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MECHANISM OF THE SOLID STATE FORMATION OF LEAD ZIRCONATE TITANATE

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Abstract - The solid phase reactions which occur during the calcination of PZT ceramics have been studied on two kind of raw materials. A new mechanism reaction for the PZT solid solutions formation is proposed.

I - INTRODUCTION

In an attempt to clarify the reactions occurring in the PZT formation ceramics, many papers have been addressed to such an objective by a number of researchers /1/-/6/. In a general manner the results reported by the major contributors coincid in accepting that the lead titanate (PT) is the first reaction product to be formed when the mixed oxides technique were used /1/, /2/, /5/, /6/. However, if a submicron zirconia powder chemically prepared is used then the PZ formation is previous to the PT formation /4/. This PZ intermediate product was not observed in the majority of other papers, with the only exception of Ohno et al /7/ who also reported the PZ formation which subsequently reacts with PT to form PZT solid solution. On the other hand, Yamaguchi et al /8/ report the possible formation of PZ but only under determined conditions. The presence of an intermediate PbO solid solution was reported by Speri /9/, and confirmed later by Hankey /10/.

It seems obvious that the PZT can be synthesized by the solid state reaction PbO+ZrO₂+TiO₂ → PZT, and that this reaction cannot proceed in only one step. In the powder mixture of the oxides reactants three types of intergranular contact points are to exist, where those intermediate products with the lower formation heat will be firstly formed, which then reacts further to form the PZT solid solution as the final reaction product. The objective of the present work was undertaken to study the effect of reaction temperature, time and powder reactivity in order to determine the kinetics and mechanism of the PZT solid state formation.

II - EXPERIMENTAL PROCEDURE

The mixtures were made from crystalline raw materials with high purity PbO≥99.9% (orthorhombic massicot), TiO₂≥99.9% (tetragonal anatase), and
ZrO$_2$~99.8% (monoclinic baddeleyite), 1.5% HfO$_2$ included. To study the effect of ZrO$_2$ reactivity on PZT formation, an amorphous ZrO$_2$ obtained by precipitating the hydroxide with ammonium from a ZrOCl$_2$.8H$_2$O aqueous solution was used. The complex zirconium hydroxide was further calcined at 500°C for several hours. Average particle size was measured for all powders using a Coulter Counter, and specific surface area measurements were carried out by BET technique using N$_2$ as an absorbant. In order to determine which is the first reaction product to be formed during the PZT formation, a DTA/TGA technique was utilized with Al$_2$O$_3$ as a reference material.

A PZT composition with Zr/Ti/53/47, which is closed to the phase boundary, was chosen. Powder were mixed in stoichiometric ratios in a ball mill for 4 hours with alumina balls grinding media in acetona, and the slurries were dried at 50°C. The oxides mixture was remilled by attrition for 1 hour and dried. After drying the powders were pressed at 100 MPa into pellets 5 mm in diameter and 4 mm thick. These pellets were placed in a small platinum crucible and subjected to reaction temperature in a preheated furnace. The heat-treatments were carried out in air at a fixed temperature between 500°C and 850°C. Above 750°C the pellets were placed in a sealed platinum crucible to avoid the evaporation of lead oxide. After subjecting the samples to the different reaction temperatures, they were air quenched and ground in an agata mortar.

The phase composition of the reaction products was determined by X-ray diffraction analysis with a Philips diffractometer using CuK$_\alpha$ radiation and a nickel filter. Although the PbO-ZrO$_2$-TiO$_2$ is a very complex system, however the different phases formed during the PZT formation are characterized by a good symmetry and, therefore, the intensity of the diffraction lines could be taken to do an approximate estimation of the reaction progress. In this way, the equation $x_i = K I_i/I_0i$ was used to calculate the approximate concentration of the different phases ($x_i$=phase concentration, $I_i$=intensity of the diffraction line for the phase $i$ in the reaction product, $I_0i$=intensity for the same diffraction line in the pure phase, and $K$=constant). The diffraction lines (111), (110), (200), (220) and (311) for PbO, ZrO$_2$, TiO$_2$, PbTiO$_3$, PbZrO$_3$ and PZT respectively were used. In the case of the PZT phase, its relative concentration was estimated by reference to a standard prepared from a composition Pb(Zr$_{53}$Ti$_{47}$)O$_3$ sintered at 1230°C.

III - RESULTS AND DISCUSSION

Fig. 1 shows the DTA curves obtained for the two kind of PZT samples prepared. For mixed oxides sample, in which the average particle size after attrition milling was <2 µm, an exothermic peak at about 560°C, attributed to the PT formation, was observed. A second thermal effect at approximately 740°C was also found. In this case the endothermic peak must be attributed to the PZT formation which is an endothermic process. For the sample in which a ZrO$_2$ chemically prepared was used, the DTA curve only shows an endothermic effect at approximately 750°C which is related to the PZT formation, and no exothermic peak was observed. The se results are quite different to those found by Chandratrey et al /37 who attributed the endothermic peak to the PZ formation which compound was, on the other hand, not observed in their X-ray diffraction experiments. Hankey and Biggers /2/ found a complex DTA curve in which the PT formation was an endothermic effect. A second endothermic peak attributed to the PbO solid solution formation was also reported. Further more, a third peak, endothermic, in this case corresponding to the PZT formation was also reported. At present time the DTA curves from Hankey and Biggers /2/ are difficult to be interpreted with clearness.
As previously mentioned, the complete quantitative analysis of the phases composition during the PZT formation would be extremely difficult to obtain. However, as shown in Fig. 2 an estimation of the phase composition in the reacting mixture as a function of temperature was made as follows:

From mixed oxides
A set of preliminary experiments with oxide mixtures of composition Pb(Zr, Ti)O, showed that after heating at 500°C for several hours the products contain PbO, ZrO, TiO, and traces of PbTiO, which indicates that below 500°C the reaction proceeds only at intergranular PbO-TiO contacts according to the following equation:

PbO + TiO → PbTiO

This reaction was completed at approximately 600°C as shown by the disappearance of the X-ray diffraction lines corresponding to TiO.

As the temperature was increased a very important feature was observed between 600 and 650°C. In that narrow temperature range the reaction simultaneously proceeds at intergranular PbTiO-PbO and PbTiO-ZrO contacts, and some of PbO and ZrO diffuses into the lead titanate perovskite lattice taking place there the formation of a lead titanate solid solution. This assumption was supported by the observed increase for the lattice parameters of the lead titanate compound. On the other
hand, neither diffraction lines of the lead zirconate compound nor PbO solid solution formation were observed. Furthermore, the intensity of the diffraction lines for lead titanate did not shift, and those corresponding to the PbO and ZrO$_2$ oxides slightly decreases. Therefore, the second reaction step taking place before PZT formation is: PbTiO$_3$ + PbO + ZrO$_2$ + (PbTiO$_3$)$_{ss}$.

Beyond 650$^\circ$C, the saturated lead titanate solid solution acts as a support for the PZT formation. It seems probable that the diffusion of Pb$^{2+}$ and Zr$^{4+}$ ions in the lead titanate perovskite surface which results in the formation of PZT was more favourable. Although the diffusion in the PbO-ZrO$_2$ contact points to give PZ is not improbable, however that compound was not detected in the lead step of the PZT reaction synthesis. It is possible that the diffusion rate for the Pb$^{2+}$ and Zr$^{4+}$ ions into the lead titanate ss perovskite lattice was higher than that for the formation of PZ. In this way, the final reaction in the PZT formation can be established as follows: (PbTiO$_3$)$_{ss}$ + PbO + ZrO$_2$ + (PZT)$_{ss}$.

From ZrO$_2$ chemically prepared

Taking into account that this oxide is the least reactive of the three oxides mixture, a submicronized ZrO$_2$ with a high specific surface (149 m$^2$/g) for these experiments was used. As can be seen from Fig. 2, PbTiO$_3$ is always the first reaction product to be formed and two stages of the reaction may clearly be distinguished: a initial period in which practically all the PbTiO$_3$ is formed and, before this reaction was finished, starts the PbZrO$_3$ formation. That reaction sequence takes place between 450$^\circ$ and 600$^\circ$C. Therefore, the reaction occurring in that temperature range progress mainly in the intergranular contacts PbO-TiO$_2$ with the PbTiO$_3$ formation, and can be described by the equation: PbO + TiO$_2$ + PbTiO$_3$. However, this reaction step was not detected by DTA (see Fig. 1), probably due to rapid PZ formation and its simultaneous interaction with PT to give PZT.

The subsequent reaction taking place is the PbZrO$_3$ formation which is formed into a narrow temperature range (600$^\circ$-650$^\circ$C). In that temperature interval more than 70-80% of PbZrO$_3$ is formed as it could be estimated from the intensity of the diffraction lines. Before the maximum formation of PbZrO$_3$, a decrease in the intensities of the PbTiO$_3$ diffraction lines was observed, which is related with the beginning of the formation of the PZT solid solution. The reaction in this second step can be described as follows: PbO + ZrO$_2$ + PbZrO$_3$.

This reaction, as can be observed in Fig. 2, takes place at a higher rate than the rate for the PbTiO$_3$ formation.

In the final step, taking place from 650$^\circ$ to 850$^\circ$C, the PbZrO$_3$ is consumed more rapidly than the PbTiO$_3$, which is related to a lower stability of that compound as the temperature is increased. On the other hand, it was found that the reaction rate for the PZT formation was lower than in the case in which a mixed oxides was used. Then the final step could be described by the equation: PbTiO$_3$ + PbZrO$_3$ + (PZT)$_{ss}$.

From the above described results the following reaction mechanism for the PZT formation could be advanced. In the first step, above 450$^\circ$C, reaction proceeds at the higher rate which results in the total consumption of TiO$_2$. When the PT formation was completed some of PbO and ZrO$_2$ oxides reacts further, almost immediately, with the formed PT to give a PT solid solution as a result of the second step reaction. When the PT was saturated and if the temperature is increased then takes place the third step, with the interaction of PbO, ZrO$_2$ and TiO$_2$ in the interior of the PT perovskite matrix forming the PZT solid solution as the final product of the reaction. According to our results it seems reasonable to assume that the PT perovskite lattice acts as a host matrix in which the interdiffusion of the Zr$^{4+}$, Pb$^{2+}$ and Ti$^{4+}$ ions favour the PZT formation. In this way the PZT synthesis efficiently proceeds at
approximately 800°C, although the complete formation is only achieved at higher temperatures. This fact could be explained by assuming the formation of thick layers of PZT between the grain of the reactant products which probably hindered the mass-transport. If this is so, the diffusion-rate of Zr⁴⁺ and Pb²⁺ ions in the PT host matrix could be the rate-limiting step in the final PZT solid solution formation.

When a ZrO₂ with a high surface energy was used, the kinetics for the PZT formation was strongly affected, and a new intermediate reaction product, PZ, was formed. Such an intermediate reaction product was always formed after the PT reaction formation was practically completed, and never previously to the PT formation as reported by Venkataramany and Biggers /4/. This could depend on the reactivity of the ZrO₂ powder. This seems reasonable as the formation enthalpy for PT is lower than that for the PZ formation. It this case the reaction mechanism for the PZT formation could be described by a first step reaction in which, as always, the PZ is formed. Due to the high reactivity of ZrO₂ a new intermediate reaction product, the lead zirconate, is formed in the second step reaction. When these two compound have been formed begins the PZT formation at the PT/PZ interfaces as the third step reaction. It is believed that the diffusion-rate in the PT/PZT and PZ/PZT interfaces could be the rate-limiting step in the formation of a PZT solid solution. Fig. 3 shows schematically the two reaction systems leading to the PZT formation.

According to our results a new reaction mechanism for the solid state PZT formation is proposed. The differences found with respect to the reaction mechanism reported by other authors may be due to the different experimental conditions, however the conclusions here attained are based on the experimental results obtained on oxides mixtures carefully prepared. Although became very difficult to delimit the beginning and the end of each step reaction, however the present results can contribute to elucidate the reaction phenomena which occur during the calcination in the PZT ceramics fabrication.

REFERENCES