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# *In-situ* devitrification of metallo-organic decomposition solutions in the high voltage electron microscope

C. A. LEACH, G. X. DONG, B. C. H. STEELE
*Department of Materials, Imperial College of Science, Technology and Medicine, Prince Consort Road, London, SW7 2BP, UK*

The decomposition of metallo-organic compound films to yield ceramic oxides with a composition in the lead lanthanum zirconium titanate (PLZT) phase field has been observed using an environmental cell in the transition electron microscope. Diffraction pattern analysis indicates that the first formed phase is lead oxide but that this is rapidly followed by the formation of an homogeneous PLZT composition. The results are supported by differential thermal analysis (DTA)/thermogravimetric analysis (TGA) of the precursor solutions. These observations indicate that it may be practical to prepare thin films of this important electro-optic material by this route.

## 1. Introduction

The preparation of dense, polycrystalline mixed metal oxide films is of considerable importance in many areas of electrical ceramics research [1]. Typical applications range from their use as constituent layers in electronic components exploited for their dielectric or charge carrying characteristics, to window coatings whose optical density may be modified rapidly, as in smart window technology. In many of these cases it is necessary to prepare a dense, fine, polycrystalline oxide film of known stoichiometry in order to obtain the desired properties. This can prove difficult to achieve by a conventional thermal decomposition route in situations where one constituent phase of a mixed oxide is particularly volatile or where a low melting point, incongruent, liquid phase is formed during the preparation of a mixed oxide film [2, 3]. Another feature of film production by thermal decomposition which may lead to an undesirable microstructure is that, frequently, the temperature to which it must be heated in order to produce a single phase film which is homogeneous and dense is too high to be consistent with a fine grain size within the film [2]. It is therefore generally desirable to reduce the time and temperature of the heat treatment of a thin film as far as possible in order to optimize the microstructural features.

The metallo-organic decomposition (MOD) method of producing thin films is a relatively novel approach which does not involve the significant generation of discrete intermediate single oxide phases [4]. It enables sample preparation producing a homogeneous single phase to be carried out at lower temperatures than those required by other chemical routes, commonly described as sol–gel or coprecipitation techniques. This approach involves the preparation of mixed solutions of metallo-organic (MO) compounds to form an intimately mixed, metal precursor of the correct stoichiometry, from which the desired oxide is produced by thermal decomposition [4].

Compounds formed at specific compositions within this compositional field display switchable ferroelectric behaviour, and show considerable promise for a range of electro-optical devices [5]. The multi-element composition of this ceramic makes it an ideal candidate for production by this route, since conventional processing methods suffer from many of the disadvantages described above [6].

In this paper we will describe the formation of a thin film of PLZT (lead lanthanum zirconium titanate) material *via* the decomposition of metal carboxylate precursors, as observed *in-situ* in an environmental cell in the TEM. This approach enables direct observation of the decomposition of the sample at elevated temperature at an oxygen pressure comparable with that of air. The results of the TEM investigation will be compared with some DTA/TGA results from the decomposition of the solutions.

## 2. Experimental procedure

Individual MO solutions of the metal 2-ethyl hexanoate were prepared in xylene, following the method of Vest and Singaram [4]. The reagents were general purpose reagent (GPR) grade lead nitrate, lanthanum chloride and zirconium chloride, each dissolved in deionised water and titanium ethoxide in ethanol. These solutions were reacted individually with 2-ethyl hexanoic acid and the reaction products extracted in xylene. The solutions were then mixed in such proportions as to result in the desired cation ratio, corresponding to a PLZT composition

$$(Pb_{0.93}La_{0.07})(Zr_{0.65}Ti_{0.35})_{0.965}O_3$$

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TEM samples were then prepared by painting the MO solution onto a carbon film suspended on a standard 200 μm mesh copper grid, and drying under an infrared lamp to produce a film ~ 2 μm thick. The samples were mounted on a heating stage in an environmental cell within the specimen chamber of an AEI EM7 high voltage electron microscope. This configuration enabled the sample to be heated to temperatures of around 500 °C under an oxygen pressure, $p(O_2)(= p_{tot})$, of *ca.* 11.99 kPa. The value of $p(O_2)$ for air is *ca.* 19.99 kPa. Higher oxygen pressures within the environmental cell were not possible as significant leakage of the gas into the microscope column occurred, resulting in destabilization of the electron beam. The sample temperature in the environmental cell was measured by means of a thermocouple.

Complementary to the above, DTA/TGA measurements were made in air on a sample of the mixed MO solution and its constituent components to determine the decomposition temperatures in air and to measure the associated weight changes.These were carried out on a Stanton Redcroft STA 780 series thermal analyser, heating at a rate of 10 °C min$^{-1}$ up to 850 °C.

## 3. Results

### 3.1. Diffraction pattern analysis

During heating of the film the changes in the selected area diffraction pattern of a part of the film *ca.* 10 μm in diameter was observed. The sample was heated at an average rate of 20 °C min$^{-1}$.

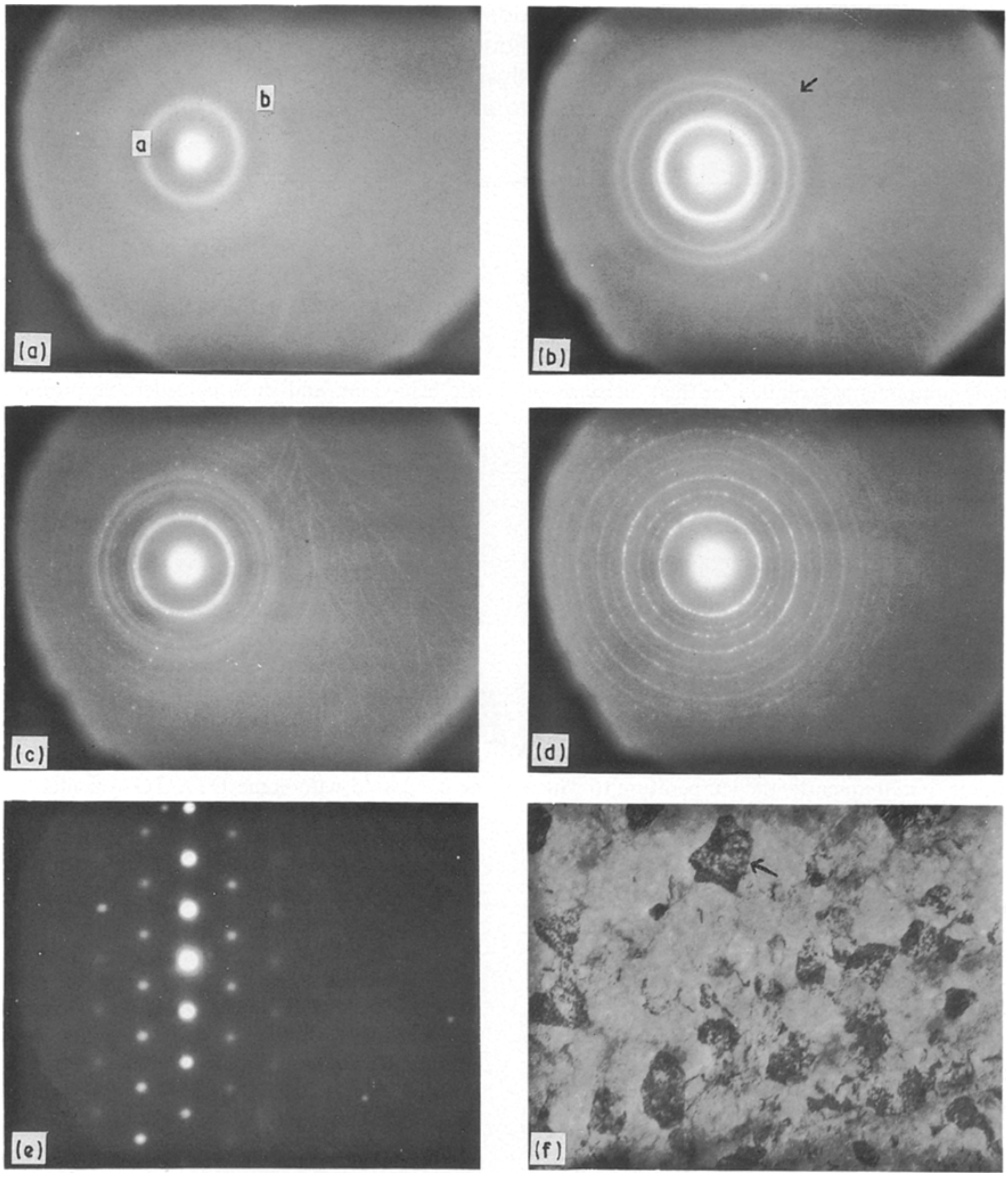

*Figure 1* (a)–(e) Selected area diffraction patterns of the thin film during its decomposition to a PLZT; (a) Heated to 390 °C, (b) heated to 480 °C, (c) heated to 480 °C and held at temperature for 4 min, (d) heated to 480 °C and held at temperature for 13 min, (e) heated to 480 °C and held at temperature for 45 min (single grain [1 1 1] orientation), (f) micrograph of the final product; a polycrystalline PLZT thin film. The arrowed grain produced the SADP shown in Fig. 1e.

In contrast with the results of the DTA observations, no structural changes, as evidenced by observing the diffraction pattern, were observed at temperatures below 400 °C, although it should be borne in mind that it was only possible to maintain the $p(O_2)$ in the cell at 60% of air, and so this discrepancy is likely to be due to a reduced oxygen activity in the atmosphere. A typical diffraction pattern, taken at a sample temperature of 390 °C, is shown in Fig. 1a and comprises a diffuse ring (a) surrounded by a very diffuse band (b). This type of pattern indicates a predominantly amorphous film with some short range order present, which would be typical of a rapidly crystallized MO compound.

On heating to 480 °C more structure is developed within the diffraction pattern (Fig. 1b). The bright ring (a) of Fig. 1a is now surrounded by a weaker ring centred on a *d*-spacing of 0.269 nm. The very diffuse band (b) of Fig. 1a is now resolved into two rings corresponding to lattice spacings of 0.189 nm and 0.161 nm. There is also evidence for a weak ring outside this doublet (arrowed). These new rings indicate the onset of a periodic structure within the film with a concomitant increase in long range order. At this stage in the decomposition, point diffraction maxima due to individual crystallites are not resolved. The appearance of these new rings, coupled with the retention of the short range order ring, suggest that a large number of nuclei of a new crystalline phase are forming. The sample temperature was maintained at 480 °C to study the subsequent crystallization of the film.

After a 4 min hold, discrete spots are visible in the diffraction pattern (Fig. 1c) arranged in rings, and indicating the development of another phase. These later rings are positioned close to, but not coincident with, the earlier rings. In particular one of the new rings lies between the original short range order ring and the secondary ring surrounding it. The first set of rings rapidly decreased in intensity and became undetectable after 13 min hold time (Fig. 1d). Further annealing only resulted in a reduction of the number of spots within the second set of rings as the oxide grains coarsened.

Fig. 1e shows a [1 1 1] diffraction pattern of an individual PLZT grain (Fig. 1f – arrowed) taken after annealing the film for 45 min. The grains have now coarsened to 0.5–0.8 μm within a fully dense film. The crystal structure at 480 °C is indexed as cubic with $a = 0.401$ nm.

### 3.2. DTA/TGA

The results of the DTA/TGA analysis are shown in Fig. 2. In the DTA trace there is a strong, broad, endothermic peak at 95 °C which occurs at 85% weight loss and is due to the evaporation of the solvent. Further heating to 200 °C resulted in very little change to the sample. Above 200 °C the initiation of an exothermic reaction is observed, accompanied by a slight increase in the rate of weight loss from the sample. The DTA trace reaches a local exothermic peak at 260 °C and this is followed by a much stronger exothermic peak at 320 °C. After this peak the sample is stable up to 800 °C.

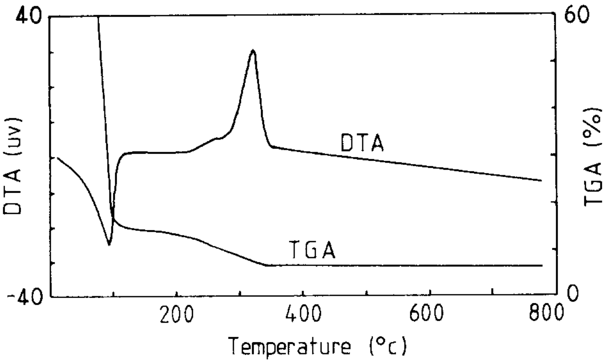

*Figure 2* Differential thermal and thermogravimetric analyses showing sample variations during the crystallization and the decomposition of the MOD solution used in this study.

## 4. Discussion

Diffraction pattern analysis in the environmental cell of the TEM suggests that only one transient phase is formed before the development of the mixed oxide PLZT. The lattice parameters of the intermediate phase corresponds to PbO. Similarly, in the DTA trace of the mixed metal solution we observe only two exothermic peaks after the evaporation of the carrier solution, at 260 and 320 °C. The results of these two experiments are correlated and the first exothermic peak at 260 °C assigned to the initial decomposition of the metal carboxylate involving the loss of some volatile material and the formation of an intermediate PbO phase. The second peak is therefore associated with the formation and crystallization of the PLZT oxide film, which remains stable up to 850 °C.

It is, however, noted that the reactions observed in the TEM occurred at higher temperatures than those measured by DTA. This is believed to be due to the reduced $p(O_2)$ and the increased heating rate in the TEM compared with the DTA runs, resulting in changes in the kinetics of the reaction steps.

Since PbO has been identified as an intermediate phase in the formation of the PLZT film, it might therefore be expected that similar DTA peaks for the decomposition of the solution to yield lanthana, zirconia and titania would be observed. These are not seen. Although data for the decomposition temperature of a MO solution to yield lanthana is not available, values corresponding to zirconia and titania formation are quoted in the literature as 450 and 600 °C, respectively [6]. The absence of these peaks prior to the formation of the PLZT phase indicates that no additional intermediate steps are involved in the formation of PLZT by this route. It is thus concluded that mixing the solutions, and hence the cations, on the molecular level has caused these individual decomposition processes to interact over a narrow temperature range (around 320 °C) to form the mixed metal oxide directly. This has occurred with only minor formation and redissolution of lead oxide prior to the development of the final product. Other work by the authors suggests that the final decomposition temperature is a function of the PLZT composition and in fact increases slightly as the Ti/Zr ratio is increased.

The TGA analysis indicates that below 850 °C there was no sample weight loss after the MO decomposition which occurred at 320 °C. Coupled with the EDAX analysis of the final film, this suggests that, even though lead oxide is formed as an intermediate phase, there is no lead loss from the system at temperatures up to 850 °C, and therefore a PLZT composition of the solution's stoichiometry has been formed.

## 5. Conclusions

1. It is possible to prepare dense, thin films of PLZT by the MOD process.
2. The decomposition of the MO precursor solution occurs by the formation of an intermediate lead oxide phase, which is subsequently resorbed into the PLZT solid solution.
3. Thermal decomposition takes place at a sufficiently low temperature as to permit an exceptionally fine grain size in the film.

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