm thick intergranular layer of oxy-nitride glassy phase between two Si_3N_3 grains in Si_3N_4:Yb_2O_3 ceramics.

The wear mechanism of structural ceramics is affected by the temperature, by their reactivity with the counter material, as well as by the presence of active species in the environment (humidity, lubricants etc.). In the case of Si_3N_4 in contact with itself under dry conditions, brittle fracture of Si_3N_4 grains prevails, resulting in severe wear and a high coefficient of friction. In the case of the presence of humidity, a protective oxide layer is formed resulting in a significantly lower wear rate. Identification of the reaction products formed in dry or lubricated contact between the two parts is of major importance for understanding (and reduction of) the wear of ceramics in different environments. Such products were examined using methods of analytical electron microscopy in isostatically hot pressed silicon nitride plates on top of which a Si_3N_4 ball was oscillating. It was found that the fretting wear of silicon nitride depends on the amplitude of oscillation and on the environmental conditions, at least in the range examined /21/.

Figure 5 shows a TEM micrograph (bright field) of an area in the wear scar on a Si_3N_4 plate exposed to fretting at an amplitude of 15 μm for 30 minutes. The microcracks which were found around the silicon nitride grains severely deteriorate the mechanical properties of this part of the ceramic material.

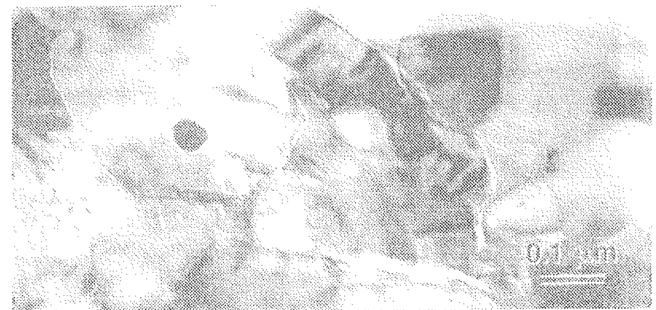

Fig. 5: TEM micrograph of an area in the wear scar on a Si_3N_4 plate exposed to fretting at an amplitude of 15 μm for 30 minutes.

Superficially completely different, but actually a very similar case of the use of AEM in the identification of erosion products is the determination of asbestos fibres in drinking water. Asbestos fibres are a health hazardous material that increase the risk of lung cancer when they are inhaled. In waterworks and piping systems, built several decades ago, asbestos-cement pipes were used. This material incorporates asbestos fibres as a hardening agent. When water flows through this type of pipes, the walls are eroded and the asbestos fibres are carried away. In the last decade the potential health effects of asbestos fibres in drinking water have received much attention. There has been some concern that populations exposed to high concentrations of asbestos in their drinking water over long periods of time could show an increased incidence of gastrointestinal tract cancers. Asbestos often occurs naturally in

drinking water, and concentrations of several million fibres per litre are not uncommon. The normal use of asbestos-cement pipe contributes relatively low levels of fibres to the water which is conveyed through them. Today it is believed that asbestos fibres are carcinogenic only when inhaled, and not when ingested /22/.

The only method that could positively identify asbestos fibres is analytical electron microscopy /23-26/. As a positive identification high matching of the morphology (aspect ratio), chemical composition (ratio of elements Na, Mg, Ca, Fe to Si) and the structure (using electron diffraction) to standard values should be achieved.

In Figure 6a TEM micrograph, an electron diffraction pattern and an EDXS spectrum of chrysotile asbestos fibre from drinking water (waterworks in a city in Slovenia) is shown.

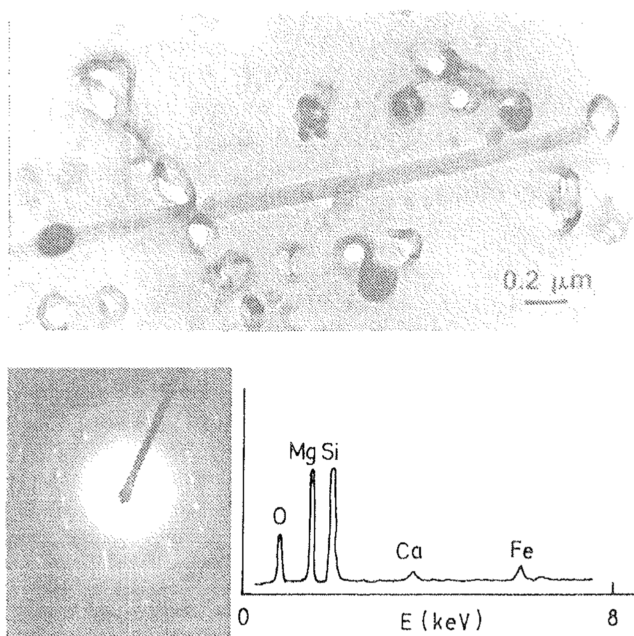

Fig. 6: TEM micrograph, electron diffraction pattern and EDXS spectrum of a chrysotile asbestos fibre from drinking water.

3. 4. Electronic ceramics; properties vs. microstructure

In the ZnO - NiO system two solid solution phases (ZnOss: solid solution of NiO in ZnO phase and NiOss: solid solution of ZnO in NiO phase) coexist. It was found that this material posseses a positive temperature coefficient of electrical resistivity (PTCR) if it contains a suitable ratio of the two phases. The origin of the PTCR anomaly was explained on the basis of the percolation model. The conductivity of ZnOss is much higher than that of NiOss grains in the ceramic material. On the other hand, the linear thermal conductivities of the two phases are very different, and thus on heating the interconnections between the particles of the highly conductive phase are loosened and the bulk conductivity is substantially decreased.

A TEM micrograph is given in Fig. 7, showing the stress field (S) at the top of a microcrack (M) at the ZnOss-NiOss boundary in a thermally treated sample with 40 wt.% of ZnOss /27, 28/. The thermal expansion differences cause mechanical stresses at the grain boundary during cooling of the sample. These stresses are relaxed by the formation of microcracks which could not be annealed at lower temperatures, and therefore provoke ageing and finally, after repeated thermal cycles, the collapse of the material. This effect prevents the practical use of the material.

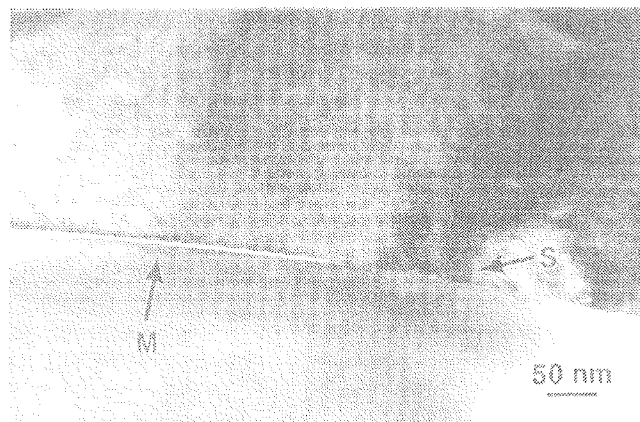

Fig. 7: TEM micrograph showing the stress field (S) at the top of a microcrack (M) at the ZnOss-NiOss boundary in a thermally treated sample with 40 wt.% of ZnOss

A similar example where only AEM techniques could confirm suspected reasons for distinctive electrical properties is the influence of the microstructure on the gauge factors in thick film resistors /29/. The gauge factor of a resistor is defined as the ratio of the relative change in resistance and the strain applied. As well as geometrical reasons alone (change in dimensions due to applied stress), it was found that the size and distribution of the particles of the conductive phase also plays an important role in this phenomenon. In Figure

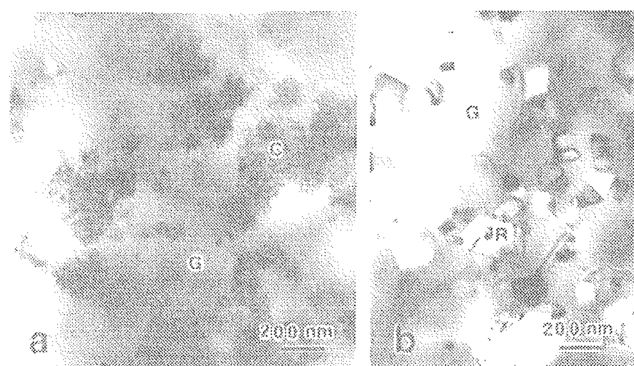

*Fig. 8: (a) - TEM micrograph of a DuPont 8041 sample (C - clusters of RuO_2 particles)
(b) - Heraeus 8241 sample (R - RuO_2 grains). In both micrographs G is the matrix glass phase.*

8a a TEM micrograph of a sample of DuPont 8041 thick film resistor material is displayed. Clusters of very small (< 10 nm) RuO_2 crystalls were found, up to 200 nm in size. This material posesses a relatively small gauge factor (3.5). On the other hand, material with larger RuO_2 particles (up to 200 nm) which are more or less uniformly distributed in a glassy matrix exhibit a much larger gauge factor (16). The microstructure of such material is shown in Figure 8b (Heraeus 8241 sample). From these findings it was concluded that materials with larger average distances between the conductive grains exhibit larger gauge factors than materials with a shorter average distance between the grains /29/.

3. 5. Ferroelectric thin films

Materials based on lead zirconate-titanate ($Pb(Zr,Ti)O_3$) or lead-lanthanum zirconate-titanate ($(Pb,La)(Zr,Ti)O_3$) are currently being extensively investigated due to their potential use in electronic and electro-optic devices. The use of these materials in non-volatile memories, piezoelectric SAW devices, microactuators, pyroelectric sensors and electrooptic modulators requires miniaturization, which is achieved by using thin films on substrate materials. For ferroelectric thin film fabrication, various methods are used, amongst which the sol-gel method appears to be the one with the highest possibility of controling the stoichiometry of composition /30/.

In Figure 9 a dark-field TEM micrograph of a cross-section of a sol-gel derived PLZT (9.5/65/35) thin ferroelectric film is shown. The sample was thermally treated at 600°C for 20 hours. Due to its very small thickness (0.5 μm), transmission electron microscopy is again the only method which enables the observation of the microstructure across the film. Seven different layers could be observed in Figure 9. First from the bottom is an amorphous (800 nm) SiO_2 layer which is on the top of a Si monocrystal wafer. Then follows a 40 nm thick amorphous Pb-Si-O reaction layer, a 20 nm thick crystalline TiO_2, 100 nm Pt (electrode) layer, 20 nm thick $PbTiO_3$ (seeding) layer, a 300 - 400 nm thick perovskite layer and finally a 50 - 100 nm thick fine-grained pyrochlore

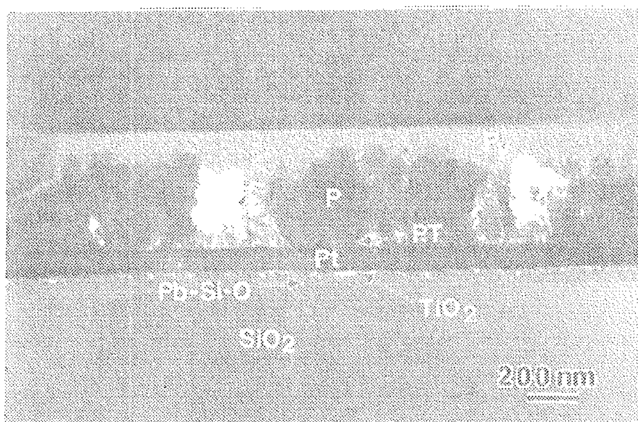

Fig. 9: TEM micrograph of the cross-section of a sol-gel derived PLZT thin ferroelectric film on <Si>/SiO_2/TiO_2/Pt substrate fired at 600 °C for 20 hours.

layer. Due to a defective Pt layer, the PbO from the PLZT film reacted with SiO_2 during the firing procedure, forming a reaction layer. Lead-oxide deficient PLZT film did not completely crystallize in perovskite form but a thin pyrochlore layer was formed on the top of the sample.

Applications of AEM techniques in the study of various ferroelectric materials, such as quantitative EDXS analysis of bulk PZT materials, chemical line profiles across thin PLZT films, determination of the degree of homogenization, etc. are to be found in /31/.

4. CONCLUSIONS

In this work some examples of the investigation of various inorganic materials in the form of powder, bulk ceramic and thin films using techniques of analytical electron microscopy are described. Detection of submicron phases, intergranular layers, microcracks and the distribution of phases throughout thin ferroelectric were presented and discussed. In many cases it was found that TEM sample preparation is the critical step that can introduce artifacts or deteriorate the structure or chemical composition. Analytical electron microscopy is an indispensable tool in the research and development of modern ceramic materials.

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Dr. Goran Dražič, dipl.ing.
Jožef Stefan Institut,
Jamova 39,
SI-1000 Ljubljana, Slovenija
tel.: +386 61 1773 271
fax: +386 61 1261 029
goran.drazic@ijs.si

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