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Kinetic Aspects of the Formation of Lead Zirconium Titanate

O. Babushkin,[a] T. Lindbäck,[a]* J.-C. Luc[b] & J.-Y. M. Leblais[b]

[a] Division of Engineering Materials, Luleå University of Technology, S-971 87 Luleå, Sweden
[b] Quartz et Silice Research Institute, B.P. 95, F-77792 Nemours, France

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Abstract

The kinetics of the second calcination step in the formation of PZT solid solution (with perovskite ABO_3 lattice) has been investigated by using two different particle sizes of the B-site precursor (1·91 and 5·08 μm), the finer size being obtained by prolonged milling. In-situ *analysis performed by high-temperature X-ray diffractometry in a non-isothermal mode (20-800°C) revealed a reduction of the calcination temperature by 100°C with a decrease in particle size of the precursor. In order to clarify the mechanism of the solid-state reaction to PZT, isothermal heat treatment of the mixtures was performed in the temperature range 540–700°C. The activation energies for the fine and the coarse powders were estimated as 150 and 210 kJ mol^{-1} respectively, and the reaction was found to follow the Jander model for diffusion-controlled solid-state reaction kinetics.* © *1996 Elsevier Science Limited*

1 Introduction

The basic electrical and mechanical properties of PZT ceramics are strongly influenced by the chemical composition of the raw materials and the subsequent calcination and sintering processing. As far as the calcination stage is concerned, it can have a large influence on the piezoelectric properties since it can affect the homogeneity of the final solid solution. In the calcination to PZT, studies of solid-state reaction sequences have shown the dependence of the formation mechanism of PZT on powder characteristics (particle size, impurities, morphology of the precursors, etc.). When the calcination is performed in one step, i.e. starting from the three individual oxides, the problem of PbO vaporization limits the calcination temperature and as a consequence prolongs the calcination. It has been shown that increased homogeneity, which enhances the final properties of the PZT solid solution, can be achieved by carrying out the calcination in two steps.[1–3] In the first step the B-site oxides are prereacted to form a B-site zirconium titanate precursor according to the following reaction.

$$0{\cdot}52ZrO_2(s) + 0{\cdot}48\ TiO_2(s) \rightarrow Zr_{0{\cdot}52}Ti_{0{\cdot}48}O_2\ (ss)\ (1)$$

The formation of the precursor without PbO suppresses intermediate phases when forming the perovskite phase in the second stage as given in the following expression

$$Zr_{0{\cdot}52}Ti_{0{\cdot}48}O_2(ss) + PbO(s) \rightarrow PbZr_{0{\cdot}52}Ti_{0{\cdot}48}O_3(ss)(2)$$

The present investigation, made using high-temperature X-ray diffractometry, was performed in order to clarify the influence of particle size of the B-site precursor on the kinetics of the second reaction.

2 Experimental

Two $PbO/Zr_{0{\cdot}52}Ti_{0{\cdot}48}O_2$ powder mixtures were prepared having two different particle sizes of the $Zr_{0{\cdot}52}Ti_{0{\cdot}48}O_2$ precursor. Both powders were attrition-milled. One of them, termed the 'fine' powder, had an average particle size of 1·91 μm and the other 'coarse' powder had a particle size of 5·08 μm. The commercial PbO had a purity of 99·6% (orthorombic crystal structure plus several wt% of tetragonal form). The powders were carefully mixed and isostatically pressed to pellets at 100 MPa with a maximum thickness of 1·0–1·5 mm.

X-ray diffractograms were obtained using a Philips PW-1710 automatic diffractometer with a step and a continuous scanning device. The basic unit in this system is a Philips powder diffractometer with a vertical goniometer PW 1050/25, graphite mono-chromator PW 1752/00, proportional counter for reflected beam PW 1711/10 and a PW

*To whom correspondence should be addressed.

1730/25 generator. Diffraction patterns were measured in a 2θ range of 20–40° using Cu K_α radiation of 50 kV and 30 mA. The at-temperature investigations were performed in an Anton Paar high-temperature attachment re-engineered by the authors.[4] The temperature of the sample was measured with a Pt–13% Rh/Pt thermocouple placed close to the sample. The measurements of the developing lead zirconate titanate phase were made in two different modes. The first set of measurements was made during heating to 800°C with a nominally constant heating rate of 10°C min^{-1} and 3 min scans in the above-mentioned 2θ range starting from 500°C with a scan at every 50°C. The second set was made during isothermal heat treatments in the temperature range 450–800°C with a maximum soaking time of 120 min.

The quantitative estimation of phase content was derived from an equation which relates the intensity of the diffraction peaks to the phase abundance[5]

$$I_{ij} = \frac{K_j C_{ij}}{\rho_j \mu_{li}} = \frac{\beta_j C_{ij}}{\sum_{j=1}^{n} \mu_j C_{ij}} \qquad (3)$$

where

K_j is a constant.
C_{ij} is the weight fraction of the jth phase in the ith sample.
I_{ij} is the intensity of a diffraction peak of phase j.
μ_{li} is the mass absorption coefficient of the sample.
μ_j is the mass absorption coefficient of phase j.
ρ_j is the density of phase j.
$\beta_j = K_j/\rho_j$) is the calibration constant, defined by the crystal structure, the composition of the analysed phase and the instrumental conditions.
n is the number of phases in the sample.
i is the sample number.
j is the phase number.

It is evident that the determination of C_{ij} from eqn (3) requires a knowledge of β_j and μ_{li}. Fortunately, the equation is simplified especially if it is assumed that chemical composition of the investigated sample remains unchanged during heat treatment and by ignoring texturing effects (because of *in-situ* mode data collection). Then, assuming that the mass absorption coefficient of the sample is constant, eqn (3) becomes

$$C_{ij} = B_j I_{ij} \qquad (\text{where } B_j = 1/\beta_j) \qquad (4)$$

Then the conversion of PbO to PZT can be written as

$$C_{PZT} = \frac{S_{PZT}}{S_{PZT} + S_{PbO}} \qquad (5)$$

where C_{PZT} is the fraction of newly formed PZT phase, S_{PZT} is the integrated intensity of the cubic PZT (1 1 0) peak and S_{PbO} is the integrated intensity of the PbO (1 1 1) peak.

Precise quantitative phase analysis requires accurate measurement of the integrated intensities of the diffracted lines. Count integration techniques work very well, when the lines are isolated and on simple backgrounds. However, when one or more lines overlap the line of interest, or if a complex background is present, profile fitting techniques are required in order to eliminate interferences. In order to fit the main peaks of PbO (1 1 1) and PZT (1 1 0) a profile model based on asymmetric Lorentzians for fitting the instrument- and wavelength-related components of the powder diffraction profile, together with a Marguardt non-linear least-squares algorithm, were used.[6]

3 Results and Discussion

3.1 Dynamic heat treatment

The phase composition of the initial mixtures contained two polyforms of PbO, namely massicot as the main phase and a small amount of litharge formed during preparation. In many commercial powders the metastable massicot is stabilized by the addition of small amounts of impurities (dopants), preventing its transformation to stable litharge at room temperature but allowing transformation to litharge when a mechanical force is applied. The other main phase was $Zr_{0.52}Ti_{0.48}O_2$, the main diffraction peaks of which were strongly overlapped by PbO. *In-situ* analysis made in the non-isothermal mode (temperature range 20–800°C) revealed dissolution of the main phases and corresponding formation of the PZT phase with cubic symmetry (Fig. 1). Special attention was paid to scanning in the temperature range 400–600°C, where the formation of a pyrochlore phase was expected. Diffractograms of samples in that temperature interval did not reveal the main peak of the pyrochlore phase located at $29° < 2\theta < 30°$ (Fig. 1). From this it was concluded that the formation of the PZT phase in this investigation can be considered as a uniform process without formation of intermediate phases.

The quantitative analysis showed that during the non-isothermal treatment the rate of formation of PZT was dependent on the particle size of the $Zr_{0.52}Ti_{0.48}O_2$ powders (Fig. 2). In both cases the curves are characterized by a sigmoidal shape, the main stages of the process being: the start of the reaction between 400 and 500°C, a constant rate stage between 500 and 700°C and a decreasing reaction rate at temperatures over 700°C. Figure 2

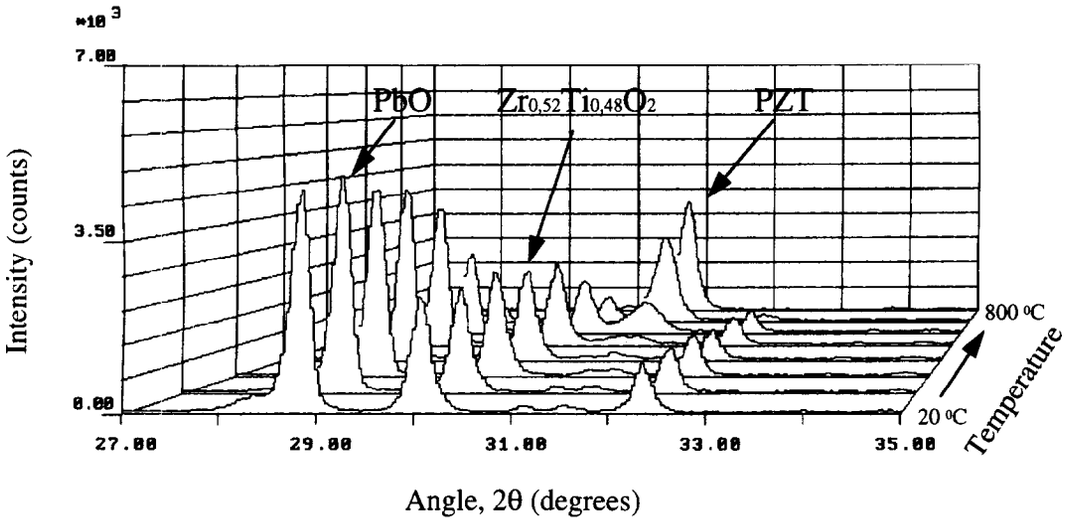

Fig. 1. Phase composition for the coarse $Zr_{0.52}Ti_{0.748}O_2$–PbO powder during heating.

clearly shows that the reaction to PZT is not autocatalytic and that the maximum rate of PZT formation for the two powders differs by approximately 100°C. A similar particle size effect on the calcination temperature was observed by Shrout[1] and Fukai *et al.*[7] The latter also showed that PZT was produced at a lower temperature than 600°C without formation of intermediate phases.

3.2 Isothermal heat treatment

Heat treatment of the powders was performed in an isothermal mode in the temperature range 540–700°C, in order to obtain more information about the solid-state reactions taking place during the PZT formation [Figs 3(a) and (b)]. As can be seen from the figures, the isothermal runs showed the absence of a measurable incubation time for the reaction. For the fine powder, the temperature of reaction is around 100°C lower than for the coarse. As a further quantitative assessment of the powder mixtures, the reactivity of the powders was estimated from the value of the apparent activation energies of reaction.

The overall rate of change of a microscopic transformation that proceeds via a large number of atomic processes is given by[8]

$$\text{rate} = v \exp(\Delta S/k) \exp(-\Delta H/kT) \qquad (6)$$

where v is a complex function that depends on the vibration frequency of the atoms, ΔS the activation entropy, k the Boltzmann constant, T the absolute temperature and ΔH the activation enthalpy. In condensed systems the activation enthalpy and the activation energy (ΔE_a) are nearly the same. Therefore, on the molarity scale, the rate of transformation may be expressed as an exponential function of an empirical activation energy which is characteristic of the transformation process

$$\frac{d\alpha}{dt} = f(\alpha) \cdot A e^{-\Delta E_a/RT} \qquad (7)$$

where α is the fraction converted, $f(\alpha)$ is a function of α and A is a constant. Integration of eqn (6) gives

$$\int_0^{t_{\alpha_f}} dt = \int_0^{\alpha_f} [Af(\alpha)]^{-1} e^{\Delta E_a/RT} d\alpha \qquad (8)$$

or

$$\ln t_{\alpha_f} = \ln\left\{ \int_0^{\alpha_f} [Af(\alpha)]^{-1} d\alpha \right\} + \frac{1}{R} \cdot \frac{E_a}{T} \qquad (9)$$

where t_{α_f} is the time required to obtain a certain fraction converted, α_f.

In this case the activation energy can be estimated in a straightforward manner, without assuming a specific kinetic model. It follows from eqn (9) that the activation energy is found by plotting the logarithm of time versus $1/T$ for a given constant fraction converted (α_f). Plots of ln t versus $1/T$ shown in Fig. 4 are reasonably straight parallel

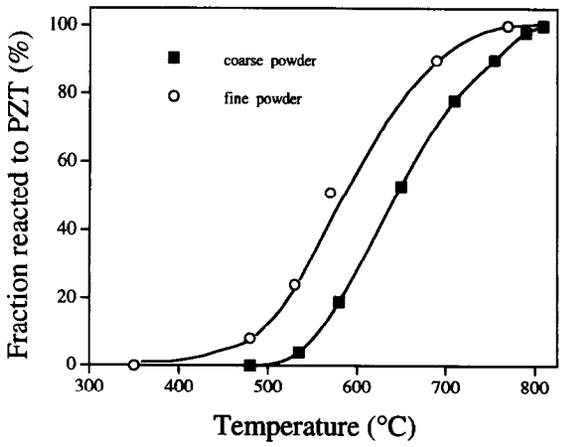

Fig. 2. Fraction of PZT formed versus temperature.

lines, indicating that the PZT formation reactions are characterized by a uniform mechanism. The calculated values of activation energy for the fine and the coarse powders are 150 and 210 kJ mol^{-1} respectively. In the literature,[9-12] quoted values for the activation energy vary from 100 to 500 kJ mol^{-1}. It is obvious that the physical meaning of the activation energy obtained from solid-state reactions in powder systems cannot be directly related to concepts used for describing kinetic processes in, for example, gas systems. In solid-state reactions the numbers of reacting species and reaction steps are more uncertain. Generally, these depend on the type of atomic interaction, the extent and geometry of the contact regions in the particle system, the type of crystal lattice and its degree of perfection. An example is provided by investigations performed on the reaction between PbO and ZrO_2.[10] The growth of the product layer between bulk PbO and ZrO_2 samples could be described by parabolic kinetics and the activation energy of the reaction was approximately 500 kJ mol.$^{-1}$ In contrast, in studies of mixed powders with different thermal prehistories, morphology and chemical activity, the phase transformations were shown to follow the Jander and the Kolmogorov–Erofeev models having activation energies of 188 and 100 kJ mol^{-1}, respectively.[11,12] The values for the activation energies obtained in this investigation are consistent with the literature data and indicate that the activation energy for solid-state reactions mainly reflects the reactivity of the powders used in the investigation.

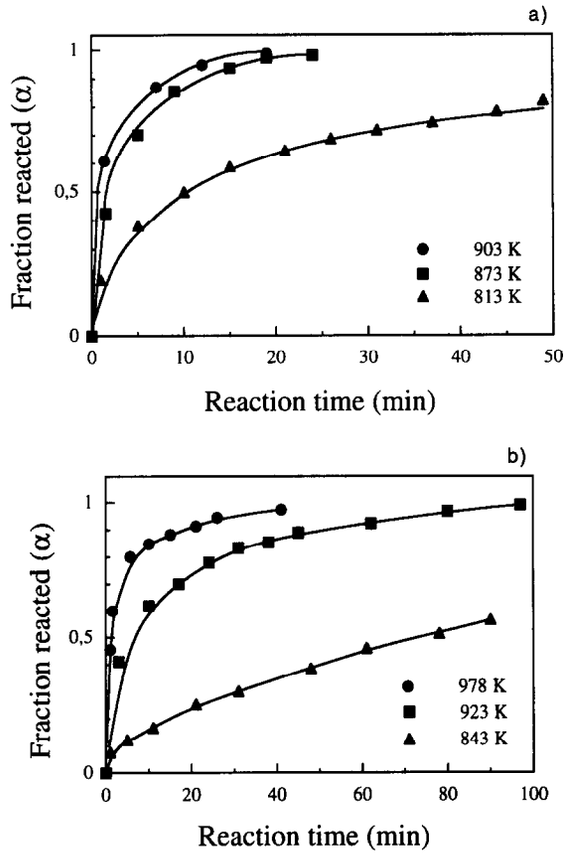

Fig. 3. Fraction of PZT formed versus time at different temperatures: (a) fine and (b) coarse powder.

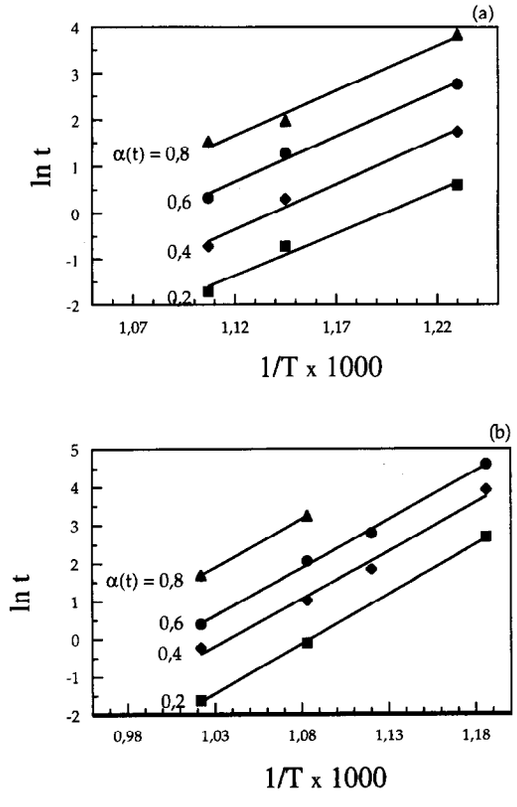

Fig. 4. The logarithm of time as a function of reciprocal temperature for various extents of the reaction, where (a) and (b) are the fine and the coarse powders, respectively.

3.3 Evaluation of the kinetic model

Investigations performed on PbO–TiO_2 and PbO–ZrO_2 systems have revealed that the formation of the binary compounds proceeds via reactions with material transport as the rate-controlling process.[7,10,11] It was also shown that, for powder compacts, the formation of $PbTiO_3$ and $PbZrO_3$ followed the Jander model for diffusion-controlled solid-state reaction kinetics.[11] In diffusion couples it was observed that the lead diffuses faster than the zirconium and titanium; thus few Ti^{4+} and Zr^{4+} ions were found in the PbO plate, while large numbers of Pb^{2+} ions were found in both the TiO_2 and ZrO_2 plates.[10] Attempts have been made to apply rate equations to powder mixtures with a distribution of sizes. It was found that the Valency–Carter diffusion model was applicable in all temperature intervals, when describing a particle size distribution of precursors reacting to $PbTiO_3$ and $PbZrO_3$.[9,13]

The above observations suggest that the formation of the ternary $Pb(Zr,Ti)O_3$ compound would occur predominantly by solid-state diffusion of Pb^{2+} and O^{2-} ions. Three diffusion-controlled models are chosen here to help identify the nature

of the diffusion mechanism: (i) the Jander model which is based on the solution for diffusion in a plane interface, without any change in volume or motion of the interface; (ii) the Ginstling and Brounshtein equation for a diffusion-controlled reaction starting on the exterior of a spherical particle[14] and (iii) the Valesi and Carter equation for spherical particles, taking into account the difference in volume of the reaction product and the initial material.[14 16] When the experimental data were fitted to these equations, the best fit was obtained with the Jander equation

$$r_A^2[1 - (1 - \alpha_t)^{1/3}]^2 = 2k\,t \qquad (10)$$

where α_t is the relative amount of A transformed into reaction product, r_A is the radius of the original spherical particles of A and k is the parabolic rate constant. The derivation of the equation is based on the premise that equal-sized spheres of reactant A are embedded in a quasi-continuous medium of reactant B. The closeness of fit is demonstrated in Figs 5 and 6 for the fine powder mixture. On the basis of this it is proposed that, when the fine powders are heated, either rapid surface diffusion or a high vapour pressure of PbO provides a uniform supply of Pb^{2+} and O^{2-} ions over the entire surface of the $Zr_{0.52}Ti_{0.48}O_2$ particles. Since the vapour pressure of PbO is rather low, varying from 1.5×10^{-9} atm at 500°C to 5×10^{-7} atm at 700°C,[17, 18] the second alternative seems less probable. Thus the extent of contact regions, together with the activation energy for bulk diffusion of Pb^{2+} and O^{2-} ions, will play a dominant role in the formation rate of the PZT solid solution.

In the derivation of the Jander equation, a parabolic growth law has been assumed. This is only valid for a diffusion-controlled one-dimensional reaction process, and not for a process with spherical geometry. Therefore it may appear somewhat surprising that the Jander equation gives the best fit to the experimental data. However, after milling, the $Zr_{0.52}Ti_{0.48}O_2$ particles consist of finely divided, far from spherical, nanometre-sized crystallites with a high defect density.

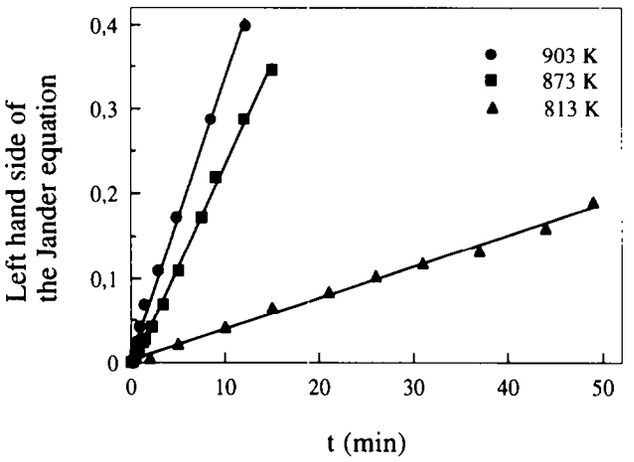

Fig. 5. Fitting of the Jander equation to experimental date of the reaction $Zr_{0.52}Ti_{0.48}O_2 + PbO \rightarrow Pb(Zr_{0.52}Ti_{0.48})O_3$ in the fine powder mixture.

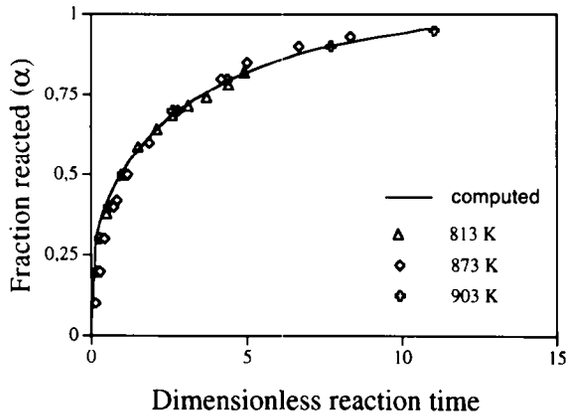

Fig. 6. Amount of PZT formed (α), for the fine powder mixture, as a function of reduced time, $t/t_{0.5}$. The full line is computed on the basis of the Jander model.

4 Conclusion

The second calcination stage in the formation of PZT solid solution was investigated by means of high-temperature X-ray diffractometry. The constant heating rate experiment of the powder mixtures of PbO and $Zr_{0.52}Ti_{0.48}O_2$ showed a direct formation of PZT solid solution without any intermediate X-ray-crystalline phases. By reducing the particle size of the B-site precursor from 5·08 to 1·91 μm, the calcination temperature was reduced by 100°C. The measured activation energy of the reaction was 150 kJ mol^{-1} for the mixture containing the fine precursor activated by prolonged milling and 210 kJ mol^{-1} for the mixture containing the coarse precursor. The reaction was found to follow the Jander model for diffusion-controlled solid-state reaction kinetics.

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