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PZT Formation in the Presence of Dopants

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Abstract: The formation of PZT from the oxides Pb_3O_4, TiO_2 and ZrO_2 in the presence of NiO, Fe_2O_3 and Ta_2O_5 additives has been investigated by thermal analysis (DTA and TG), X-ray diffraction and chemical techniques. It is shown that the formation of PZT is accomplished through several steps: decomposition and formation of Pb_3O_4 between 240 and 390°C; formation of $PbTiO_3$ above 350°C and of its solid solutions at 650°C. The PZT solid solution appears without formation of $PbZrO_3$. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Lead titanate–zirconate (PZT) solid solution ceramics are well-known as piezoelectric ceramics with a perovskite structure.[1–3] The reaction sequence through which PZT solid solutions are formed by solid state reactions has been investigated by many authors but with varying conclusions.[1–10] In this domain, different parameters have been investigated: quality of raw materials,[1,4] time and mode of milling[4,5] and calcination conditions.[1] In general, the $PbTiO_3$ formation, which is the first step in the PZT formation reaction, is accompanied by the formation of one of the following solid solutions:

- solid solution of $(PbTiO_3)_{ss}$ characterized by a slight modification of the lattice parameters.[6]
- an intermediate PbO solid solution of a tetragonal form whose lattice is different from the starting one.[7]
- an intermediate PZT solid solution which becomes homogeneous with temperature and calcination time.[8]

A $PbZrO_3$ formation is observed either with SiO_2 addition,[2] or when chemically prepared ZrO_2 is used.[6] The present study is undertaken to investigate the reaction sequence of PZT solid state formation from the the oxides Pb_3O_4, TiO_2 and ZrO_2 in presence of NiO, Fe_2O_3 and Ta_2O_5 additives. DTA, TG, XRD and wet chemical techniques are used to determine the calcination reactions.

2 EXPERIMENTAL PROCEDURE

A single composition 0.49 $PbTiO_3$–0.46 $PbZrO_3$–0.05 $Pb(Fe_{0.2}Ni_{0.2}Ta_{0.6})O_3$ was prepared from an oxide mixture of high purity Pb_3O_4 (99.9%), ZrO_2(99.9%) and TiO_2 as rutile (99.56%). The following oxides were used as additives: NiO (99.9%), Fe_2O_3 (99.0%) and Ta_2O_5 (99.0%).

Powders were mixed in an agate mortar for 10 h in distilled water. After grinding, the particle size was obtained by image analysis (automated SEM technique); the powder morphology is shown in Fig. 1. The mixtures were dried and pressed with 103 MPa into pellets, which were sintered at different temperatures in a PbO atmosphere for 2 h.[11,12] The specimens were examined by X-ray diffractometry (D500-Siemens) with CuKα radiation. The data were processed with a PDP 11/23 computer using the Diffrac-11 program library.[12,13] For the thermal analysis a Rigaku thermobalance and a DSC analyser were used.

3 RESULTS AND DISCUSSION

After the heat treatment the samples were analysed qualitatively (X-ray diffraction) for any remaining Pb_3O_4, TiO_2 and ZrO_2, as well as for possible reaction products, e.g. PbO, $PbZrO_3$ and $PbTiO_3$. Interplanar spacings and the indices of the characteristic lines of the oxides are shown in Table 1.

The thermogravimetric study of a small quantity of the mixture shows a mass loss of 1.2% between

Fig. 1. Scanning electron micrograph (SEM) of unreacted powder: $0.49PbTiO_3$–$0.46PbZrO_3$–$0.05Pb(Fe_{0.2}Ni_{0.2}Ta_{0.6})O_3$

230 and 440°C [Fig. 2(a)], which is caused by the decomposition of Pb_3O_4. This decomposition is confirmed by the first endothermic effect, observed on the DTA curve, at about 240°C [Fig. 2(b)], as well as by the decrease in the Pb_3O_4 lines intensity, which has been observed on the X-ray diagram of the mixture after calcination at 300°C (Fig. 3). The total decomposition of Pb_3O_4 is characterized by a second loss of mass of 2.20%, at 530°C [Fig. 2(a)] and by a second endothermic effect at the same temperature [Fig. 2(b)].

The analysis of the characteristic line intensity of Pb_3O_4 and of PbO in the diffractograms of the uncalcined sample and those of the calcined material at temperatures of 300°C and 350°C (Fig. 3) shows a variation of the relative quantities of these oxides. This variation is connected to a competition between the Pb_3O_4 decomposition reaction and that of its formation, according to the following reaction:

Table 1. Interplanar spacings and indices of the characteristic lines of the oxides

Oxide	Diffractograms notation	d_{hkl}	hkl
Pb_3O_4	P1	6.2445	110
	P2	3.3781	211
	P3	3.1131	220
	P4	2.9015	112
	P5	1.911	213
PbO	P'1	3.0716	111
	P'2	2.9497	002
	P'3	2.3776	020
TiO_2	T1	3.2511	110
	T2	2.4884	101
	T3	1.6877	211
	T4	1.6243	220
ZrO_2	Z1	3.6958	011
	Z2	2.3297	021
$PbTiO_3$	PT1	4.1456	001
	PT2	2.8371	101
	PT3	2.2927	111
	PT4	1.7619	201
	PT5	1.7414	210
$PbZrO_3$	PZ1	2.5548	132
	PZ2	2.3919	042
	PZ3	2.3448	230
	PZ4	1.9312	310

$$3PbO + \frac{1}{2}O_2 \rightarrow P_3O_4 + Q$$

The observation of the exothermic effects on the DTA curves [Fig. 2(b)] and those of DSC (Fig. 4) at 280°C can be a consequence of the Pb_3O_4 formation. At 350°C, the first step in the PZT formation occurs which is the $PbTiO_3$ formation. This is proved by the observation of two exothermics effects; one at 330°C on the DSC curve (Fig. 4) and the other at 340°C on the DTA curve [Fig. 2(b)]. The $PbTiO_3$ formation

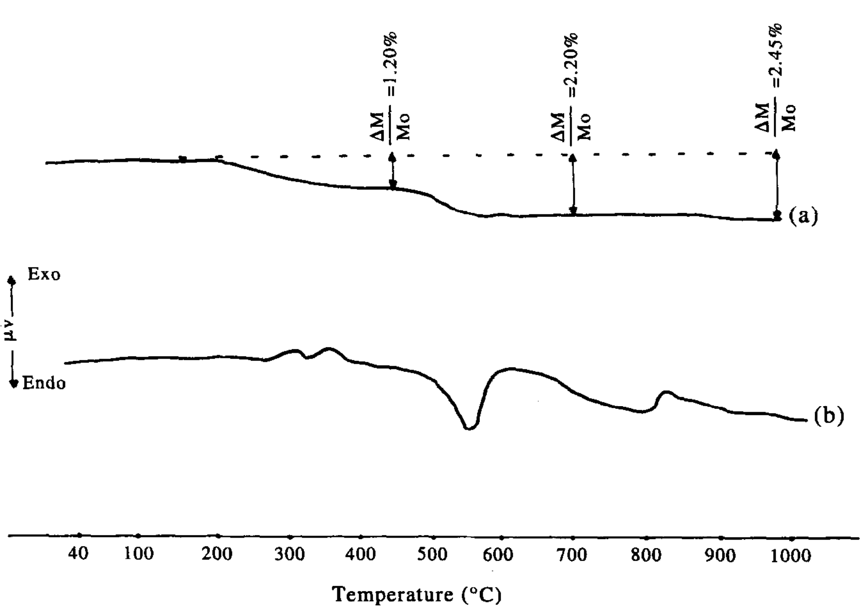

Fig. 2. (a) Thermogravimetric (TG) and (b) differential thermal analysis (DTA) of powder mixture.

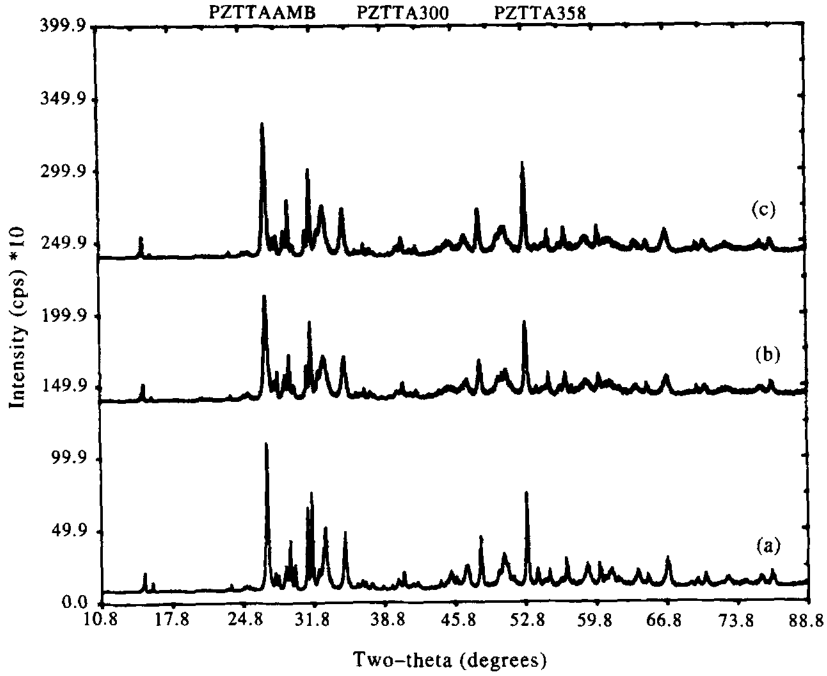

Fig. 3. X-ray diagrams of (a) uncalcined powder mixture and mixtures heat treated at (b) 300°C and (c) 350°C.

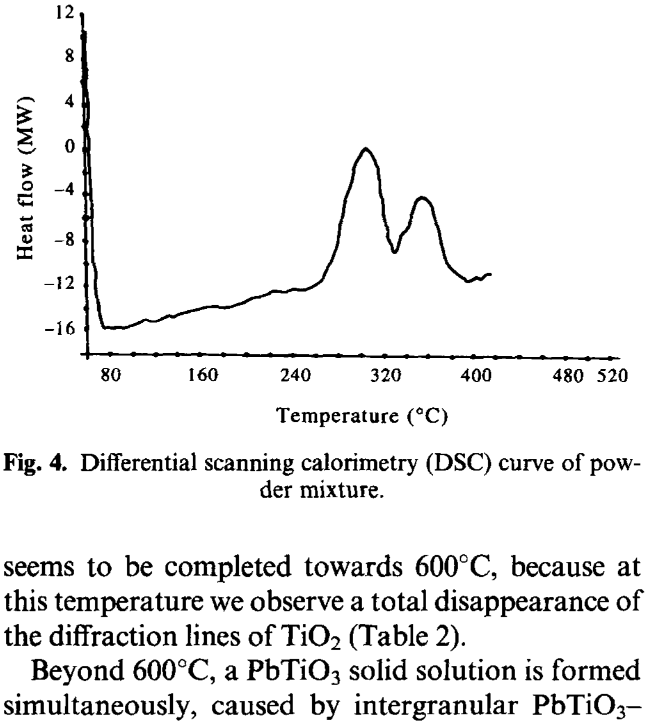

Fig. 4. Differential scanning calorimetry (DSC) curve of powder mixture.

Table 2. Intensity variation (I_{max}) of the characteristic TiO_2 reflections with calcination temperature

Peak notation	I of mixture calc. at 300°C	I of mixture calc. at 350°C	I of mixture calc. at 500°C	I of mixture calc. at 600°C
T1	146	104	24	—
T2	49	62	31	—
T3	116	108	—	—
T4	47	36	34	—

seems to be completed towards 600°C, because at this temperature we observe a total disappearance of the diffraction lines of TiO_2 (Table 2).

Beyond 600°C, a $PbTiO_3$ solid solution is formed simultaneously, caused by intergranular $PbTiO_3$–ZrO_2 contacts.[6] This assumption is established by the relative constancy of the PbO and ZrO_2 amounts and by the slight variation in the *a* and *c* parameters of the $PbTiO_3$ lattice[12] and by the absence of the $PbZrO_3$ phase. The observation of the endothermic effect on the DTA curve [Fig. 2(b)] at 640°C is associated with the $(PbTiO_3)ss$ formation, according to the following reaction:

$$PbTiO_3 + PbO + ZrO_2 \longrightarrow (PbTiO_3)ss$$

The $(PbTiO_3)ss$ saturation by PbO and ZrO_2 facilitates the PZT formation. The X-ray diffraction pattern of the mixture calcined at 750°C (Fig. 5), as well as the last endothermic effect from 820°C on the DTA curve [Fig. 2(b)], indicates the formation of the PZT solid solution. This is confirmed by the density measurement (7.02) of the sample calcined at 750°C[11] and by the disappearance of the X-ray diffraction lines of ZrO_2 and PbO. The X-ray diffraction pattern of the sample calcined at 1200°C (Fig. 5) shows a better resolution of the diffraction lines.

The calcination process can be described by the following reaction sequence:

a) $Pb_3O_4 \xrightarrow{240-450°C} 3\,PbO + 1/2\,O_2$

b) $3\,PbO + 1/2\,O_2 \xrightarrow{280-390°C} Pb_3O_4 + Q$

c) $TiO_2 + PbO \xrightarrow{T>350°C} PbTiO_3$

d) $PbTiO_3 + PbO + ZrO_2 \xrightarrow{T>650°C} (PbTiO_3)ss$

e) $(PbTiO_3)ss + PbO + ZrO_2 \xrightarrow{T=750°C} Pb(Zr,Ti)O_3$

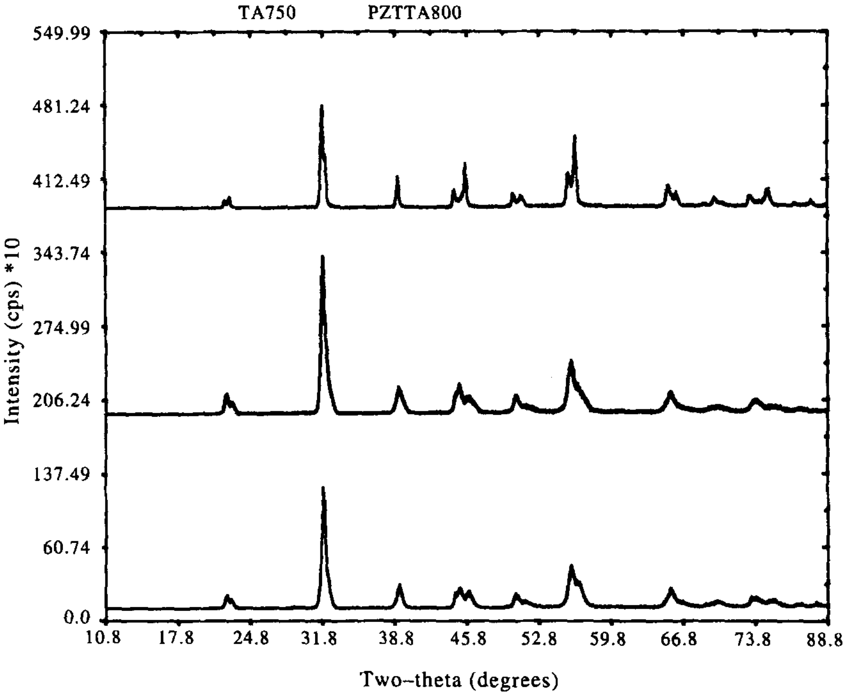

Fig. 5. X-ray diffraction of standard reactants calcined at (a) 750°C, (b) 800°C and (c) 1200°C.

4 CONCLUSION

The formation of PZT from Pb_3O_4, TiO_2 and ZrO_2 in the presence of NiO, Fe_2O_3 and Ta_2O_5 additives has been investigated with DTA, TG, X-ray diffraction and chemical analysis techniques. It is shown that the formation of PZT takes place in several steps: decomposition and formation of Pb_3O_4 between 240 and 390°C; formation of $PbTiO_3$ above 350°C and of its solid solution at 650°C. The PZT solid solution appears without formation of $PbZrO_3$.

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