

Microwave calcination of conventionally and sol-gel prepared lead zirconate titanate

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Microwave calcining of conventionally prepared (mixed oxides) as well as sol-gel prepared lead zirconate titanate (PZT) powders was investigated. Conventionally prepared PZT was calcined with microwave power at 720°C for 45 min, whereas conventional calcination requires 4 h at 800°C. The sol-gel PZT was calcined with microwave power at 600°C for 40 min, whereas 5 h are needed when a conventional furnace is used at the same temperature. Beside reducing the calcining temperature and time, microwave heating also leads to a more uniform particle size distribution in both cases.

1. Introduction

Microwave processing of ceramics has emerged as a successful alternative to conventional processing in the last few years. It offers the advantages of a rapid and uniform heating at lower temperatures and times than in the conventional case. Sheppard [1] reviewed the application of microwave energy in the various steps of ceramics processing developed by researchers at different universities. He pointed out the potential for an economical production on a large scale. He also noted the importance of determining the specific conditions optimizing the use of microwave energy for each application. Selmi et al. [2] have determined the optimum microwave calcining conditions for barium strontium titanate (BST). They concluded that the use of microwave absorption for calcining and sintering of BST ceramics leads to the development of a fairly uniform and fine microstructure. Harrison et al. [3] have investigated the use of a commercial microwave system for calcining lead zirconate titanate. They calcined the PZT material at 840°C for 12 min and at 565°C for 95 min. In both cases, however, the calcination was not complete as determined by X-ray diffraction analysis. The X-ray patterns showed peaks of unreacted lead titanate, lead oxide and zirconium oxide.

Microwave energy, if combined with the sol-gel method can produce very fine powders at yet lower temperatures and shorter processing times. Sol-gel processing of PZT has been reported as a way to fabricate thin films [4–6] as well as bulk gels [1]. The advantages of sol-gel processing over the conventional mixed-oxide techniques are a greater purity, better compositional control at the molecular level, a more homogeneous liquid-mix, lower processing temperatures, and the possibility of making fibers, thin coatings and films as reported by Budd et al. [4]. Selvaraj et al. [5] have shown that complete calcination of sol-gel processed PZT fibers was achieved at 600°C. Yi et al. [6] showed the possibility of firing PZT thin films prepared by the sol-gel technique at temperatures as low as 550°C.

In this paper, we study the favorable conditions to microwave calcining of PZT using the PKI 400 composition (a proprietary composition of Piezo Kinetics Inc.). We investigate the effects of conventional calcining versus microwave calcining of the conventionally and the sol-gel prepared PZT powders.

2. Experimental procedure

2.1. Conventional preparation of the PZT powder

Lead oxide, strontium oxide, titanium and zirconium oxide were mixed in the desired stoichiometry and milled for 24 h in zirconia grinding media and ethanol. After drying at 80°C, the resulting powder was sieved then divided into two batches. The first batch was calcined in a conventional furnace at temperatures ranging from 700 to 850°C for 4 h, the remaining powder was calcined in a commercial microwave oven (2.45 GHz, 600 W) at 720°C for 45 min. The powder was placed in a thermally insulating cavity and the temperature was monitored with the aid of a K-type thermocouple probe inserted in the powder. The power of the oven was regulated to maintain the proper calcining temperature throughout the soaking time. The powders were then milled

again then characterized by X-ray diffraction analysis (XRD) for phase purity and scanning electron microscopy (SEM) to determine particle morphology and size.

2.2. Sol-gel preparation of the PZT powder

Fig. 1 shows a flow diagram for the preparation of sol-gel PZT. Lead acetate trihydrate $[\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}]$, strontium metal $[\text{Sr}]$, zirconium *n*-propoxide $[\text{Zr}(\text{C}_3\text{H}_7\text{O})_4]$ 70% in butanol and titanium isopropoxide $[\text{Ti}(\text{CH}_3)_2\text{CHO}]_4$ were used as precursor materials. 2-methoxyethanol was used as a solvent. First, $[\text{Pb}(\text{CH}_3\text{CO}_2)_2 \cdot 3\text{H}_2\text{O}]$ was dissolved in 2-methoxyethanol and dehydrated at 120°C. Next, after cooling to about 70°C, strontium was added in the solution which was continuously stirred by a magnetic stirrer. Zirconium *n*-propoxide and titanium isopropoxide were then added and the

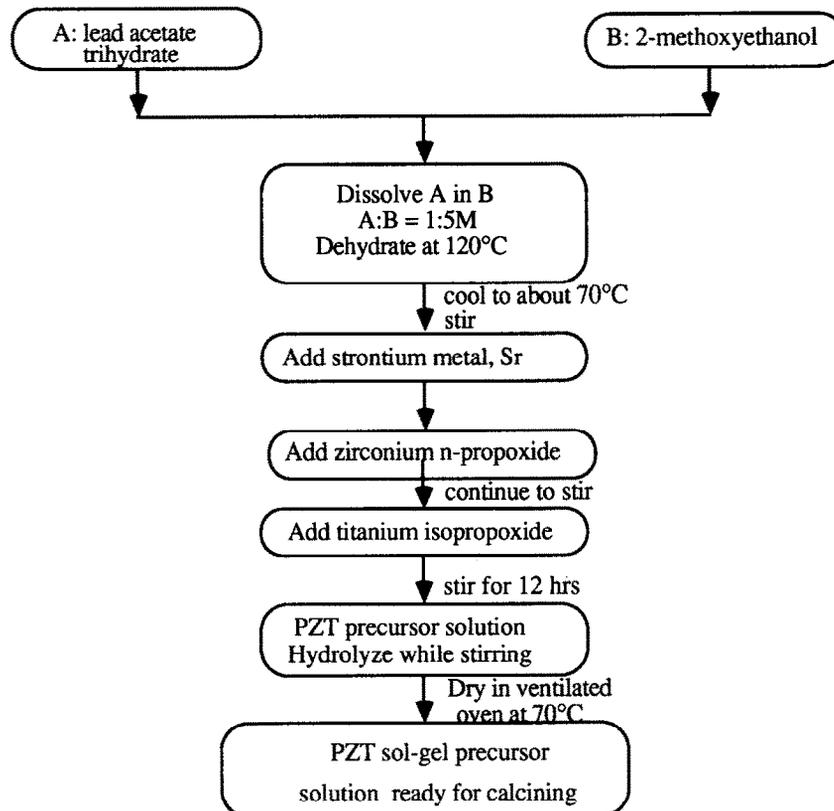


Fig. 1. Flow diagram for sol-gel processing of PZT powder.

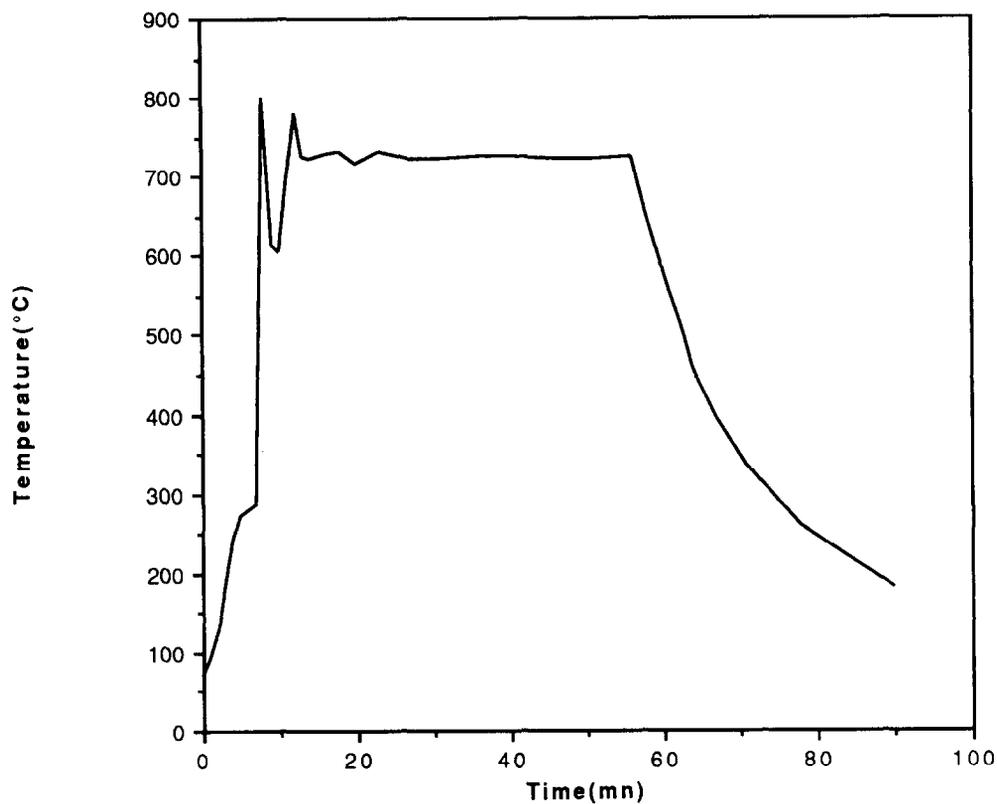


Fig. 2. Microwave heating profile of lead zirconate titanate.

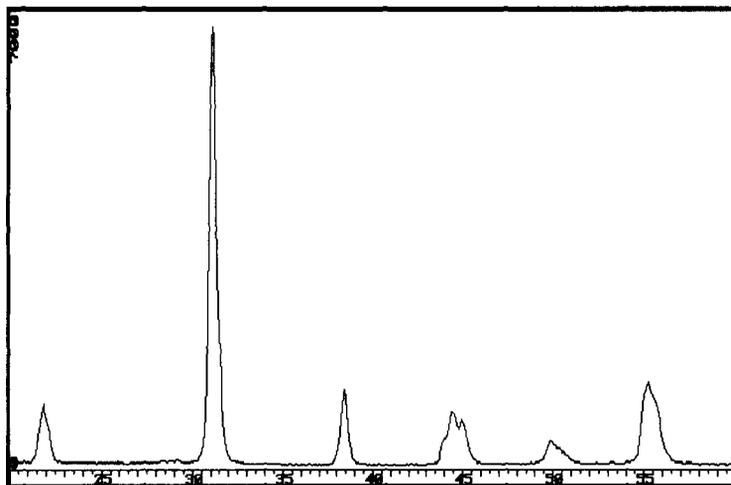


Fig. 3. X-ray patterns of conventionally prepared PZT calcined by microwave power at 720°C for 45 min.

resulting solution was refluxed at 70°C for 12 h. The PZT precursor solution was then hydrolyzed with a mixture of distilled water and ethanol. The precu-

sor solution was then placed in a ventilated oven at 70°C to form a viscous sol or gel. The sol-gel PZT was calcined according to the following procedure

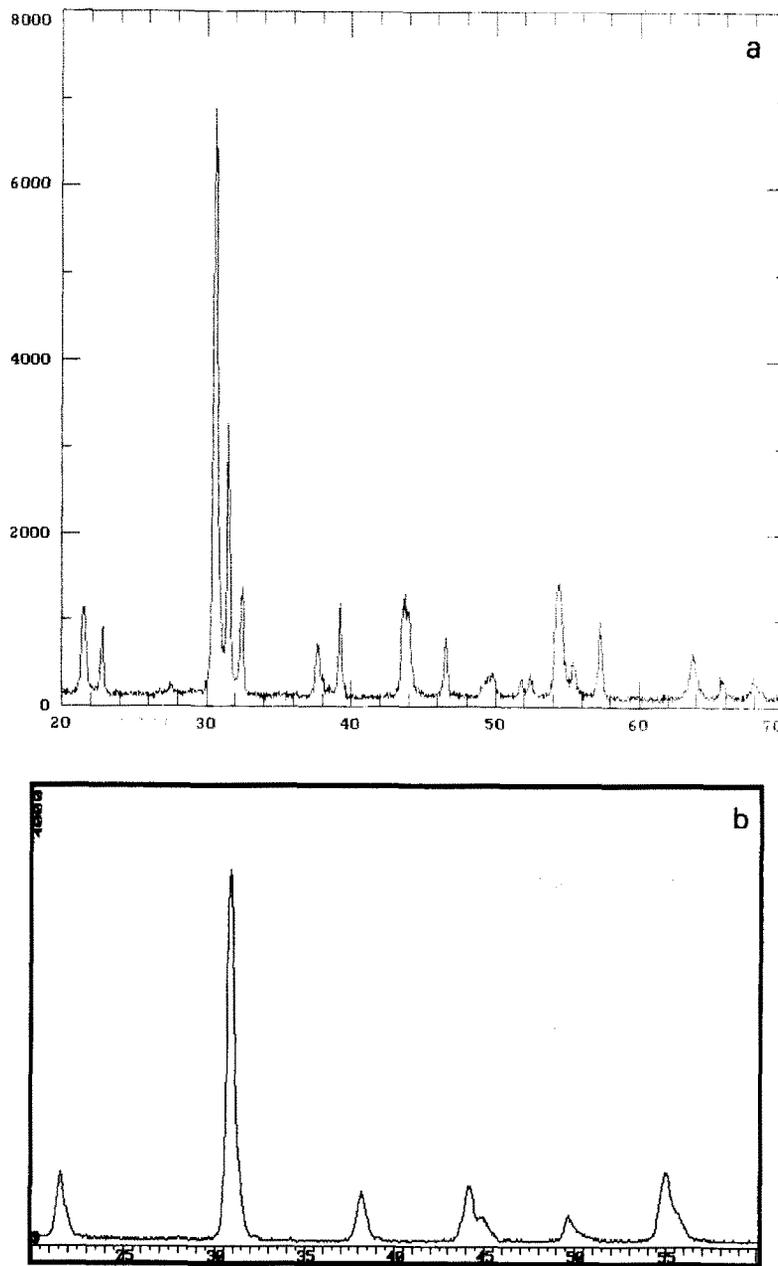


Fig. 4. X-ray patterns of conventionally prepared PZT calcined in a conventional furnace: (a) at 750°C for 4 h and (b) at 800°C for 4 h.

and conditions: in a conventional furnace at 700°C for 4 h and 600°C for 5 h, and in the microwave oven at 600°C for 40 min. The powders were then characterized by XRD and SEM.

3. Results and discussion

3.1. Conventional versus microwave calcining of conventionally prepared powder

Fig. 2 shows the microwave heating profile of the

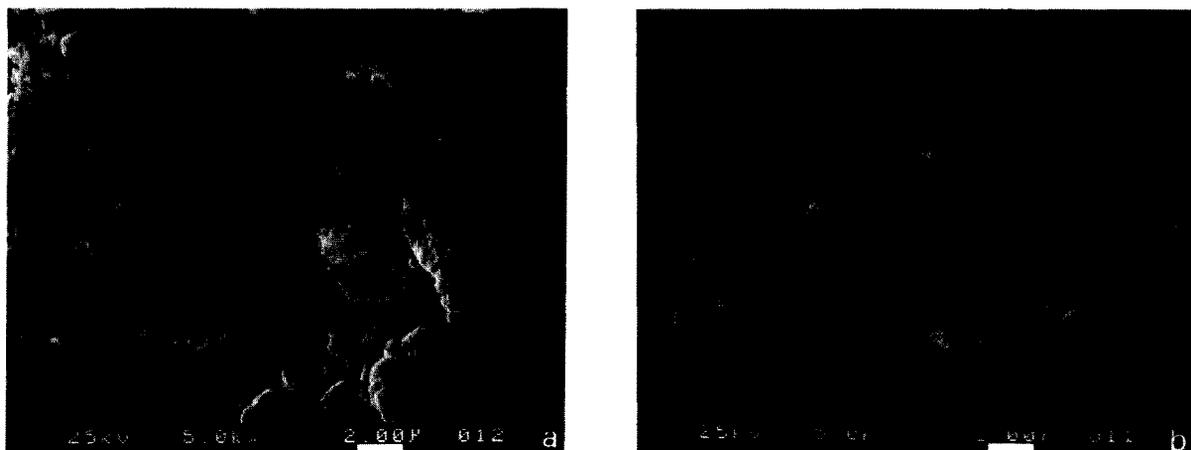


Fig. 5. Particle size distribution as revealed by SEM: (a) for conventionally calcined conventionally prepared PZT powder and (b) for microwave-calcined conventionally prepared PZT powder.

Table 1
Comparison of the particle size distribution of the conventionally and microwave-calcined mixed oxides PZT powders

% pass	Particle size (μm)	
	microwave	conventional
10	0.33	0.36
50	0.70	0.79
90	2.00	10.0

PZT powder. The temperature increased at a rate of $25^\circ\text{C}/\text{min}$, but once it reached 200°C , it increased sharply to 800°C and had to be brought down to 720°C where it was maintained. X-ray analysis of the microwave-calcined material showed the presence of a complete perovskite phase as shown in fig. 3. Figs. 4a and 4b show the X-ray diffraction patterns for the conventionally calcined powders at 750 and 800°C respectively. From fig. 4a, it can be seen

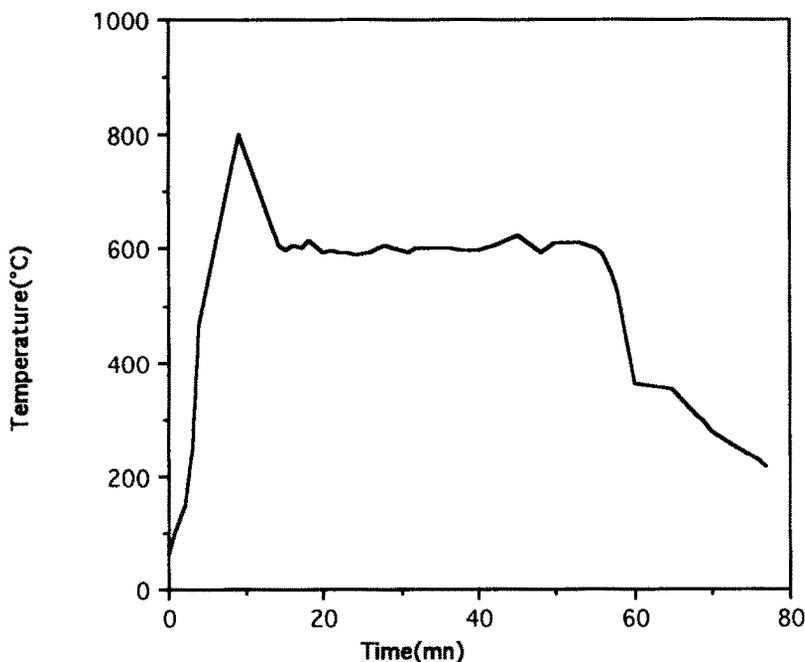


Fig. 6. Heating rate of microwave-calcined sol-gel PZT.

that complete crystallization of the PZT composition was not achieved at 750°C as peaks of unreacted PbO, ZrO₂ and PbTiO₃ are still present. In fig. 4b, however, it is clear that calcination at this temperature is complete and only the PZT phase is present as indicated by the peaks. Figs. 5a and 5b are SEM pictures of PKI 400 powders calcined at 800°C in a box furnace and at 720°C in the microwave oven respectively. Particle size analysis was also performed for these two powders to better analyze particle size distribution in both cases. It is found that although both powders have about the same average particle size (0.7 μm), the particle size distribution in the case of the microwave calcination is more uni-

form than in the case of conventional calcination. In the former case, 10% of the particles were smaller than or equal to 0.33 μm and 90% of them were smaller than or equal to 2 μm; in the latter case, 10% were equal to or smaller than 0.36 μm and 90% were smaller than or equal to 10 μm. This supports the fact mentioned earlier that a more uniform microstructure can be obtained by microwave calcining over conventional calcining (see table 1). Also, conventional calcining usually takes about 8 h for the entire cycle to be completed whereas microwave calcining takes about 70 min.

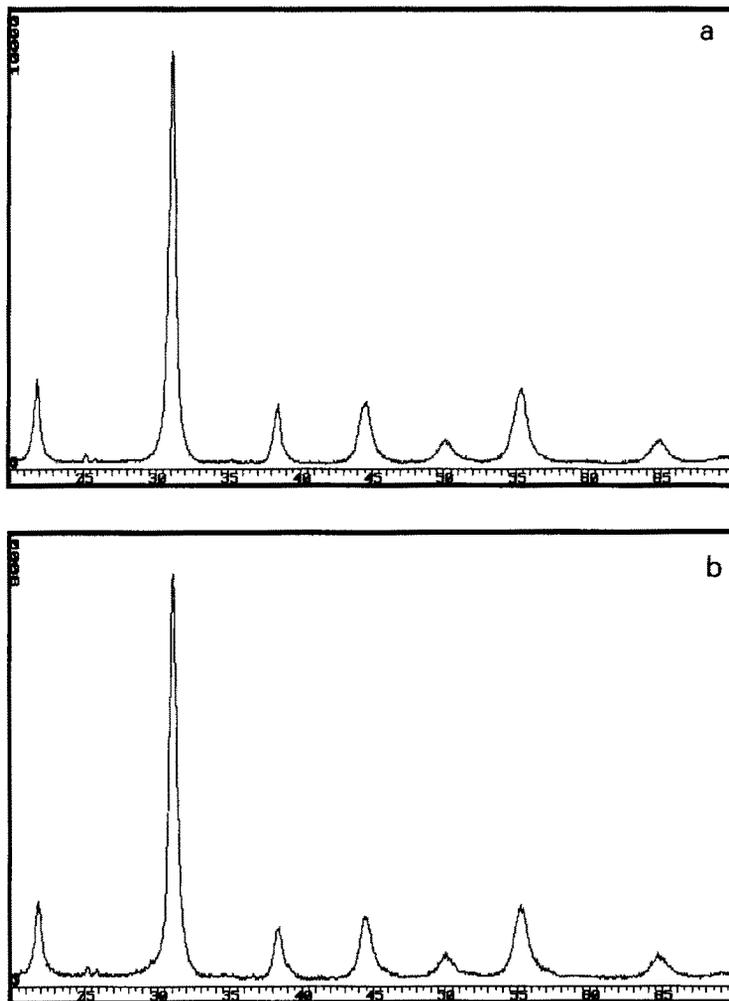


Fig. 7. X-ray patterns of sol-gel prepared PZT calcined in a conventional furnace: (a) at 700°C for 4 h and (b) at 600°C for 5 h.

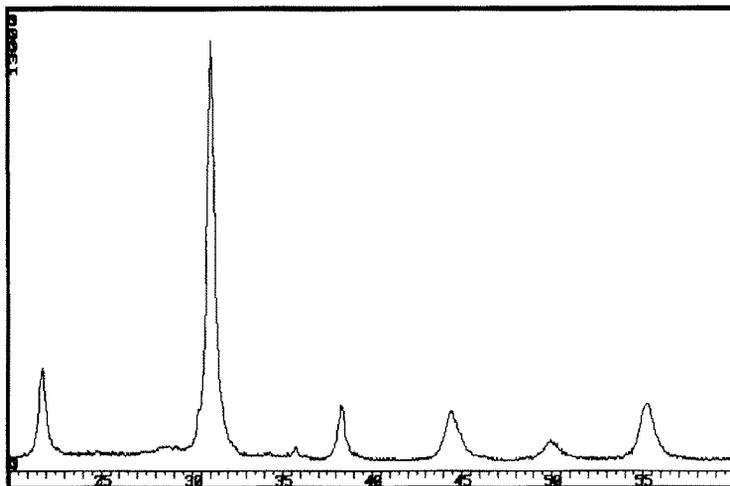


Fig. 8. X-ray pattern of sol-gel prepared PZT calcined by microwave power at 600°C for 40 min.

3.2. Conventional versus microwave calcining of sol-gel prepared powders

Fig. 6 shows the microwave heating profile of the sol-gel powder calcined at 600°C for 40 min. Figs. 7a and 7b show the XRD of the conventionally calcined sol-gel at 700 and 600°C respectively, and fig. 8 shows the XRD of microwave-calcined sol-gel at 600°C. These figures indicate that a complete phase formation of the PZT phase has occurred at these various combinations of time and temperatures. Note again that microwave heating reduces the required

calcining temperature and time as compared to conventional calcining as well for the sol-gel prepared powder. Figs. 9a and 9b are the SEM pictures of the conventionally calcined and the microwave-calcined PZT powders respectively. Particle size analysis was also performed for these two powders. It is again confirmed that microwave calcining of the sol-gel powder leads to a more uniform distribution of particle sizes (see table 2). For the conventionally calcined sol-gel, 90% of the powder is smaller than 4 μm and 10% of it is smaller than 0.2 μm, as compared to microwave calcining of sol-gel where 90%

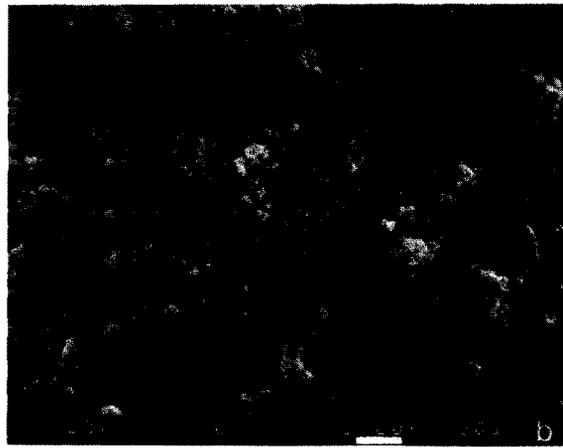
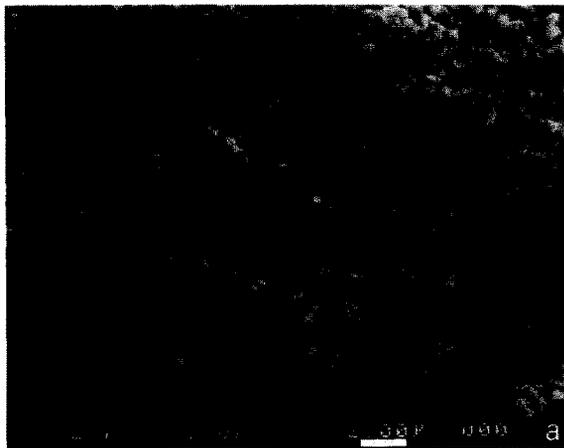


Fig. 9. Particle size distribution as revealed by SEM: (a) for conventionally calcined sol-gel prepared PZT powder and (b) for microwave-calcined sol-gel prepared PZT powder.

Table 2
Comparison of the particle size distribution of the conventionally and microwave-calcined sol-gel PZT powders

% pass	Particle size (μm)	
	microwave	conventional
10	0.20	0.20
50	0.52	0.60
90	2.00	4.00

of the powder was smaller than $2 \mu\text{m}$ and 10% of it was smaller than $0.2 \mu\text{m}$. The average size is $0.6 \mu\text{m}$ for the conventionally calcined and $0.52 \mu\text{m}$ for the microwave-calcined sol-gel.

4. Conclusion

Microwave calcination of conventionally prepared

as well as sol-gel prepared PZT powders has been shown to be a successful alternative to conventional calcining. Its use for calcination has the advantage of reducing the total processing time and the soak temperature. In addition, the combination of sol-gel and microwave processing leads to smaller particles and a more uniform distribution of their sizes.

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