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Microstructure and chemical reactions in the PFN–PFW–PZN system

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Microstructure, phase compositions and reaction mechanisms were studied in the solid solution system of perovskites composed of 0.48 PFN–0.36 PFW–0.16 PZN as the function of sintering temperature and time. At temperatures above 750° C, perovskite grains were partly decomposed to zinc ferrite and a liquid phase with a composition close to Pb_2WO_5. Consequently, the perovskite solid solution was enriched in the PFN component. At longer sintering times large pyrochlore grains appeared, presumably due to PbO evaporation from the liquid phase.

1. Introduction

Dielectric ceramics, based on solid solutions of different lead perovskites with the general formula $Pb(B_1B_2)O_3$, due to their high dielectric constant and relatively low firing temperature, are of considerable interest for manufacture of multilayer ceramic capacitors with low-cost silver internal electrodes [1–5].

Yonezawa [4] described dielectric ceramics that fire at temperatures less than 900° C, composed of 0.48 $Pb(Fe_{1/2}Nb_{1/2})O_3$–0.36 $Pb(Fe_{2/3}W_{1/3})O_3$–0.16 $Pb(Zn_{1/3}Nb_{2/3})O_3$ (designated as PFN–PFW–PZN). He also found that around 800° C liquid phase appeared, with a composition close to Pb_2WO_5, which enhanced sintering and consequently improved the mechanical strength of the capacitors and reduced dielectric losses. Small additions of manganese also reduced dielectric losses [6].

The formation of PFZNW solid solution is accomplished through a series of intermediate reactions where pyrochlores are initially formed and then above 700° C transform to single perovskite solid solution.

In the present study, the mechanism of phase changes in PFZNW solid solution during firing of ceramics above 700° C was investigated. In addition, the microstructures were investigated, using SEM–EDX, TEM–EDX and stereological methods.

2. Experimental details

Solid solutions of PFN–PFW–PZN with different amounts of added manganese (from 0.1 to 5.0 mol %) were prepared from PbO, Fe_2O_3, ZnO, Nb_2O_5, WO_3 and $Mn(CH_3COO)_2$. All chemicals were reagent grade (p.a.). The homogenized mixtures were pressed into compacts and calcined at 750° C for 2 h. After milling in a ZrO_2 mill, the powdered calcine was pressed into pellets 10 mm in diameter which were sintered in air at temperatures between 750 and 1000° C. Sintering times were between 1 and 64 h. Microstructures and chemical compositions were examined with a scanning electron microscope (Leitz-AMR 1600 T) and EDX system (PGT–IV). For phase identifications, electron diffraction (TEM, Jeol 2000 FX) and X-ray diffraction (XRD) (Philips, PW1710) were used.

Volume fractions of phases and grain size were measured from micrographs using a semi-automatic device (MOP-AM 03 from Kontron).

3. Results and discussion

By XRD it was found that after calcination and sintering of the powder at 750° C for 1 h, only traces of pyrochlore phase were present besides perovskite. In samples sintered at 850° C submicron particles of ferrite appeared in the microstructure. In samples sintered at temperature above 850° C, liquid phase (PW), ferrite grains (ZF) and perovskite (P) grains could be found (Fig. 1). The volume fractions of the liquid and ferrite phases increased with increasing firing temperature (Table I).

Longer sintering at temperatures above 850° C caused the appearance of large, regularly shaped grains. According to TEM–ED and XRD analysis, they have the pyrochlore (Py) structure (Fig. 2).

With increasing firing time the volume fraction of ferrite and pyrochlore phases increased, while the

TABLE I Volume % of phases present and average intercept length of perovskite grains in samples prepared at different sintering temperatures and times

Sample	phases				l(P)(μm)
	ZF	PW	Py	P	
750/1				100	0.9
850/1	trc*			100	1.0
850/1	trc.			100	1.3
910/1	5	5		90	1.3
910/11	7	< 5	15	75	3.0
910/58	8	< 5	20	70	6.0
1000/1	6	21		70	4.0
1000/15	10	12	30	50	10.0

*trc.–traces could be found on SEM picture.
ZF–zinc ferrite, PW–liquid phase, close to Pb_2WO_5, Py–pyrochlore, P–perovskite, l(P)–average intercept length of perovskite grains.

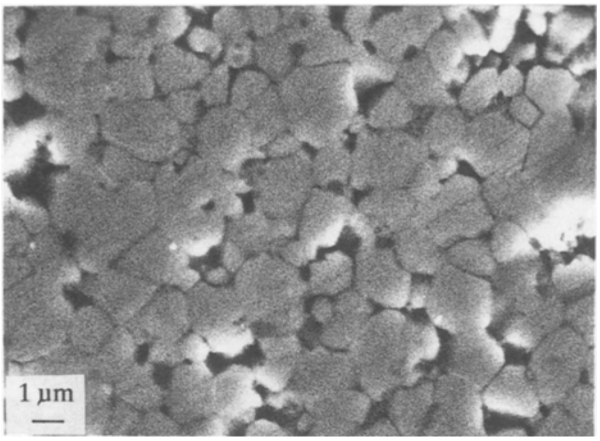

Figure 1 Microstructure of sample fired at 910° C, 1 h.

volume fraction of liquid phase and perovskite decreased (Table I). In samples sintered at 1000° C for 64 h, all perovskite decomposed to pyrochlore, liquid phase and ferrite.

In Table II the relative intensity of the strongest XRD lines of the phases present in samples prepared at different sintering temperatures and times are listed.

Despite careful covering of the samples, there was some weight loss at sintering temperatures above 850° C and at longer sintering times, as shown in Fig. 3.

It was found that the liquid phase (PW) is composed of 0.8 mol % Pb_2WO_5–0.2 mol % PbO, and that ferrite is $(Mn, Zn)Fe_2O_4$ (if Mn is added to the composition). Manganese is incorporated predominantly in ferrite (in the approximate ratio of 10 : 1 with respect to perovskite grains). The compositions of perovskite and large pyrochlore grains varied with sintering time and temperature. Figure 4 presents the molar ratios of constituent perovskites in solid solution as a function of sintering temperature and time. The fraction of PFN increased, while the fractions of PFW and PZN decreased with increasing sintering temperature and time. Table III lists the compositions (at %, normalized to lead) of perovskite and pyrochlore grains in samples sintered at 910° C for 11 h and at 1000° C for 15 h. The composition of Py grains changes with increasing firing temperature and time. It may be noted that in comparison with perovskite, the pyrochlore phase is characterized by considerably higher tungsten and lower iron contents.

TABLE II The relative intensities of the strongest XRD lines of the phases present in samples prepared at different firing conditions

Sample	P	PW	ZF	Py
750/1	100	/	/	3
850/1	100	/	/	3
850/11	100	12	1	3
910/1	100	/	/	3
910/22	70	100	4	10
910/58	100	2	7	17
1000/1	90	100	2	
1000/15	40	100	15	12

P–perovskite, PW–liquid phase, ZF–ferrite, Py–pyrochlore.

With increasing sintering time, the homogeneity of the samples was improved, as demonstrated by the decreased standard deviations of the concentration measurements (wt %) of perovskite grains shown in Table IV.

Samples sintered for 1 h showed much higher scattering of chemical composition in the perovskite grains than in the case of samples sintered for 11 h. The reproducibility (relative standard deviation) of EDX measurements, obtained by repetitive measurements of the same perovskite grain are shown in Fig. 5.

To confirm that zinc is responsible for the appearance of ferrite and PW liquid phase, diffusion couples were prepared. A monocrystal of PZN (perovskite) and of previously sintered ZnO were embedded in calcined PFN–PFW (1 : 1) composition. The diffusion couples were fired at 910° C for 22 h. In Fig. 6 the interface of the PZN/PFNW junction is shown. The PZN monocrystal decomposed to lead niobate (P_xN_y) and ZnO. On the PFNW side large ferrite grains (dark) with interesting liquid-like shapes appeared besides PW liquid phase. Zinc was found in the first 100 μm layer of the PFNW perovskite grains.

In the case of the ZnO/PFNW diffusion couple (Fig. 7), a layer composed of fine ferrite and pyrochlore grains near the interface and larger ferrite grains in the matrix of the PFNW grains with dissolved zinc ions were observed. The chemical composition of the pyrochlore grains was very close to the composition of samples prepared from a solid solution of PFN–PFW–PZN under the same conditions. In Fig. 8, the

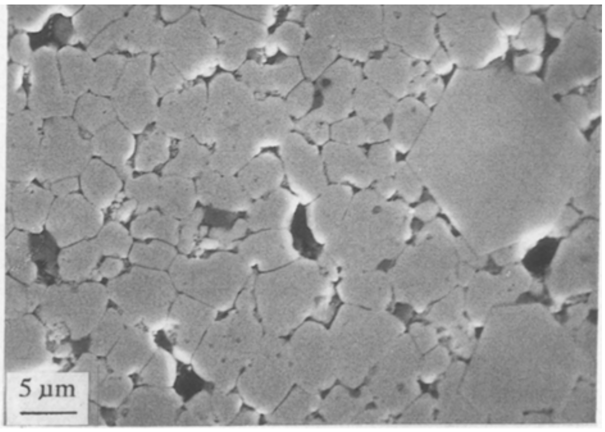

Figure 2 Microstructure of sample fired at 910° C, 11 h.

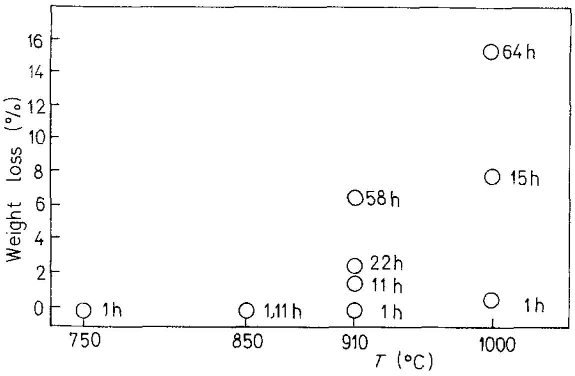

Figure 3 Weight loss (%) of samples against firing temperature and time.

TABLE III Atomic ratio of elements (normalized to lead) in perovskite (P) and pyrochlore (Py) grains in samples sintered at 910° C for 11 h and at 1000° C for 15 h

Sample	Phase	Atomic ratio					
		Pb	Fe	Zn	Nb	W	O
910/11	P	1.00	0.47	0.03	0.40	0.10	3.00
	Py	1.00	0.28	0.01	0.50	0.21	3.40
1000/15	P	1.00	0.48	0.02	0.43	0.06	3.00
	Py	1.00	0.28	0.00	0.60	0.16	3.50

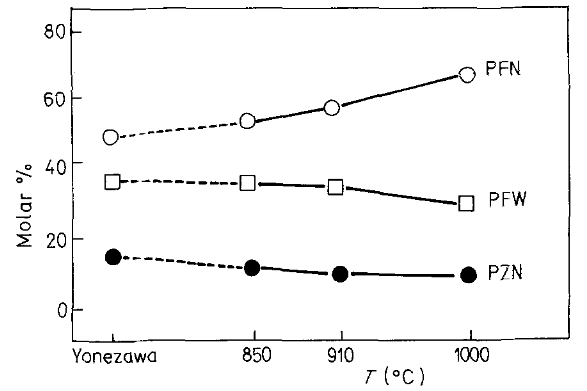

Figure 4 Molar ratios of constituent perovskites in solid solution against firing temperature (firing time was 1 h).

TABLE IV Standard deviations of the concentration measurements (wt %) of perovskite grains for the samples sintered at 850° C for 1 and 11 h

Sample	Element	Average concn (wt %)	Standard deviation (%)
850/1	Fe	7.8	5
	Zn	0.8	20
	Nb	8.9	8
	W	6.1	10
850/11	Fe	7.8	3
	Zn	0.8	9
	Nb	10.2	2
	W	5.7	7

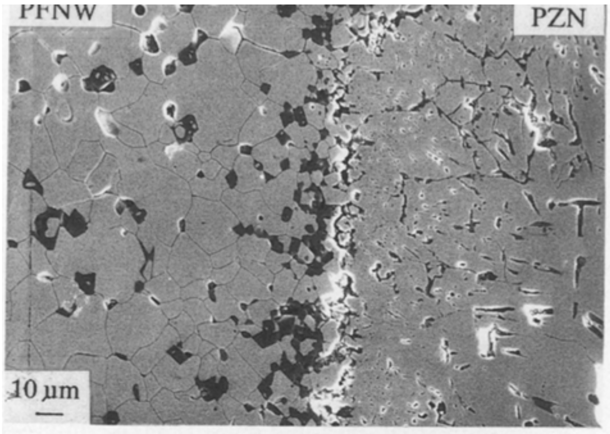

Figure 6 Microstructure of PZN/PFNW diffusion couple fired at 910° C, 22 h.

diffusion couple WO_3/PFZNW (910° C, 22 h) is shown. Regions of lead tungstenate (very close to $PbWO_4$) and a region of pyrochlore grains can be seen.

Diffusion experiments confirmed that Zn-containing compounds (ZnO or PZN) react with iron in PFNW to form zinc ferrite. This reaction creates an excess of Nb^{5+} and W^{6+} ions in the perovskite grains. Lead oxide and tungsten oxide form liquid phase (PW), while Nb^{5+} ions remain in the perovskite structure. For each firing condition there is some quasi-stable perovskite composition which tends to be enriched in PFN and reduced in PZN (and PFW) with increasing temperature and time.

To confirm this assumption, a composition was prepared based on EDS analyses of the perovskite grains when fired at 910° C for 58 h (i.e. 0.68 PFN–0.24 PFW–0.08 PZN). In samples of this composition, fired at 910° C 22 h, neither ferrite, nor liquid phase, nor large pyrochlore grains could be detected, as shown in Fig. 9. Sintering of this composition was poor, as expected for solid state sintering in this case, so we added 3 vol % of prereacted PW. Sintering was improved but no other phase except perovskite grains and the added liquid phase could be seen. From these results we can state that for each sintering condition there is some limiting content of zinc ions in the perovskite grains. If this content is exceeded, ferrite and PW liquid phase are formed.

If the amount of ferrite generated (and PW) is small, then perovskite could include additional niobium and does not decompose to pyrochlore. However, if the

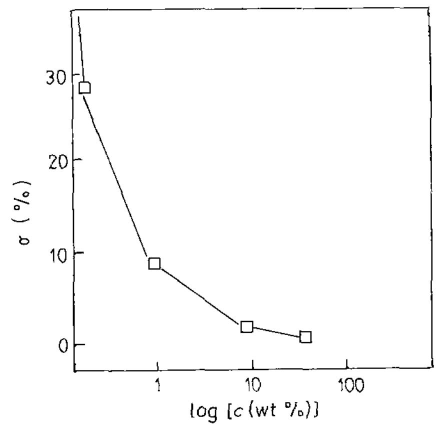

Figure 5 Relative standard deviations of measurements (in %) against log of concentrations (in wt %).

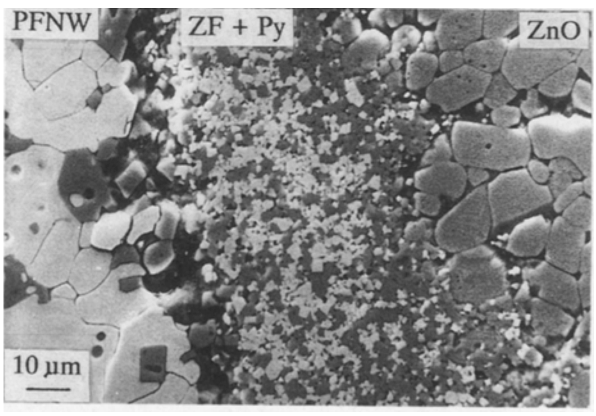

Figure 7 Microstructure of ZnO/PFNW diffusion couple fired at 910° C, 22 h.

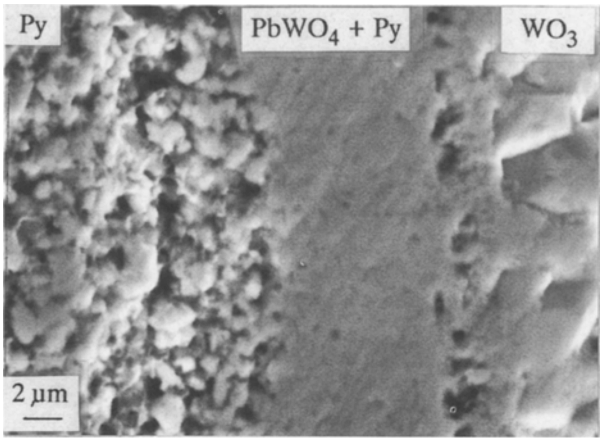

Figure 8 Microstructure of WO_3/PFZNW diffusion couple fired at 910° C, 22 h.

amount of ferrite produced is large (there is marked deficiency of iron ions and an excess of tungsten ions), the pyrochlore phase is more stable. Pyrochlore is also formed if there is just an excess of tungsten ions (and a lack of lead, which reacted with tungsten to form some of the lead tungstenate), as in the case of the WO_3/PFNW couple.

In the case of sintered PFZNW for longer times, presumably PbO from the liquid phase (PW) evaporates, and thus the PW phase becomes enriched in WO_3. This tungsten excess causes perovskite decomposition and formation of pyrochlore grains. Pyrochlore grains grow from the liquid phase in such a way that certain cubic facets grow very quickly (exaggerated grain growth).

Figure 10 shows a TEM micrograph of the liquid phase between two grains of a PFZNW sample (910° C, 22 h). Precipitates of ferrite and of pyrochlore phase are seen in the PW phase. TEM examinations did not reveal ferrite particles inside the perovskite grains; all of them were in corners between grains or attached to the grain boundaries between two perovskite grains. From this result we could assume that decomposition of perovskite to ferrite and PW took place at the grain boundaries, and that ferrite grains grow inside the melt (this could also explain the interesting shape of the ferrite grains in diffusion couples).

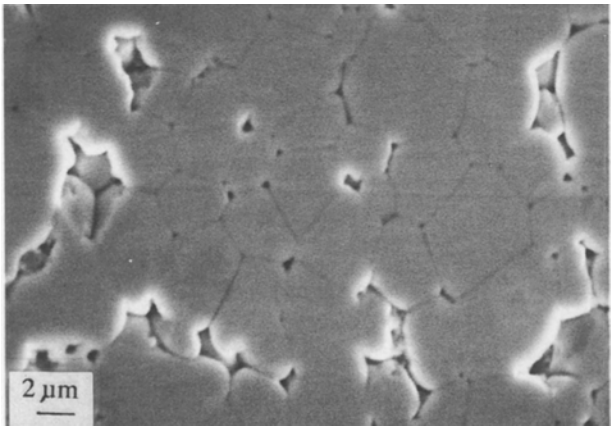

Figure 9 Microstructure of composition 0.68 PFN–0.24 PFW–0.08 PZN fired at 910° C, 22 h.

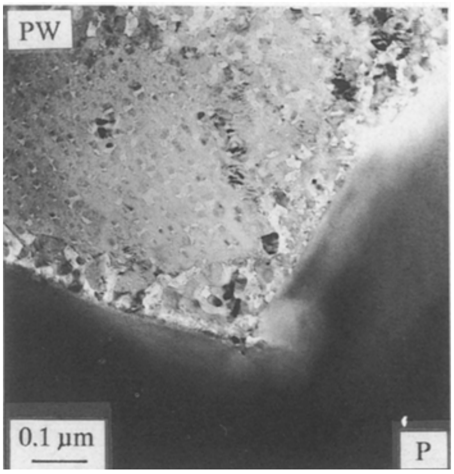

Figure 10 TEM micrograph of sample fired at 910° C, 22 h. Particles of ferrite and pyrochlore in PW melt.

4. Conclusions

Perovskite with "Yonezawa" composition, which is formed at around 750° C, decomposes at higher temperatures to ferrite and PW liquid phase:

$$\text{PFZNW(p)} \rightarrow \text{ZF} + \text{PW} + \text{PFZNW}_i(\text{p})$$

Due to PbO evaporation from PW and consequent enrichment of the melt with WO_3, large W-rich pyrochlore grains are formed at longer firing times:

$$\text{PFZNW}_i(\text{p}) + \text{PW} \rightarrow \text{ZF} + \text{PFZNW(py)} + \text{PbO} + \text{PFZNW}_j(\text{p})$$

(where p stands for perovskite, py for pyrochlore, ZF is zinc-ferrite and PW is liquid phase with composition 0.8 Pb_2WO_5–0.2 PbO, i and j represent different compositions).

Sintering temperature and time strongly influenced the chemical composition of the perovskite grains. With higher temperatures and longer times, the concentration of niobium increased, while the concentration of tungsten and zinc decreased.

For each firing condition there is a limiting concentration of zinc ions in the perovskite structure. If this concentration is exceeded zinc ferrite is formed. To accomodate the excess of tungsten and niobium ions during ferrite formation, liquid phase with composition 0.8 Pb_2WO_5–0.2 PbO is formed. Niobium ions remain in the perovskite structure, which is the reason that with increasing sintering temperature and time the PFN content of the PFN–PFW–PZN solid solution increased.

The formation of pyrochlore grains is due to a high depletion of iron content or a large excess of tungsten content in the system. Ferrite particles are formed at the perovskite grain surfaces and migrate through the liquid phase to the corners between grains, where they grow.

The chemical transformations described influence the dielectric properties of the fired ceramics, as reported in [7].

Acknowledgement

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