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REACTION MECHANISMS IN THE FORMATION OF PZT SOLID SOLUTIONS

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ABSTRACT

The solid-state reactions occurring in the $\text{PbO-TiO}_2\text{-ZrO}_2$ system were investigated using constant heating rates up to 1000°C . DTA, dilatometric length changes, and X-ray diffraction analysis were used for characterization. PbO and TiO_2 reacted exothermally to form the product PbTiO_3 with a large volume expansion between 450 and 600°C . Formation of PbZrO_3 from PbO and ZrO_2 occurred endothermally with a large volume expansion between 700 - 800°C . The expansion was due to reaction topology, differential molar volumes of products and reactants and the pellet microstructure. In the formation of PZT from ternary powder mixtures, PT formed between 450 and 600°C followed by PZT formation above 700°C with no measurable amounts of PbZrO_3 formed as determined by XRD analysis. The analysis of the mechanisms indicate that the overall kinetics of homogeneous PZT solid

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solution formation are determined by either the ionic transport within the perovskite lattice or the phase boundary reactions leading to perovskite formation and not by the diffusion of Ti across PbO which is relatively rapid.

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I. INTRODUCTION

The PbZrO_3 - PbTiO_3 (PZ-PT) solid solution system exhibits many desirable electrical properties such as pronounced ferroelectric-piezoelectric behavior and high Curie temperatures. Investigations have been conducted to control stoichiometry and to study the effect of impurities and dopants on the final properties and microstructure. It has been well documented that the fabrication process determines to a significant extent the electrical properties such as dielectric constant, loss factor, coupling coefficients, etc. Using available data, ceramic bodies in the PZT system can be sintered to high densities by proper selection of a composition and suitable control of ambient PbO vapor pressure. Phenomena involved in the process of calcination, on the other hand, have not yet been fully understood though their importance has been noted. (1,2)

The reaction sequence through which PZT solid solutions are formed by solid state reactions in a mixture of $\text{PbO-TiO}_2\text{-ZrO}_2$ has been investigated by many workers but with differing conclusions. Matsuo and Sasaki (3), Gesemann and Neels (4) and Harris (5) did not observe formation of PbZrO_3 as an intermediate phase while Ohno et.al.(6) reported that PZT solid solution was synthesized after formation of both PbTiO_3 and PbZrO_3 . Mori et.al.(7) reported formation of PZ as an intermediate phase only when the

ZrO_2 content of the mixture exceeded 60 mole %. Similarly Yamaguchi et.al.(8) found that a ball milled oxide mixture showed no presence of PZ as an intermediate phase, while precipitation mixing resulted in PZ formation. None of the authors have provided a systematic discussion of the atomistic processes involved in the solid state reactions. Also, the thermodynamic heat effects associated with the formation of various compounds have not been clear. Whereas Speri (9) reported an endothermic heat effect associated with PbTiO_3 formation, others (5,7) observed an exothermic reaction. Moreover, the temperature and time range over which various reactions were observed differ considerably in various reports. The present study was undertaken to investigate the reaction sequence and the temperature range for each reaction step under constant heating rate conditions using DTA, dilatometry and X-ray diffraction analysis.

II. EXPERIMENTAL PROCEDURES

Preparation of Powder Mixtures

Lead monoxide used for the mixtures was reagent grade Massicot (PbO) with less than (0.5%) impurity content. Anatase (TiO_2) of 99.9% purity and reactor grade unstabilized baddeleyite (monoclinic) with hafnium content less than 0.2% were used. The volatile content as measured by weight loss up to 500°C was less than 1% for all of the powders. Average particle size as

measured by Fisher subsieve sizer and specific surface area as measured by three point BET apparatus using nitrogen as an adsorbant were 0.7 micron and $1.5 \text{ m}^2/\text{g}$ for PbO , 0.6 micron and $10.7 \text{ m}^2/\text{g}$ for TiO_2 , and 1.7 micron and $14.1 \text{ m}^2/\text{g}$ for ZrO_2 . SEM photographs indicated that the TiO_2 and ZrO_2 powders were agglomerated with the crystallite size much smaller than the particle size. Five compositions chosen for the study are shown in Table I. Powders were mixed in stoichiometric ratios in a vibratory mill for two hours with ZrO_2 grinding media in isopropyl alcohol. The mixture slurries were dried at 80°C .

To study the effect of the crystal structure of TiO_2 on lead titanate formation, rutile was substituted for anatase. Rutile was obtained by quenching anatase heated at 1100°C for 48 hours. To study the effect of monoclinic to cubic transformation of ZrO_2 on the reaction temperature, calcia-stabilized-zirconia (CSZ) was prepared (15 wt% CaO) and mixed with PbO .

Differential Thermal Analysis

A multi-sample nickel block was used with cells 9.5 mm in diameter and 16.5 mm in depth. The sample reference temperature was assumed to be the same as the block temperature. DTA runs using Pt-Pt 10% Rh thermocouples were made up to 1000°C ; some runs were terminated at intermediate temperatures by rapid cooling in order to identify the phases at those temperatures. Samples were

removed, crushed to -200 mesh in a mortar and subjected to qualitative X-ray analysis. A scanning rate of 1 degree/min was used with Cu(K α) radiation and a graphite monochromator.

Dilatometric Measurements

A fused quartz tube and rod assembly with a LVDT attachment was used for dilatometric measurements. Samples 6.4 mm in diameter and 19 mm in length were prepared by isostatically pressing the powder mixtures in a latex rubber tube up to 2.1×10^8 N/m². A thin platinum foil was then wrapped around the sample to avoid any direct contact between sample and the fused quartz sample holder. Temperature was monitored by a chromel-alumel thermocouple placed close to the sample. The following heating rates were used: 3.2, 5.6, and 8.2°C/min. As with DTA, many dilatometric runs were terminated at temperatures below 1000°C in order to identify the phases present in the quenched samples.

III. RESULTS AND DISCUSSION

The DTA thermograms for compositions V, IV and II are shown in Fig. 1. The curves for compositions I and III were similar to that for II. The PT formation starts at about 450°C and is exothermic in nature. X-ray diffraction analysis of quenched samples indicated that formation of PT was complete at about 600°C.

C even at rapid heating rates. When rutile was used instead of anatase, the reaction was also exothermic and ranged from 450 to 650°C indicating no significant effect of the TiO_2 crystal structure on the nature of the reaction. As seen in Fig. 1, formation of PZ is endothermic and begins at about 700°C. Patterns with ZrO_2 supplied by two different manufacturers gave similar results. The DTA trace of the ternary composition II shows an exothermic peak starting at about 450°C and an endothermic peak starting at about 725°C. The pattern is essentially a composite of the two binary mixtures.

It is known that a phase transformation in one of the reactants can alter the kinetics and thermodynamics of solid-state reactions (Hedval effect). To determine if the monoclinic to cubic transformation of ZrO_2 usually observed at about 1000°C has any effect on the formation of PZ, cubic CSZ was substituted for baddeleyite. The DTA pattern up to 900°C of the $\text{PbO} + \text{CSZ}$ mixture was similar to that of the $\text{PbO} + \text{ZrO}_2$ mixture, and an XRD pattern indicated the formation of a $\text{PbZrO}_3\text{-CaZrO}_3$ solid solution. To check if the formation of a PZ surface layer of crystallites on monoclinic ZrO_2 catalyzes the martensitic transformation to cubic ZrO_2 , a mixture of 10 mole % PbO with baddeleyite was subjected to DTA and XRD. The DTA pattern did not show any peak in addition to that for PZ formation. It can be concluded that up to 900°C the structural transformation of ZrO_2 is not promoted by PZ formation and that the substitution of CSZ for monoclinic ZrO_2

has no detectable effect on the PZ formation. The observed endothermic heat effect must thus be associated solely with the chemical reaction between ZrO_2 and PbO .

From the thermodynamic principle of successive entropy states, reversible reactions are characterized by an endothermic heat effect while irreversible reactions exhibit an exothermic effect on increase in temperature. Therefore, the endothermic formation of PZ suggests reversibility of reaction at an as yet undetermined equilibrium temperature below 700°C . Exothermic synthesis of lead titanate on the other hand points out to irreversibility of the reaction.

It has been reported (10) that in the formation of PT, PbO is transported to the TiO_2 particles where the reaction proceeds at the interface. If vapor pressure data (11) for PbO are extrapolated to 500°C , calculations show that the vapor pressure will be 1.5×10^{-9} atm. This value suggests that at the lower temperatures the reaction starts at the contact points and that surface diffusion of PbO probably plays the major transport role.

The thermal expansion curves for mixtures V, IV and II obtained at a heating rate of $8.2^\circ\text{C}/\text{min}$ are shown in Figure 2. Curves for heating rates of 3.2 and $5.6^\circ\text{C}/\text{min}$ were essentially the same. A P+T mixture shows normal volume expansion up to about 450°C , fol-

lowed by a sharp volume increase up to about 600°C and rapid shrinkage with further heating. This temperature range corresponds to the exothermic peak on the DTA curve. The expansion behavior of the P+Z mixture also shows a large volume expansion beginning at about 700°C followed by shrinkage at temperatures above 800°C. This temperature range corresponds to the endothermic peak on the DTA curve and was associated with the formation of PZ. The curve for the ternary mixture is essentially a composite of the curves for the binary mixtures. Changes in (ZrO_2 / TiO_2) ratio in the ternary compositions only changed the extent of expansion during each of the two reactions.

Theoretical calculations of volume changes due to the solid state reactions can be made. Since PbO is the mobile species, it can be assumed that PT forms as a 'shell' on the particles of TiO_2 . Based on X-ray density values, molar volumes of PT and anatase are 37.8 and 20.8 cm^3 , respectively. Therefore, if a dense spherical single particle of TiO_2 is completely converted to a dense particle of PT, the radius of the resulting PT particle will be 22% larger than the parent anatase particle. If primarily the TiO_2 particles form a skeletal structure in the original $\text{PbO}+\text{TiO}_2$ mixture with PbO packed into the interstices, the large radial expansion of TiO_2 particles can be expected to be translated into an overall expansion of the pellet. The actual amount of pellet expansion may in addition be affected by the external load and ability of the particulate matrix to accomodate rearrangement. A

similar analysis applied to the formation of PZ indicates a radial expansion of 25% on complete conversion of a dense spherical particle of baddeleyite to PbZrO_3 . The smaller expansion observed experimentally than for PT formation may be due to a lesser effective skeletal structure because of the smaller ZrO_2 molar volume than for TiO_2 .

The reaction sequence for the formation of PZT solid solution has not been clear. Previous publications (3-8) have differed on whether the PT, which forms first, reacts directly with PbO and ZrO_2 without the formation of PZ as an identifiable intermediate product, or with PZ that forms from PbO and ZrO_2 . Samples of ternary mixtures with $\text{ZrO}_2/\text{TiO}_2=65/35$ were subjected to XRD analysis after quenching from several temperatures (Fig. 3). Specimens quenched from 580°C and 655°C showed peaks for PT but no detectable peaks for PZ or PZT. At 715°C features appeared in the pattern which can be interpreted as reflecting the initial formation of PZT solid solution. Formation of PZT solid solution is virtually complete by 785°C . No peaks attributable to PZ alone were observed indicating that significant amounts of PZ were not formed. However, formation of small amounts of PZ can not be ruled out due to difficulty in interpretation of the X-ray patterns. Above the Curie temperatures, PT and PZ form a continuous solid solution of cubic structure. On cooling to room temperature, the solid solutions can exist in one of three structures: tetragonal, rhombohedral or orthorhombic depending on the

Zr/Ti ratio (12). As a result, XRD patterns are complex involving overlaps and shifts of peaks due to solid solution formation. Nevertheless, the XRD analysis rules out the PZT formation based primarily on the initial formation of PT and PZ in large amounts followed by slow interdiffusion of Ti^{4+} and Zr^{4+} to form PZT. The DTA and thermal expansion data support the XRD data that PT is formed first and with increasing temperature ZrO_2 takes part in the reaction. The three reactants PbO , ZrO_2 , and PT then form a reactive system in which the perovskite formation can proceed at two interfaces, ZrO_2/PbO and ZrO_2/PT , as schematically shown in Figure 4.

Assuming that oxygen does not diffuse over a long range and the charge balance in solid solution formation is achieved by proper interdiffusive fluxes of cations, following critical factors should be noted:

- (i) A Ti^{4+} gradient exists in PbO from Ti saturated PT/ PbO interface to its interface with the perovskite providing a driving force for Ti^{4+} transport across PbO . The ratio Zr/Ti in the perovskite formed will be determined by the rapidity of such transport.
- (ii) The initially formed PT phase in contact with PbO and ZrO_2 continues to grow as PZT at the expense

of these reactants probably with a lower Zr/Ti ratio.

(iii) A net gradient of quadrivalent ions exists from ZrO_2 to PbO in perovskite products forming at both the original interfaces as long as the reaction continues, as shown in Fig. 4. A flux of Pb^{2+} exists in the opposite direction.

(iv) Interdiffusion of Ti^{4+} and Zr^{4+} within and between the PZT phases forming at the original PbO/ZrO_2 and PT/ZrO_2 interfaces results in an overall PZT of homogeneous composition.

As evident from PZT formation at the PbO/ZrO_2 interface, titanium transport through PbO is relatively rapid and does not form the rate limiting step in the overall formation of a homogeneous PZT solid solution. The rate limiting mechanism must therefore be associated with the ionic transport across the perovskite or the phase boundary reactions at the perovskite interfaces, as evident from the nature of reaction sequences with the increasing temperature.

In the above discussion, it was implicitly assumed that the contact between the reactants at various interfaces was ideal. Discrepancies in the reaction mechanisms observed by various authors (3-8) may be attributed to the different experimental

conditions to the extent that processing operations like mixing, particulate characteristics and the volume fractions of the reactants determine ideality of an experimental set-up.

IV. CONCLUSIONS

Formation of PT begins at about 450°C and finishes at about 600°C , is exothermic in nature suggesting irreversibility, and is accompanied by a large volume expansion. Since the vapor pressure of PbO at these temperatures is low, mass transport of PbO to the TiO_2 particle surfaces is believed to be due to surface diffusion. Formation of PZ begins at about 700°C and is almost complete at about 800°C also accompanied by a large volume increase. The reaction is endothermic and hence theoretically reversible at some undetermined equilibrium temperature below 700°C .

The large volume increases during the formation of the binary compounds can be attributed to (a) the relative specific molar volumes of reactants TiO_2 and ZrO_2 and the products and (b) the topology of reaction whereby the product layer is formed on the surface of the reactants TiO_2 and ZrO_2 , and (c) the particulate packing is such that TiO_2 and ZrO_2 form a skeletal structure.

In the ternary mixture of $\text{PbO} + \text{ZrO}_2 + \text{TiO}_2$ the DTA and the dilatometric data are a composite of the data for the binary mixtures

of P+Z and P+T. In the formation of PZT solid solution, PT forms first or most rapidly. The formation of PZT is believed to occur by a coupled reactive exchange of 2 Pb^{2+} and Zr^{4+} at the PT/ZrO_2 and 2 Pb^{2+} and Ti^{4+} at the PbO/PT interfaces followed by counter-diffusion of Zr^{4+} and Ti^{4+} within the perovskite lattice. Similarly, the reaction at PbO/ZrO_2 contact points proceeds by the exchange of 2Pb^{2+} and Zr^{4+} . This is followed by interdiffusion of quadrivalent cations within the product where transport of Ti across PbO to the PbO/PZT interface forms a source of Ti. The diffusion of Ti across PbO was rapid enough that no significant peaks of PZ were detected in X-ray diffraction analysis. Thus, the rate determining step in the overall kinetics of homogeneous PZT solid solution formation appears to be the ionic transport within the perovskite lattice or the phase boundary reactions leading to perovskite formation at PT/ZrO_2 as well as PbO/ZrO_2 interfaces. The DTA and dilatometry data support the proposed mechanism on the basis that the positions of endothermic and expansion peaks for binary P+Z and ternary P+Z+T mixtures are the same.

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Table I. Experimental Compositions from PbTiO_3 - PbZrO_3 System

COMPOSITION	MOLAR RATIOS		
	PbO	TiO ₂	ZrO ₂
I	1.00	0.35	0.65
II	1.00	0.50	0.50
III	1.00	0.65	0.35
IV	1.00	0	1.00
V	1.00	1.00	0

FIGURE CAPTIONS

- Fig. 1. DTA plots for $(\text{PbO} + \text{TiO}_2)$, $(\text{PbO} + \text{ZrO}_2)$ and $(\text{PbO} + 0.5 \text{TiO}_2 + 0.5 \text{ZrO}_2)$ mixtures at the constant heating rate of $10^\circ\text{C}/\text{min}$ in air (V, IV, and II in Table 1).
- Fig. 2. Dilatometric expansion characteristics of $(\text{PbO} + \text{TiO}_2)$, $(\text{PbO} + \text{ZrO}_2)$ and $(\text{PbO} + 0.5 \text{TiO}_2 + 0.5 \text{ZrO}_2)$ mixtures at constant heating rate of $8.2^\circ\text{C}/\text{min}$ (II, IV and V in Table 1).
- Fig. 3. Room temperature X-ray diffractometry patterns for Composition I ($\text{PbO} + 0.65 \text{ZrO}_2 + 0.35 \text{TiO}_2$) showing various phases. Samples were heated to the shown temperatures at the constant rate of $5.6^\circ\text{C}/\text{min}$ and quenched rapidly after reaching the shown temperature.
- Fig. 4. Schematic of reaction system after lead titanate formation is complete. The dotted line is not a true interface since PZ-PT form a continuous solid solution above Curie temperatures.

DIFFERENTIAL THERMAL ANALYSIS (D.T.A.)

XBL 756-6525

Fig. 1

Fig. 2

XBL 765-6867

Fig. 3

XBL 807-5511

Fig. 4

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