Title
KINETICS OF FORMATION OF LEAD ZIRCONATE TITANATE

Permalink
https://escholarship.org/uc/item/9341r733

Author
Chandratreya, Sudhir Shantaram.

Publication Date
1976-06-01
KINETICS OF FORMATION OF LEAD ZIRCONATE TITANATE

Sudhir Shantaram Chandratreya (M. S. thesis)

June 1976

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48

For Reference
Not to be taken from this room
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
KINETICS OF FORMATION OF LEAD ZIRCONATE TITANATE

Contents

Abstract ........................................ v
I. Introduction .................................... 1
II. Experimental Procedure ....................... 5
   A. Preparation of Powder Mixtures ............ 5
   B. Differential Thermal Analysis ............ 5
   C. Dilatometric Expansion .................... 6
   D. X-Ray Analysis ........................... 7
III. Results and Discussion ....................... 8
   A. Differential Thermal Analysis ............ 8
   B. Dilatometric Expansion .................... 13
IV. Summary and Conclusions ..................... 17
Acknowledgements ................................ 19
References ...................................... 20
Tables ........................................... 21
Figure Captions ................................ 23
Figures ......................................... 24
KINETICS OF FORMATION OF LEAD ZIRCONATE TITANATE

Sudhir Shantaram Chandratreya

Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Materials Science and Engineering, University of California, Berkeley, California 94720

ABSTRACT

The solid state reactions occurring in PbO-TiO$_2$-ZrO$_2$ system were investigated using constant heating rate method. The temperature range involved was from room temperature up to $1000^\circ$C, the range normally associated with the calcining step in the processing of PZT. Experimental techniques used included DTA, dilatometric expansion and the X-ray diffraction analysis.

PbTiO$_3$ was found to form exothermally as an intermediate product between 450°C and 600°C. PbZrO$_3$ formation was observed to be endothermic and starting at 700°C followed immediately by its interdiffusion with PbTiO$_3$. Both PZ and PT formations are accompanied by large volumetric changes and yield products of very fine particle size and high resultant reactivity. Hence the interdiffusion of PZ and PT is rapid to completely form PZT solid solution around 800°C. Formation of PbZrO$_3$ as an intermediate product is supported by the results of DTA and dilatometric expansion studies. Approximate estimation of the kinetic parameters from the DTA data using Kissinger's method was attempted. The method was found to be not useful due to broad nature of the DTA peaks.

Samples were observed to shrink rapidly after the expansions associated with the intermediate reactions. A model has been proposed to account for such behavior which also explains the high reactivity.
exhibited by the intermediate phases. Based on this analysis it should be possible to optimize the calcination process to obtain highly reactive fine sized powders in the PZT system. The method could be extended to other systems involving large volumetric changes in the course of solid state reactions.
I. INTRODUCTION

The lead zirconate-lead titanate solid solution system has the perovskite crystal structure and exhibits pronounced ferroelectric properties. Devonshire\(^1\) has shown thermodynamically that for ferroelectric perovskites, three polarized crystal structures can be formed with decreasing temperature in the following sequence:

1. Unpolarized cubic phase above the Curie temperature,
2. Tetragonal phase polarized along (001),
3. Orthorhombic phase polarized along (011),
4. Rhombohedral phase polarized along (111).

In the lead titanate-lead zirconate system, all three of these structures are seen as shown in Fig. 1(a).

Above the Curie temperature, the ideal cubic perovskite structure consists of the lead atoms at the corners of the unit cell, oxygen atoms at the face centers and Ti or Zr atoms at the body center position (Fig. 2). Below the Curie temperature the ionic positions shift to give a net electric dipole moment. The Curie temperature for lead titanate is 490°C while that for lead zirconate is 230°C. For the ternary compositions in the pseudobinary system of PbTiO\(_3\)-PbZrO\(_3\), the Curie temperature changes continuously between 230°C and 490°C. It is because of the high Curie temperatures, along with superior electric properties, that the compositions in PbO-TiO\(_2\)-ZrO\(_2\) system have been extensively investigated. Many of the studies have been associated with the control of stoichiometry and effect of additions of impurities and dopants on the electrical properties. Sintering and grain growth behavior has also been studied under various conditions. It is now well
documented that the processing determines to a significant extent the 
electrical properties like the dielectric constant, dielectric loss, 
coupling coefficient, etc. Thus the development of high permittivity 
ceramics of predictable properties in PZT system reduces to the 
selection of proper compositions and well defined processes of manufacture.

One of the first steps involved in the manufacture of PZT ceramics 
is the formation of the compound itself. This is done by calcining a 
mixture of powdered oxides (PbO, TiO$_2$ and ZrO$_2$) at a temperature high 
enough to cause solid state reactions yielding the perovskite structured 
product. The calcined product is then ground, compacted, and sintered 
to give a dense body. Unfortunately, little work on the properties 
of PZT ceramics has been reported with a full understanding of the 
process of calcination. It has been assumed that uniform fully reacted 
powder ready for sintering can be obtained simply by calcining between 
800°C to 1000°C for a few minutes to a few days.

A study of calcination is essentially a study of solid state 
reactions. The first step involved in such investigations is to 
determine the reaction path, i.e., various intermediate phases formed 
during the course of a reaction, and the time-temperature domain in 
which they form. A study of reactions in PZT formation has been 
reported by Matsuo and Sasaki who conducted isothermal studies between 
500 and 800°C up to maximum of 32 hr. They suggested the following 
reaction sequence:

\[
\begin{align*}
\text{PbO} + \text{TiO}_2 & \rightarrow \text{PbTiO}_3 \\
\text{PbTiO}_3 + \text{PbO} + \text{ZrO}_2 & \rightarrow \text{Pb}(\text{Zr}_\alpha \text{Ti}_{1-\alpha})_3 \\
\text{Pb}(\text{Zr}_\alpha \text{Ti}_{1-\alpha})_3 & + \text{PbTiO}_3 + \text{Pb}(\text{Zr}_\lambda \text{Ti}_{1-\lambda})_3
\end{align*}
\]
Later Ohno, Takahashi and Tsubouchi\textsuperscript{3} conducted similar studies in which a constant heating rate method was used instead of the isothermal technique. While Matsuo and Sasaki\textsuperscript{2} had observed no formation of PbZrO\textsubscript{3}, the latter reported that Pb(Ti\textcdot Zr) O\textsubscript{3} was synthesized after passing through formation of both PbTiO\textsubscript{3} and PbZrO\textsubscript{3}. Also the temperatures and times over which reactions occurred were widely different in the two studies.

The second step involved in the study of solid-state reactions involves kinetic measurements like the extent of reaction at a particular time and temperature. Various models like those proposed by Jander\textsuperscript{4}, Ginstling-Brounshtein\textsuperscript{5} and Komatsu\textsuperscript{6} have been used to describe the progress of solid state reactions under isothermal conditions and differing rate controlling mechanisms. Hangel and Doskocil\textsuperscript{7} conducted such studies on the formation of PbZrO\textsubscript{3} and PbTiO\textsubscript{3} and reported reaction isotherms for the two products. They concluded that both the reactions have identical activation energies of 45 kcal/mole with the rate controlling step being diffusion of the mobile species PbO through the product layer. Though their discovery of PbO being the mobile species is in agreement with Matsuo and Sasaki\textsuperscript{2}, it does not match the findings of Harris and Cook\textsuperscript{8}. The latter reported that in the formation of PbTiO\textsubscript{3} both PbO and TiO\textsubscript{2} are the mobile species. It should be noted, however, that their investigations were carried out at 1180°C which is considerably above the typical range of calcination temperatures.

Isothermal reaction rate studies do not reflect the actual conditions in the manufacture of PZT. This is because of the large
amounts of material involved giving uneven temperature distributions and slow heating rates causing difficulty in establishing "zero" time for the reaction.

Robinson and Joyce\textsuperscript{9} were the first to report that even at very high temperatures, as much as 3 mole\% of the oxides may remain unreacted in PZT. Robinson and Luff\textsuperscript{10} simultaneously reported that any unreacted PbO and ZrO\textsubscript{2} in particular can severely deteriorate the dielectric constant and coupling coefficient in the final ceramics. Buckner and Wilcox\textsuperscript{11} conducted investigations on the sinterability of Niobia-doped PZT powder based on its calcining history. They reported that the calcining history had a profound effect on the sinterability of PZT to the extent that the final fired density depended primarily on the calcining temperature.

Noting that from point of view of sinterability as well as electrical properties, calcination is an important process step, the present study was undertaken to characterize the calcination process. The reaction path was investigated and the temperature ranges in which the various reactions occur were established. The study involved use of various techniques like differential thermal analysis (DTA), dilatometric expansion measurements and X-ray diffraction analysis.
II. EXPERIMENTAL PROCEDURE

A. Preparation of Powdered Mixtures

Five compositions were chosen from the pseudobinary phase diagram of the PbTiO$_3$-PbZrO$_3$ system as shown in Table I. The mixtures were made from raw materials of high purity and known crystalline morphology (Table II). Average particle size was measured for all powders using a Fisher Subsieve Sizer and thermogravimetric analysis in air was conducted on each component to determine the volatile content up to 500°C. The appropriate corrections were made to account for the volatile content during weighing and the powders in stoichiometric ratios were mixed in a polyeurethene lined Sweco Vibratory Mill for 2 hr. The details of the powder preparation are shown in the flow chart in Fig. 3.

To study the effect of crystal structure on lead titanate formation, rutile was also used in place of anatase. Rutile was prepared by heating anatase to 1100°C for 48 hr and rapidly quenching. It was then mixed with PbO in the same manner as anatase.

B. Differential Thermal Analysis

A multi-sample nickel block was used with cavities 3/8 in. in diameter and 0.65 in. in depth. The differential thermocouples were placed into each cavity through a hole in the nickel cover plate. The differential temperatures were measured with Pt-Pt 10% Rh thermocouples and were recorded on a multi-pen recorder. Al$_2$O$_3$ was used as a standard. The temperature program was controlled by a potentiometric fully proportional controller. The sample temperature was assumed to be the same as the block temperature which was monitored continuously.
Different heating rates were used (5°C/min, 12°C/min, 20°C/min) to study the effect of the heating rate on the reaction kinetics. Samples were heated between room temperature and 1000°C. Some experimental runs were terminated at intermediate temperatures by rapid cooling to study the various phases present at those temperatures. Samples were removed and crushed to (-200) mesh in a mortar and pestle and subjected to qualitative X-ray analysis.

C. Dilatometric Expansion

Samples of dilatometric expansion experiments were prepared by isostatically pressing the powders in a latex rubber tube to 30,000 psi. The pressed slug was then cut to the required length. Typically, samples were 1/4 in. in diameter and 3/4 in. in length for mixtures of two oxides. For the mixtures of three oxides, samples were 1 in. long.

The sample was placed inside a fused quartz tube and rod assembly. To avoid any direct contact between the sample and the fused quartz, a very thin platinum foil (0.006 in.) was wrapped around the inner surface of the quartz tube. Also, two similar pieces of Pt foil were put between the sample and the quartz tube as well as the sample top and the end of the quartz rod. Failure to take this precaution would have resulted in a reaction between fused quartz and PbO yielding a low melting eutectic.

The entire tube-rod-sample assembly was fixed at the center of a cylindrical shell furnace tilted at 30° to the vertical. A chromel-alumel thermocouple was placed in air very close to the sample. The temperature monitored was assumed to be the sample temperature. The cold junction of this thermocouple was maintained at 0°C in an ice-
-7-

distilled water bath and the output was fed directly into the X input of an X-Y recorder. Another thermocouple placed nearby was connected to a controller-recorder for temperature control.

Expansion of the sample was monitored via the differential displacement of the quartz rod and tube by a linear variable differential transformer (LVDT). The output from LVDT was fed into a dc amplifier which in turn was connected to the "y" input of an X-Y recorder. The linearity of the range of LVDT used was assured before every experiment by use of a calibrating micrometer. Since typical expansion encountered was only 1/5 of the linear range, linearity in output was easily obtained when proper nulling was done.

The following heating rates were typically used in the dilatometric study: 190°C/hr, 335°C/hr, 490°C/hr. The temperature range used was between room temperature and 1000°C. As with DTA, many dilatometric runs were conducted up to an intermediate temperature and the sample was rapidly quenched. This was done in order to determine phases formed below the quenching temperature by X-ray analysis.

D. X-Ray Analysis

X-ray diffraction was used to identify the various phases formed during the course of the reactions. Typically powders to be analyzed were crushed to ~200 mesh and were mixed with a small amount of water. The suspension was then dropped on a glass slide used as a sample holder. After the water had evaporated, the sample was mounted in a diffractometer. A scanning rate of 1°/min was used with CuKα radiation. No attempts were made to make any quantitative measurements using X-ray diffractometry.
III. RESULTS AND DISCUSSION

A. Differential Thermal Analysis

Every chemical reaction or physical transformation liberates or absorbs heat, causing a change in temperature. Reactions may also be accompanied by a change in weight due to reaction with or formation of a gas phase. Differential thermal analysis is capable of determining changes that are not accompanied by a change in weight and also has the advantage of determining whether the reaction is exothermic or endothermic. Differential thermal analysis is a dynamic technique based upon changes in the thermal gradient across a sample. Hence the reactive temperatures determined by this method do not correspond to the thermodynamic equilibrium temperatures. Many investigations of solid-state reactions have been carried out using DTA as an analytical tool. Coupled with X-ray diffraction, DTA was used to show the initiation of spinel formation in the reaction of ZnO with Cr$_2$O$_3$. Borchardt and Thompson studied a number of solid state reactions with DTA. Templeton and Pask studied the synthesis of BaTiO$_3$ from BaCO$_3$ and TiO$_2$. Moon used this method to study the high temperature phase equilibria in PbTiO$_3$-PbZrO$_3$ system.

Results of the DTA study for compositions V(PbO + TiO$_2$), IV(PbO + ZrO$_2$) and II(PbO + 0.5 TiO$_2$ + 0.5 ZrO$_2$) are shown in Fig. 4. The DTA curves for composition I(PbO + 0.35 TiO$_2$ + 0.65 ZrO$_2$) and III(PbO + 0.65 TiO$_2$ + 0.35 ZrO$_2$) were similar to that for composition II.

A major and rather broad peak is observed starting at 450°C in the case of the PbO + TiO$_2$ mixture. The nature of the peak indicates that the reaction is exothermic. There is no other major thermal effect seen
up to 1000°C. Other DTA runs on the same mixture but quenched at intermediate temperatures were used to determine the various phases present at those temperatures. Up to 450°C, no formation of PbTiO$_3$ was detected by X-ray analysis. Above 450°C PbTiO$_3$ was observed to have been formed rapidly and by 600°C no significant amounts of unreacted components were detected indicating that the reaction was complete. Even at very rapid heating rates, the reaction was found to be complete by 600°C. The reaction then can be represented by

$$\text{PbO(s) + TiO}_2(\text{s}) \rightarrow \text{PbTiO}_3(\text{s})$$

The experiment was repeated using rutile instead of anatase. The reaction started at around 450°C and was complete at 650°C thus giving a broader peak than anatase. The reaction was exothermic in both cases.

For a PbO + ZrO$_2$ mixture (composition IV) no thermal effect was observed up to 700°C—starting at 700°C a large endothermic peak was observed with the apex around 780°C and returning to the baseline at approximately 850°C. X-ray analysis of samples quenched at various temperatures indicated no detectable reaction up to 700°C. Unlike in the case for PbTiO$_3$, however, some unreacted constituents were found up to 1000°C even at a heating rate as low as 5°C/min. The phase formed during the solid state reaction was PbZrO$_3$ with an orthorhombic crystal structure at room temperature. The reaction can be stated to be as follows:

$$\text{PbO(s) + ZrO}_2(\text{s}) \rightarrow \text{PbZrO}_3(\text{s})$$

That the above reaction does not go to completion even at high temperatures for a long time has also been reported by other investigators,$^7,9$ while Matsuo and Sasaki$^2$ report that isothermally PZ forms
within 2 hr at 750°C. The latter have also reported that PbTiO$_3$ formation begins after nearly 12 hr at 500°C and after 30 min at 600°C. Probable reasons for the above could be inadequate mixing of reacting powers, large particle sizes of reactants or inadequate sensitivity in the method of analysis.

The DTA of ternary composition II is shown in Fig. 4. Two thermal effects are observed, one starting at 450°C and exothermic in nature and the other starting about 700°C and endothermic in nature. The former peak, based on the quench-X-ray analysis technique was found to correspond to lead titanate formation. At 700°C the phases observed were PbTiO$_3$ and unreacted PbO and ZrO$_2$. The second peak was found to correspond to PbZrO$_3$ formation as well as Pb(Ti$_{\lambda}$Zr$_{1-\lambda}$)$_3$O$_9$ formation. It is not possible to say with absolute certainty which of the phases, PZ or PZT forms first or dominates the reaction. This is due to the nature of the room temperature X-ray diffraction patterns for PbZrO$_3$ and Pb(Ti$_{\lambda}$Zr$_{1-\lambda}$)$_3$O$_9$ solid solutions. It should be noted that at elevated temperatures both PZ and PT exist as cubic perovskites with complete solid solubility (Fig. 1). Therefore, the lattice parameter of the PZT solid solution should vary continuously with the ratio of ZrO$_2$ to TiO$_2$ in the solid solution. If the reaction sequence consists of PbTiO$_3$ and PbZrO$_3$ forming independently as indicated by the DTA results and then the products interdiffusing, zoned crystals should be formed. On cooling to room temperature, these zoned crystals would give broad peaks with considerable overlap between the rhombohedral and tetragonal patterns which would exist for a homogeneous material. The same is true for detecting a room temperature orthorhombic PbZrO$_3$ phase.
if it is formed during the reaction sequence. Thus, it is almost impossible to detect with certainty any PbZrO₃ formed as an intermediate product using room temperature X-ray diffractometry.

If considering formation of PZT solid solution after formation of PbTiO₃, two possible reaction paths exist:

\[
\begin{align*}
\text{PbTiO}_3 + \text{PbO} + \text{ZrO}_2 & \rightarrow \text{Pb(Ti,Zr)O}_3 \text{ (S.S.)} \\
\text{Reaction I} & \\
\text{PbTiO}_3 + \text{PbZrO}_3 & \rightarrow \text{Reaction III}
\end{align*}
\]

Reaction I and III are essentially solid solution forming reactions, while reaction II involves compound formation. Previous publications have not been clear as to which reaction path is more likely to dominate in the calcining temperature range. There are no reported methods of separating PbZrO₃ from PZT by use of wet chemical analysis techniques. Also, because there are no reported data on the diffusion characteristics of the various species in the perovskite lattice, quantitative estimates of reaction paths are difficult to make. However, as shown in Fig. 4, the ternary mixture exhibits a prominent endothermic effect very similar to the one exhibited by the binary mixture of PbO and ZrO₂. It is, therefore, highly likely that in the ternary mixture, formation of PbZrO₃ precedes the formation of PZT solid solution. Moreover, it should be noted that reaction I involves interaction of three species simultaneously. Hence it is assumed to be less probable than reaction II which involves reaction between only two species, PbO and ZrO₂. PbO is known to be quite mobile in the temperature range involved. Ohno et al. have reported formation of PbZrO₃ as an intermediate product which
is in agreement with the above deduction. While they used X-ray diffractometry as the principal mode of analysis, the present study involves use of DTA and dilatometric expansion in addition to the X-ray analysis to support the conclusion.

Many investigators have attempted to draw kinetic information from DTA measurements. Kissinger\textsuperscript{17} developed a mathematical treatment for DTA for first order reactions. In his method the variation of peak temperature with heating rate is measured and if it is assumed that in the DTA curve the peak corresponds to the maximum reaction rate, then the following relation holds:

\[
\frac{-E}{R} = \frac{d(\ln \frac{\phi}{T_m^2})}{d(1/T_m)}
\]

where

- \( E \) = the activation energy,
- \( T_m \) = the peak temperature at a given rate of heating,
- \( \phi = dT/dt \) = the heating rate,
- \( R \) = the gas constant.

By plotting \( \ln(\phi/T_m^2) \) vs \( 1/T_m \) for various clays and minerals Kissinger obtained a linear relationship for heating rates between 3°C/min to 20°C/min. The slope was used to calculate the activation energy \( E \).

Levski\textsuperscript{18} developed a similar correlation between DTA and the kinetic parameters based on a similar assumption.

Attempts were made to apply Kissinger's method and obtain a crude estimate of the activation energy for PZ and PT formation. The heating rates used were 5°C/min, 12°C/min and 20°C/min but no significant variation in the peak temperature was observed. The resolution required
for accurate measurement of $\Delta T$ is difficult to obtain due to rather broad peaks observed in these reactions. Furthermore, this method does not take into consideration the heat transfer affects involved in DTA and also the assumptions involved are rather tenuous. Consequently, the method should be used only for approximate estimations.

**B. Dilatometric Expansion**

Dilatometric expansion studies take advantage of the volumetric changes taking place during the course of a solid state reaction. If the densities of the product phases and the reactants differ significantly from each other, the volume changes become large enough and, therefore, can be used as means of monitoring the progress of a reaction under ideal conditions. Like DTA, dilatometry is a widely used method of detecting reactions or phase changes in solid state studies.

A summary of the dilatometric experiments conducted on the P-Z-T system is shown in Figs. 5-8. Figure 5 shows the dilatometric curves obtained for PbO-TiO$_2$ mixtures at various heating rates. Normal thermal expansion of the sample is observed up to 450°C, after which a sharp volume increase occurs up to 600°C. Further heating causes shrinkage of sample at a rapid rate. It should be noted that the start of expansion at 450°C corresponds very well with the beginning of exothermic peak on the DTA curve. Quench-X-ray analysis indicated that PbTiO$_3$ starts forming at 450°C and the reaction is essentially complete at about 600°C which corresponds to the maximum expansion. Change of heating rate had essentially no effect on the extent of expansion or the beginning of the reaction.
The expansion behavior of PbO-ZrO₂ mixtures is shown in Fig. 6. As with the PbO-TiO₂ system, these curves essentially corroborate the DTA data. The beginning of PbZrO₃ formation is accompanied by sharp change in the expansion behavior at 700°C. X-ray analysis, however, indicates that the apex of the curve does not correspond to the reaction being complete. In fact, the reaction was found to be incomplete at 1000°C even at heating rates as low as 190°C/hr. This is corroborated by the earlier report by Robinson and Joyce. Very little effect of heating rate change is seen on the expansion behavior.

The ternary mixtures of PbO, TiO₂ and ZrO₂ exhibit two anomalous expansion peaks with the first one starting at 450°C. As shown in Fig. 7, the behavior of the ternary composition II is similar to the super-imposition of the expansion characteristics of the two binary mixtures PbO-TiO₂ and PbO-ZrO₂. Differential thermal analysis behavior of the above compositions agrees well with the dilatometric findings. Changing the (ZrO₂/TiO₂) ratio in the ternary composition has little effect except that the extent of expansion (i.e., the peak height) during each reaction changes. Composition I having a larger amount of ZrO₂ shows less expansion under first peak as compared to composition III containing a larger amount of TiO₂ (Fig. 8).

X-ray analysis of samples of composition I heated at 335°C/hr and quenched at various temperatures is shown in Fig. 9. PbTiO₃ formation is almost complete at 580°C while PZ and PZT is observed at about 715°C. As stated earlier, it is not possible to distinguish between PbZrO₃ and Pb(TiₐZr₋₁₋ₐ)O₃ solid solution by using X-ray diffractometry. PZT formation is seen to be rather extensive at 785°C.
Theoretically it is possible to calculate the volumetric change occurring during the course of a reaction. Based on X-ray measurements of lattice parameters, the molar volumes of PbTiO$_3$ and PbZrO$_3$ would be 38.0 cc and 42.7 cc respectively. Volume occupied by 1 mole of TiO$_2$ and ZrO$_2$ would be 20.8 cc and 22.0 cc respectively. It is reported that PbO is the mobile species in the formation of PbTiO$_3$ and PbZrO$_3$. It can then be assumed that PbTiO$_3$ and PbZrO$_3$ form as shell-like layers on the particles of TiO$_2$ and ZrO$_2$. A spherical particle of TiO$_2$ will react to become a spherical particle of PbTiO$_3$, accompanied by 22% radial expansion. Similarly a spherical particle of ZrO$_2$ will react to become a spherical particle of PbZrO$_3$ with 24% radial expansion. Such large volumetric changes would be accompanied by large strains in the product layer and subsequent cracking, chipping and peeling. Thus, after a certain extent of growth, the product layer thickness would be decided not only by the rate of reaction but also by the rate of "spalling". In such a case the expansion would no longer indicate the extent of reaction. The resulting product would exist as particles of sizes much smaller than the particle size of the original reacting species. If the reactants were submicron in size, the product would be very fine particulates of very large specific surface area. In a favorable range of temperature these fine particles would sinter or react rapidly. In fact, such a phenomenon is observed in the present system as evidenced by the rapid shrinkage of PbO-TiO$_2$ samples above 600°C and PbO-ZrO$_2$ samples above nearly 800°C. The samples were found to possess enough mechanical strength to remain integral even after large dimensional changes. This
indicates that some form of strengthening mechanism similar to sintering was taking place at the elevated temperatures.

In the case of a ternary composition PbTiO₃ forms at lower temperature range. Thus it exists as highly reactive fine particulates at the higher temperatures when PbZrO₃ begins to form. The fine crystallites of PbZrO₃, as they form and spall off, react rapidly with the PbTiO₃ almost as soon as PbZrO₃ forms. Thus at no time is there enough accumulation of PbZrO₃ in presence of PbTiO₃ that X-ray analysis could resolve it from the other species. However, it appears certain that PbZrO₃ forms prior to the formation of ternary solid solution on the basis of the dilatometric expansion and DTA data (Figs. 4 and 7).

If the temperature is not raised beyond that necessary for completion of reaction, the product would exist in very fine particle size and consequently will be very highly reactive. Thus, by choosing properly the heating rate, duration and temperature of calcination it should be possible to obtain a highly reactive product. Any over-calcination would reduce the reactivity while under-calcination would result in incomplete reaction.
IV. SUMMARY AND CONCLUSIONS

The solid state reactions occurring in the range of temperatures typically used in calcination of PbO-ZrO\textsubscript{2}-TiO\textsubscript{2} system were studied under constant heating rate conditions. Differential thermal analysis was employed to study the thermal effects of the reactions while dilatometric expansion was used to monitor the accompanying volumetric changes. X-ray diffractometry was employed qualitatively to identify various phases formed during the course of the reactions.

Lead titanate was found to form above 450°C exothermically. Reaction was rapid enough to go to completion at 600°C even at rapid rates of heating. Excellent correlation was obtained between DTA and the dilatometric experiments. Since both PbO and TiO\textsubscript{2} have low vapor pressures in this temperature range, the mass transport is thought to be due to surface diffusion of PbO.

Lead zirconate begins to form at 700°C and the reaction does not go to completion up to 1000°C even at a low heating rate of 5°C/min. The reaction is endothermic in nature. Large volumetric changes accompany both PbTiO\textsubscript{3} and PbZrO\textsubscript{3} formation.

In a ternary mixture of PbO, TiO\textsubscript{2}, and ZrO\textsubscript{2}, lead titanate formation occurs between 450°C and 600°C exothermally followed by endothermic formation of PbZrO\textsubscript{3} and Pb(Zr,Ti)O\textsubscript{3} solid solution beginning at about 700°C. The X-ray diffraction technique is deemed as of little value to differentiate formation of PbZrO\textsubscript{3} from Pb(Zr,Ti)O\textsubscript{3} solid solutions. At higher temperatures of about 800°C, Pb(Zr,Ti)O\textsubscript{3} solid solution is observed to be the only dominant phase. Thus the reactions can be summarized as follows:
a. Between 450°C and 600°C:

\[ \text{PbO} + \text{TiO}_2 \rightarrow \text{PbTiO}_3 \]

Formation of PbTiO$_3$ of very small particle size due to large volume changes involved in the reaction. The product has high specific surface area and hence enhanced reactivity.

b. Above 700°C:

\[ \text{PbTiO}_3 + \text{PbO} + \text{ZrO}_2 \rightarrow \text{PbZrO}_3 + \text{Pb}(\text{Zr}_\lambda \text{Ti}_{1-\lambda})_3 + \text{PbTiO}_3 \rightarrow \text{Pb}(\text{Zr},\text{Ti})_3 \]

Formation of PbZrO$_3$ of very fine particle size by mechanism similar to that for PbTiO$_3$. Both the intermediate products being highly reactive, PZT solid solution formation rapidly follows the formation of PZ.

Approximate estimation of kinetic parameters from the DTA data of above reactions using Kissinger's method was deemed not possible due to very broad nature of the peaks. Also the relative variation in DTA curves with differing heating rates was found to be negligible.

In dilatometry, samples were observed to shrink rapidly after the completion of the PbTiO$_3$ formation as well as PbZrO$_3$, Pb(Zr,Ti)O$_3$ formation. This has been explained on the basis of a model which accounts for generation of a product of very fine particle size and a very high resulting reactivity. Based on this analysis it should be possible to optimize thermal conditions during calcination to obtain products of very high reactivity and controlled stoichiometry.
ACKNOWLEDGEMENTS

I am deeply thankful to Professor R. M. Fulrath for his able
guidance and support during this work. I would also like to thank
Professors J. A. Pask and R. P. Merrill for having read this thesis
and approving it.

It was a pleasure to have been associated with J. J. Dih, John Dullea,
David Mentley, David Wang and V. K. Nagesh during the course of this
work. Special thanks are due to Dipak Biswas, Dan Miller and Bob
Powell for their overall help at many a difficult time.

Finally, I wish to thank Gay Brazil, Gloria Pelatowski, Shirley
Ashley, Jean Wolslegel and the entire staff of MMRD for their excellent
technical assistance.

This report was done with support from the U. S. Energy Research
and Development Administration.
REFERENCES

TABLE I. Compositions from PbTiO$_3$-PbZrO$_3$ system chosen for the present investigation.

<table>
<thead>
<tr>
<th>COMPOSITION</th>
<th>Molar Ratio</th>
<th>Weight %</th>
<th>Volume % (Approx.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PbO</td>
<td>ZrO$_2$</td>
<td>TiO$_2$</td>
</tr>
<tr>
<td>I</td>
<td>1.00</td>
<td>0.65</td>
<td>0.35</td>
</tr>
<tr>
<td>II</td>
<td>1.00</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>III</td>
<td>1.00</td>
<td>0.35</td>
<td>0.65</td>
</tr>
<tr>
<td>IV</td>
<td>1.00</td>
<td>1.00</td>
<td>0</td>
</tr>
<tr>
<td>V</td>
<td>1.00</td>
<td>0</td>
<td>1.00</td>
</tr>
</tbody>
</table>
TABLE II. Details of the raw materials used in the investigation.

<table>
<thead>
<tr>
<th>Grade</th>
<th>Crystal Structure and Comment</th>
<th>Average Particle Size</th>
<th>Volatile Content Up to 500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbO</td>
<td>Baker Reagent Grade</td>
<td>Orthorhombic Yellow Powder Massicot total impurity content less than 1%</td>
<td>0.7μ</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Pharmaceutical Grade</td>
<td>Tetragonal anatase high purity</td>
<td>0.6μ</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>Wah Chang Electronic Grade</td>
<td>Monoclinic Baddeleyite Hf-free high purity</td>
<td>1.7μ</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Fig. 1. (a) Low temperature phase diagram for PbTiO$_3$-PbZrO$_3$ system. (b) High temperature phase diagram for PbTiO$_3$-PbZrO$_3$ system. Thermal analysis data after Moon. Quenching analysis data after Fushimi and Ikeda.

Fig. 2. High temperature cubic perovskite structure and low temperature tetragonal perovskite structure of PbTiO$_3$.

Fig. 3. Flow diagram for powder preparation.

Fig. 4. DTA plots for (PbO + TiO$_2$), (PbO + ZrO$_2$) and (PbO + 0.5 TiO$_2$ + 0.5 ZrO$_2$) mixtures at the constant heating rate of 10°C/min in air.

Fig. 5. Dilatometric expansion plots for composition V(PbO + TiO$_2$) at various heating rates shown.

Fig. 6. Dilatometric expansion plots for composition IV(PbO + ZrO$_2$) at various heating rates.

Fig. 7. Dilatometric expansion characteristics of (PbO + TiO$_2$), (PbO + ZrO$_2$) and (PbO + 0.5 TiO$_2$ + 0.5 ZrO$_2$) mixtures at constant heating rate of 8.2°C/min.

Fig. 8. Dilatometric expansion characteristics of the various ternary mixtures of PbO, TiO$_2$ and ZrO$_2$ at constant heating rate of 5.6°C/min.

Fig. 9. Room temperature X-ray diffractometry patterns for composition I (PbO + 0.65 ZrO$_2$ + 0.35 TiO$_2$) showing various phases. Samples were heated to the shown temperatures at the constant rate of 5.6°C/min and quenched rapidly after reaching the shown temperature.
\[ \text{P: Paraelectric, Cubic Phase} \]
\[ \text{A}_\alpha: \text{Antiferroelectric, Orthorhombic Phase} \]
\[ \text{A}_\beta: \text{Antiferroelectric} \]
\[ \text{F}_\alpha: \text{Ferroelectric, Rhombhedral Phase} \]
\[ \text{F}_\beta: \text{Ferroelectric, Tetragonal Phase} \]


XBL765-6937

Fig. 1(a)
Fig. 1(b)
I: I n-o-t-::: Y-Q

(a) CUBIC PEROVSKITE STRUCTURE

(b) SCHEMATIC STRUCTURE FOR PbTiO₃ AT ROOM TEMPERATURE SHOWING SHIFT OF Pb AND Ti IONS RELATIVE TO THE OXYGEN OCTAHEDRON

(c) SCHEMATIC PROJECTION ON (001) OF THE ANTI-FERROELECTRIC STRUCTURE OF PbZrO₃

Fig. 2
PbO MASSICOT

WEIGHT LOSS UP TO 500 °C

TiO₂ ANATASE/RUTILE

WEIGHT LOSS UP TO 500 °C

ZrO₂ BADDELEYITE

WEIGHT LOSS UP TO 500 °C

WEIGH STOICHIOMETRIC AMOUNTS WITH CORRECTION FOR VOLATILE CONTENTS

MIXING: VIBRATORY MILL DISTILLED WATER AND ZIRCONIA BALLS AS MEDIA FOR 2 HRS

DRY 200°F 48 HRS AND CRUSH - 200 MESH

ISOSTATIC PRESSING 30,000 PSI FOR DILATOMETRY

LOOSE POWDER FOR DTA

XBL 765-6872

Fig. 3
DIFFERENTIAL THERMAL ANALYSIS (D.T.A.)

EXOTHERMIC

PT

ENDOTHERMIC

PZ

EXOTHERMIC

PZT

ENDOTHERMIC

TEMPERATURE (°C)

0 200 400 600 800 1000

Fig. 4
PbO + TiO₂
Isostatic Pressing: 30,000 psi
Sample Length: 3/4"

(a) 190°C/hr
(b) 335°C/hr
(c) 490°C/hr
PbO + ZrO₂

Isostatic Pressing: 30,000 psi
Sample Length: 3/4"
DILATOMETRIC STUDY

LENGTH OF SPECIMEN = 0.75"
HEATING RATE = 8.2°C/MIN.

Fig. 7
PbO + (λ) ZrO₂ + (1-λ) TiO₂

Isostatic Pressing: 30,000 psi
Sample Length: 1"
Heating Rate: 335°C/hr

<table>
<thead>
<tr>
<th>Composition</th>
<th>λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) I</td>
<td>0.65</td>
</tr>
<tr>
<td>(b) II</td>
<td>0.50</td>
</tr>
<tr>
<td>(c) III</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Fig. 8
PZT \([\text{ZrO}_2/\text{TiO}_2 = 65/35]\)

X-RAY: Cu K\(\alpha\), Ni filter
SCAN: 1° 2θ/min
T.C.: 3 sec

845°C

785°C

715°C

655°C

580°C

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig9.pdf}
\caption{Fig. 9}
\end{figure}
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.