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Study of modified lead titanate ceramics by Auger electron spectroscopy

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Calcium-modified lead titanate extruded and isostatically pressed ceramics have been studied, for the first time, by depth profile Auger electron spectroscopy. Our results show the high potential of the technique to determine the composition of inter- and intragranular fracture surfaces. Two different mechanisms of lead enrichment of the fracture surfaces are observed. Finally, the results are compared with a model of preferential sputtering of the different oxides.

1. Introduction

The surface composition and physical properties of powder compact particles are expected to play a major role in the growth and welding of the grains during sintering and to control the chemical nature of the final grain boundaries, which can be of primary importance when physical properties (as in the case of electroceramics) are suspected to depend on them [1].

The electron surface spectroscopy has been widely used in the determination of segregation and diffusion from the bulk to the surface in metals [2]. However, the problems associated with surface charge accumulation have prevented the extension of these techniques to the evaluation of intergranular phenomena of ferroelectric ceramics. Because of their oxide semiconductor nature, these materials present some conduction at relatively moderate temperatures ($\simeq 400^\circ$ C). This effect, combined with an appropriate surface-to-beam orientation, allows an effective surface charge drainage via bulk conduction and secondary emission. Thus, the study of the sintering process may be accomplished by means of surface techniques which provide valuable information.

Our work presents the application of depth profile Auger spectroscopy to the analysis of the initial powder compact particles and fracture surfaces of pressed and sintered material.

The calcium-modified lead titanate ceramics studied here show a strong electromechanical anisotropy, which makes them a very suitable material for ultrasonic transducers with applications in medical diagnosis and non-destructive testings [3]. It has also been found that their properties are strongly dependent on processing conditions.

Our first aim will be to find the qualitative specific composition of the fracture surfaces of extruded ceramics, prepared by a method recently developed [4], as compared with those obtained by conventional isostatic press moulding. The second implicit aim is to give a first insight into the potential and difficulties of the application of depth profile Auger electron spectroscopy technique to this specific subject.

2. Experimental procedure

The experimental results correspond to materials with the following composition:

$$\mathrm{Pb_{0.76}Ca_{0.24}((Co_{0.5},\ W_{0.5})_{0.05}Ti_{0.95})O_3} + 1\%\ \mathrm{MnO} \qquad (1)$$

Seven different kinds of ceramic specimens were prepared from three types of powders.

1. Some surfaces were prepared by fracture of fibres prepared by a recently developed extrusion method [4] in which a mixture of reactive synthesis processed powder and gel as a minority component was extruded to its final fibre shape and sintered at 1000° C for 3 h. Because of its high plasticity, the gel is used to eliminate the need of an organic agglomerant agent for extrusion. This material will be referred to here as extruded ceramic (EC). From this EC material three types of specimens were prepared: (a) fractured and polished surfaces; (b) as-fractured surfaces, on which the surface composition of extended areas as well as the specific surface of the pores will be studied; (c) surfaces exposed to air during sintering of the EC, which show the same surface composition and depth profile of the pores on the as-fractured surface.

2. From powder obtained by synthesis of the gel at 900° C for 3 h, only one type was studied: (a) Powder inclusion in an indium strip.

3. Conventionally, ceramic discs are obtained from isostatically pressed powder, which is sintered at high temperature. From the powder processed by reactive synthesis three types of samples were prepared: (a) an inclusion of powder in an indium strip to analyse the surface composition of the initial powder aggregates; (b) as-fractured surfaces from a slug, which was obtained by isostatic pressing at 2000 kg cm^{-2} of the powder; (c) as-fractured surfaces of a disc of isostatically pressed powder (2000 kg cm^{-2}) sintered at 1050° C for 3 h. This material will be referred to here as reactive synthesis ceramic (RSC).

The analysed ceramics have a tetragonally deformed perowskite structure. Their tetragonal distortions at room temperature are $c/a = 1.039$, indicating that the final composition adjusts to Equation 1.

The specimens were mounted and oriented in a heating stage the electron beam and the spectrometer

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axis were perpendicular and the normal to the sample surface was tilted ~ 52° C from the electron beam axis to minimize the surface charge effect. The ion beam impinged on the surface at an angle of 45° from normal. To obtain good SEM images or Auger spectra from the pressed or sintered specimens, they were heated at 400° C for 10 min. One basic aspect which must be known is whether the temperature produces some kind of segregation of lead to the surface. To elucidate this possible artefact, once the depth profile measurements were finished and the lead-enriched surface sputtered, several specimens were maintained at 400° C for 30 min. After this additional heating period, they did not show different Auger peak intensities than before. Stability of composition with heating time was also observed in different specimens before the ion-milling process. Thus, the observed surface compositions cannot be justified by a bulk-to-surface diffusion mechanism activated by the temperature of the measurement.

The powders encrusted on an indium strip were only measured at room temperature. The reactive synthesis processed powder allows the attainment of stable Auger spectra with minimum energy shifts. However, the powder obtained by synthesis of the gel did not allow an effective charge drainage and produced unstable spectra and important energy shifts.

On the fractures which have intergranular morphology, carbon contamination was nearly null when the time between fracture and analysis did not exceed several hours. On intragranular fracture surfaces the carbon intensity was very high, even when they were fractured immediately before their introduction into UHV. The profile of the carbon peaks provides an estimate of the shading effect due to the combined effects of rugosity and different incidence angles of the ion and electron beams. Qualitative differences were not observed for specimens with different carbon profiles.

3. Results

The depth profile results were normalized to the titanium Auger intensity. The depth profiles corresponding to surfaces of the EC material are plotted in Figs 1 to 3. The results corresponding to the materials processed by reactive synthesis are presented in Figs 4 to 7 in the order of operations during processing.

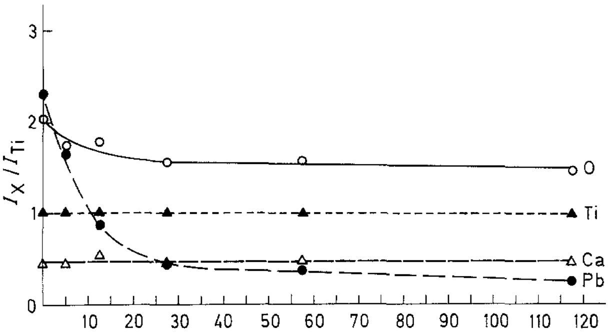

Figure 2 Depth profile Auger electron spectra for an as-fractured surface of EC material.

Fig. 1 corresponds to a polished fracture surface (surface 1a), in which apparently an enrichment of oxygen, calcium and lead appears. The profile in Fig. 2 corresponds to an as-fractured surface of EC (surface 1b). Scanning electron micrographs of this surface show an intergranular morphology and can be considered the initial surface of the polishing process. It presents a higher lead enrichment and a nearly flat calcium profile.

In Fig. 3, a profile corresponding to a grain surface in a pore on a fracture is shown. It is similar to that corresponding to an extended area on a surface exposed to air during sintering of the EC (surface 1c) material. It has the same lead behaviour as the polished fracture surface, but the calcium line is equal to that corresponding to the as-fractured surface.

Encrusted powder obtained by synthesis of the gel (specimen 2a) presents a strong surface charge effect and only very qualitative observations show a strong lead and oxygen surface enrichment, but regular spectra were not attainable.

The particles of the reactive synthesis powder encrusted on an indium strip (surface 3a) have an inhomogeneous surface composition. Fig. 4 shows two spectra from different areas which have the same qualitative composition but different intensity ratios (in this case, the diameter of the electron beam was 0.5 μm). In contrast, the fracture of the pressed slug (surface 3b) shows a surprising compositional homogeneity without substantial differences from point to

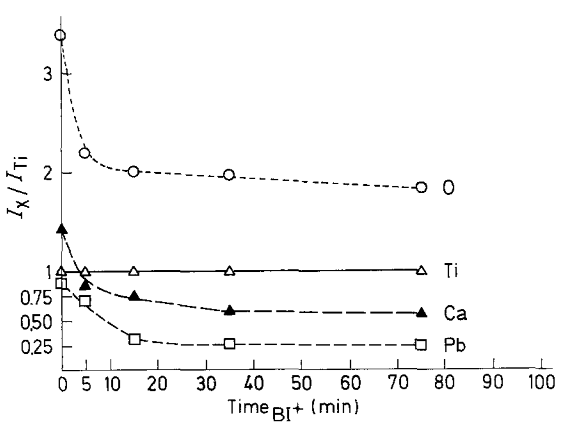

Figure 1 Depth profile Auger electron spectroscopy results for a polished fracture surface of EC material. Time$_{BI}$ = ionic bombardment time with Ar$^+$.

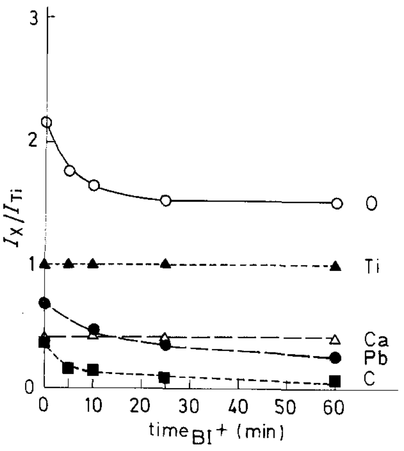

Figure 3 Depth profile Auger electron curves for a pore in an as-fractured surface of EC material.

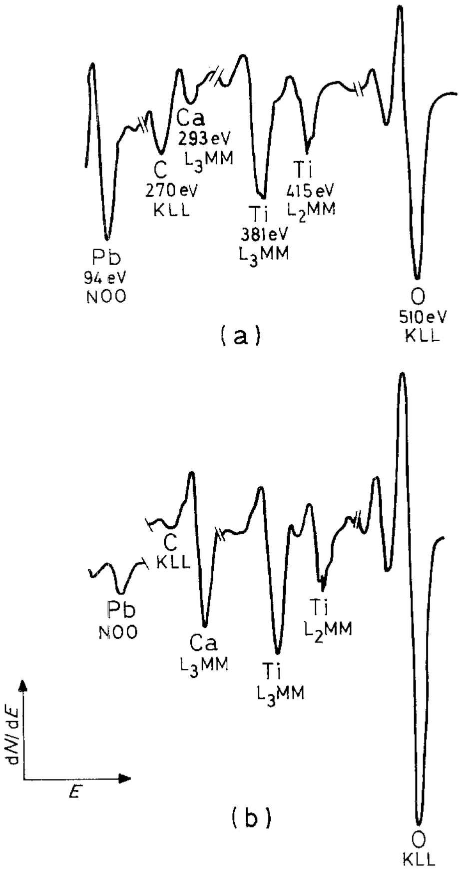

Figure 4 Auger electron spectra of two particles of the reactive synthesis processed powder encrusted on an indium strip.

point of the as-fractured surface. A characteristic spectrum of this surface is shown in Fig. 5. To determine if the fracture is produced through zones of specific composition, Auger depth profile was obtained and the result is plotted in Fig. 6. It presents a high lead relative enrichment when compared with the polished specimen of Fig. 1, but similar calcium and oxygen apparent compositions.

The as-fractured surface of the RSC material (surface 2c) observed by SEM prosents an intragranular morphology and its depth profile, Fig. 7, shows a strong lead and oxygen enrichment compared with all other specimens and a total calcium depletion. This suggests the existence of PbO on the fracture areas.

4. Estimate of the apparent surface enrichment in a homogeneous specimen

To determine if there exists a specific composition of the fracture surfaces, it is necessary to consider the ion-beam effects on the surface composition. In this discussion we will estimate the enrichment or depletion of the components for a homogeneous material. It is well known that ion bombardment reduces the surface of oxides. This reduction depends on the binding energies of oxygen and metal atoms and on their respective masses. This reduction appears in the normalized depth profile curves as an apparent oxygen surface enrichment. A practical approach to the apparent surface oxygen enrichment is given by Sigmund's expression [5]

$$R_{\mathrm{M}}^{\mathrm{O}} = (I_{\mathrm{O}}/I_{\mathrm{M}})_{\mathrm{IS}}(I_{\mathrm{O}}/I_{\mathrm{M}})_{\mathrm{FS}}^{-1} = (M_{\mathrm{M}}/M_{\mathrm{O}})^{2m}(U_{\mathrm{M}}/U_{\mathrm{O}})^{1-2m} \qquad (2)$$

where $R_{\mathrm{M}}^{\mathrm{O}}$ represents the apparent O surface enrichment in relation to the metal M. In the same way the relative apparent enrichment among metals can be estimated. $(I_{\mathrm{M}}/I_{\mathrm{O}})_{\mathrm{IS}}$ is the ratio of the Auger intensities in the initial surface before the bombardment and $(I_{\mathrm{M}}/I_{\mathrm{O}})_{\mathrm{FS}}$, the one for the final surface after bombardment. The main problem for a useful application of Equation 2 is to estimate the surface binding energies U_{O} and U_{M} and the empirical determination of m. In a recent work, Malherbe *et al.* [6] employed Equation 2, with $2m = 0.33$ and a modification of Pauling's [7] formalism in the calculation of U_{O} obtaining a satisfactory first-order agreement with the experimental values for surfaces of different simple oxides $\mathrm{M}_X\mathrm{O}_Y$. To calculate the binding energies they employed the following expressions

$$\begin{aligned} U_{\mathrm{O}} &= [X/(X+Y)]\, D(\mathrm{M{-}O}) + [Y/(X+Y)] \\ &\quad \times D(\mathrm{O{-}O}) + 1/2(\varepsilon_{\mathrm{M}} - \varepsilon_{\mathrm{O}})^2 \qquad (3) \\ U_{\mathrm{M}} &= H_{\mathrm{S}} + 1/2(\varepsilon_{\mathrm{M}} - \varepsilon_{\mathrm{O}})^2 \qquad (4) \end{aligned}$$

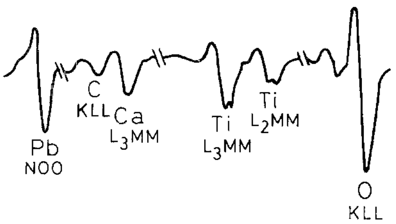

Figure 5 Auger electron spectra of the as-fractured surface of isotatically pressed powder processed by a reactive synthesis.

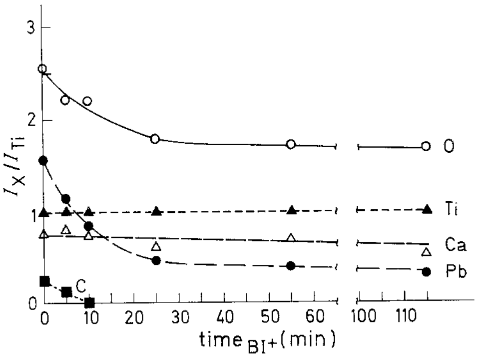

Figure 6 Results of the depth profile Auger electron spectra study of an as-fractured surface of isostatically pressed powder processed by reactive synthesis.

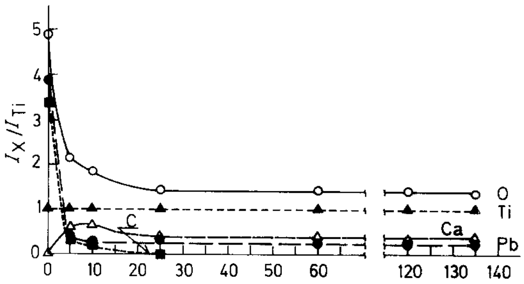

Figure 7 Depth profile Auger electron spectra of an as-fractured surface of RSC.

where D(M–O) and D(O–O) are the metal–oxygen and the oxgyen–oxygen bond energies. ε_M and ε_O are the electronegatives of the metal and oxygen, respectively, and H_S is the sublimation enthalpy. We will use Equations 2, 3 and 4 to obtain an estimate of the expected preferential sputtering of the titanate elements. In the perowskite structure [8], the titanium atom is octahedrally coordinated with six oxygen atoms and lead or calcium atoms are coordinated with twelve oxygen atoms. Each oxygen atom has two titanium neighbours and four lead or calcium neighbours (on average for the analysed composition, three lead and one calcium neighbours) on a plane perpendicular to the Ti–O–Ti bond direction. Thus, the Pauling electrostatic valency, v_i, for each Ti–O and Pb–O (or Ca–O) bond are 4/6 and 2/12, respectively. In Equation 4 we can substitute XD(M–O) by $\Sigma_i n_i v_i D$(M–O), where n represents the number of M–O bonds. This number is 2 for titanium, 3 for lead and 1 for calcium. ε_M will be substituted by an average $\bar{\varepsilon}_M$, only in Equation 3. In fact, the value of R^O_M does not differ much if values of ε corresponding to calcium or lead are employed. The values obtained for R^O_{Ti} and the apparent surface relative enrichments of lead and calcium in relation to titanium, R^{Pb}_{Ti} and R^{Ca}_{Ti}, are included in Table I. For these calculations, the needed parameters are taken mainly from Malherbe *et al.* [6]. When they were not available, H_S were taken from Gray [9], D(M–O) from Kerr and Trotman-Dickenson [10] and Engelke *et al.* [11] and ε from Knotex and Feibelman [12]. Especially, D(Ca–O) has been taken as 100 kcal mol^{-1} as the most approximate value [11].

In the reduced surface of an oxide compound, metals of different electronegativity coexist an a reduction reaction of the most electronegative metal, lead in our case, by the lesser electronegative elements can be expected. The estimated values of the reaction energies are 1.5 and 1 eV for lead replacement by calcium and titanium, respectively. This energy could be given to the lead free atom resulting in its sublimation from the surface. In the absence of a possible oxygen bond, alternatively, this free atom could remain in a physisorbed state with a low binding energy, U, thus giving a strong lead sputtering yield. In both cases the final lead concentration will be controlled by the oxygen in excess of titanium and calcium oxidation. Thus, the composition in a sputtered surface will be compatible with this model. The loss of the lowest electronegative component was qualitatively observed in the experimental results of sputtered TiO_3Sr single crystals [13], in which titantium is substituted by strontium. The XPS analysis of the same effect [14] is observed in different salts, Pb(NO_3), CO_3Pb and SO_4Pb among others. In these cases the most electronegative elements are nitrogen, carbon and sulphur, respectively, and consequently, after ion bombardment the amount of salt is drastically reduced and PbO is observed without evidence of anion oxides or reduced carbon or sulphur on the surfaces. In the following discussion it is necessary to be conscious of the approximate character of the previously estimated values.

TABLE I Values of the relative surface element enrichments with respect to titanium for the different surfaces analysed and theoretical estimates for a material of homogeneous composition

Specimen	R^O_{Ti}	R^{Pb}_{Ti}	R^{Ca}_{Ti}
(1a) Polished fracture surface of EC	1.23	3.15	1.66
(1b) Pore on as-fractured surface of EC	1.42	2.93	1.00
(1b) As-fractured surface of EC	1.33	8.18	1.00
(3b) As-fractured surface of pressed powder processed by reactive synthesis	1.47	5.06	1.5
(3c) As-fractured surface of RSC	3.70	15.00	0.00
Ideal material with homogeneous composition	1.36	1.04	1.41
Ideal material with homogeneous composition taking into account a lead reduction	1.36	2.70	1.41

5. Discussion

We will now compare the experimental R^O_{Ti}, R^{Pb}_{Ti} and R^{Ca}_{Ti} obtained from the normalized depth profiles with the estimated values. A comparison of R coefficients of different surfaces will be also established to determine the possible specific composition of the fracture surfaces.

R^O_{Ti} and R^{Ca}_{Ti} obtained from the EC polished fracture surface agree satisfactorily with the values predicted by Sigmund's expression. However, R^{Pb}_{Ti} disagrees if a lead reduction effect is not taken into account. We can now consider the possibility that the final reduced lead occupies a weak bonding state on the relatively inert oxidized surface or that the lead atom is ejected from the surface with the energy of the reduction reaction. In both cases, the final composition will agree with that calculated for a mixture of oxides or stoichiometric titanate and oxides. If we suppose that the polished fracture surface has the composition $TiO_3Pb_{0.75}Ca_{0.25}$, after ion bombardment of the surface the composition is changed to $TiO_{2.43}Pb_{0.24}Ca_{0.15}$ which corresponds to the following mixture of oxides

$$TiO_2 + 0.24\,PbO + 0.15\,CaO + 0.04\,O$$

or the equivalent mixture of modified titanate plus CaO and TiO_2. The 0.04 oxygen excess represents $\sim 2\%$ of the total oxygen amount. This would mean that a coefficient $R^{Pb}_{Ti} = 2.7$ must be expected for a process in which the non-oxidizable lead is eliminated. This value agrees satisfactorily with the observed 3.1. Thus, we conclude that the behaviour of the polished specimen does not differ qualitatively from that expected in a homogeneous specimen if the assumption of a lead reduction process is considered.

The as-fractured surface of EC has an intergranular morphology and its experimental R^{Pb}_{Ti}, R^{Ca}_{Ti} differ strongly from any prediction. As this surface is equivalent to the starting surface in the polishing, the comparison of the R coefficients shows that polishing the as-fractured surface approaches the expected homogeneous material surface. This is coherent with the nature of the polishing if the intergranular fracture surfaces, which are eliminated in the process, have a specific composition.

Comparison of R_{Ti}^{Pb} and R_{Ti}^{Ca} in the as-fractured surface with those of the polished surface show a strong lead surface enrichment and a calcium depletion. R_{Ti}^{O} is reasonably near to the estimated value for an homogeneous specimen. This would mean that lead is present in the quantity indicated by the excess in R_{Ti}^{Pb} in a near free or metallic state in the form of isolated atoms or clusters. Also, some quantity of calcium is lost in the first layers of the grain-boundary surfaces. Substitution of calcium by lead in the structure of the grain boundary gives an appropriate explanation for calcium depletion, but cannot be definitely proved from this experiment.

An excess of lead atoms can be originated by a small amount of MnO added to the composition according to the reaction:

$$MnO + PbO \rightleftharpoons MnO + Pb$$

and lead finally segregated to the intergranular surfaces under local pressure or thermal effects.

On the surface of a grain in a pore of the as-fractured surface the pressure is limited by the surface energy of the material, which is expected to be lower than that acting in the intergranular areas. The value of R_{Ti}^{Pb} is very similar to that corresponding to the polished surface. It suggests that the lead intergranular enrichment is favoured by intergranular pressure effects. Calcium depletion can be obtained by a more moderate presure and/or, alternatively, by thermal treatment. It is important to note that in an air-exposed surface during sintering, or in pore-free surfaces, the calcium depletion takes place without a lead enrichment relative to titanium.

To give an insight into the conventional forming process of the ceramic obtained by reactive synthesis, we will compare fracture surfaces from isostatically pressed slugs and the corresponding sintered discs.

In contrast to the powder encrusted in an indium strip, the fracture of the pressed material shows a uniform surface composition, and a clear lead enrichment, as can be deduced from its R_{Ti}^{Pb} value.

However, substantial differences in R_{Ti}^{Ca} were not obtained in comparison to the theoretically estimated values. In this case, the lead enrichment can only be explained in a free or metallic state. These results suggest that lead surface enrichment takes place on the powder particles until a homogeneous value is obtained on their surface. The most probable explanation is a movement of lead from interstitial positions in the bulk of the particles to an area with a high density of defects, the surface of the powder particles, as a pressure effect.

The as-fractured surface of the RSC shows an intergranular morphology. The experimental R_{Ti}^{Ca}, R_{Ti}^{Pb} and R_{Ti}^{O} values are very different from other surfaces. They show that the fracture here occurs through areas where calcium is absent and that are very rich in lead. The experimental results suggest the existence of a mixture of PbO and TiO_2 or $PbTiO_3$ as the composition separates from that of the as-fractured intragranular surface. A precipitation of PbO in some zones of the bulk of the grains can be suggested as the origin of this easiest fracture surface. The carbon content in these surfaces may come from atmospheric contamination due to a relatively higher density of active defects in the intragranular fractures. It also may appear as an impurity of the material segregated to the fracture zones. A not yet available UHV fracture experiment will be necessary to elucidate it.

6. Conclusions

1. The apparent surface enrichment of certain components of the specimen observed on the polished fracture surface of EC material is explained in terms of preferential sputtering of a homogeneous specimen when a lead reduction is taken into account.

2. The as-fractured surface of EC, which presents an intergranular morphology, shows additionally a lead enrichment and a calcium depletion with respect to the composition of the bulk of the grains, the former being related to an intergranular pressure effect and with the high density of defects in the intergranular surfaces.

3. Analysis of pore surfaces and air-exposed surfaces during sintering of free surfaces, shows a calcium depletion which is not accompanied with lead enrichment.

4. Lead enrichment on the surface of the reactive synthesis processed powder is also observed after isostatic pressing of the slugs.

5. The as-fractured surface of RSC, which occurs intragranularly, presents a lead and oxygen enrichment and a total depletion of calcium. This suggests an intragranular precipitation of PbO during sintering in some zones that became the easiest fracture surfaces.

In general, the present results show the high potential of SAM techniques in determining the specific composition of inter- and intragranular fracture surfaces in ferroelectric ceramic materials.

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