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The role of dilatancy on expansion during early stage liquid phase sintering of lead magnesium niobate

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Abstract

During an attempt to sinter (900°C/30 min) lead magnesium niobate [$Pb(Mg_{1/3}Nb_{2/3})O_3$] of average particle (aggregate) size 5.8 μm at by adding 3 wt.% excess PbO as a sintering aid, it has been observed that around 3% volume shrinkage takes place. However, an addition of excess Nb_2O_5 (6 wt.%) along with the same excess PbO gives rise to an appreciable volume expansion (upto 14%) instead of shrinkage under identical firing conditions. We have concluded after systematic studies that such expansion can be understood primarily by considering the generation of insufficient (for consolidation of powders) capillary pressure owing to the formation of a liquid phase (PbO melt with some dissolved Nb_2O_5) at 900°C and the subsequent role of dilatancy which considers the expansion of well-packed powders during shear. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

1. Introduction

Swelling or expansion due to pore coalescence, grain growth and grain boundary relaxation has been observed during certain stages of sintering of powders like thoria [1], urania [2], alumina [3], sodium chloride [4,5], cobalt oxide [6], zinc oxide [7] etc. Swelling has also been observed in isolated cases during specific heat treatments. For example, Bennison and Harmer [8] observed that fully dense alumina, prepared by hot pressing, swelled during annealing at ~1600°C in air and the swelling was attributed to the formation and diffusion of CO/CO_2 and SO_2 generated from the oxidation of carbon and sulphur impurities. Solomon and Hsu [9] reported swelling of hot pressed ZnO when the pressure was released and such swelling was attributed to the equilibration of trapped gases with externally applied pressure. Hot pressed Fe_2O_3 (~95% of theoretical density) has been found [10] to expand by ~15% when heat treated above 900°C; the swelling, according to the authors, was owing to the expansion of pores under the influence of high internal gas pressure. Huppmann [11] reported that during liquid phase sintering of densely packed planar arrays of tungsten spheres uniformly coated with copper, slight swelling could be observed if the interparticle distance was small and the liquid phase formed a high wetting angle owing to oxygen contamination on copper. It has been reported by Venkataramani [12], Venkataramani and Shrout [13] and Shrout et al. [14] that during reactive calcination of lead-based perovskite powders, volumetric expansion occurs. Such expansion is believed to be associated with the formation of phases possessing a larger molar volume than the individual components or is associated with the topology of the reaction which leads to rapid coarsening of the highly reactive product layer resulting in a porous skeletal-type structure. However, expansion (0.2–2%) of pressed pellets, when heated to temperatures lower than that required for the commencement of sintering, has been reported [15,16] for alumina and lithium fluoride. Such expansion has been attributed [17] to the release of stored anelastic and plastic strain (caused by the forming pressure) at high temperature. Here we report that under certain conditions and during the initial stage, the liquid phase sintering of lead magnesium niobate can give rise to appreciable volume expansion instead of densification. We argue that such a behaviour can be explained by considering the role of dilatancy pressure.

2. Experimental procedure

Lead magnesium niobate [$Pb(Mg_{1/3}Nb_{2/3})O_3$, referred to as PMN] powder was prepared by standard

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columbite precursor method where PbO (analytical reagent, E. Merck, Germany) was reacted with preformed magnesium niobate ($MgNb_2O_6$, referred to as MN) at 800°C for 20 h. The preparation temperature of MN from the precursors magnesium hydroxycarbonate [$MgCO_3,Mg(OH)_2,3H_2O$] (analytical reagent, E. Merck, Germany) and Nb_2O_5 (analytical reagent, E. Merck, Germany) was selected to be 1100°C and soaking time 20 h. The detailed processing steps have been given elsewhere [18,19]. The particle size of the PMN powder was determined by a particle size analyzer (Sedigraph 5100, Micromeritics).

For sintering studies, 3 wt.% excess PbO with and without 6 wt.% excess Nb_2O_5 was added to the produced PMN powder. The batches were mixed in an agate mortar and a pestle under acetone and pellets (10 mm dia/3–4 mm thickness) were pressed (pressures used were 25, 50 and 75 MPa) using 2% PVA binder. The pellets were kept on a platinum plate and directly introduced [19] inside a furnace already heated to 900°C. They were kept there for 30 min and were slowly cooled inside the furnace. Some of the pellets [pressed at the medium pressure (50 MPa)] were also heat treated (for 30 min) at different temperatures (with an interval of 50°C) in the range of 600–1000°C and the volume changes after heat treatment were measured in each case. A few samples were also slowly heated (200°C/h) inside the furnace to 900°C, followed by soaking and cooling.

The bulk densities of the samples were measured geometrically and the fracture surfaces of a few selected specimens were viewed in a Cambridge Stereoscan S-250 scanning electron microscope.

3. Results and discussion

The detailed characteristics of MN and PMN powders have been given elsewhere [18–20]. The average particle (or aggregate as can be seen from the SEM photographs given later) size of the PMN powder was found to be 5.8 μm. For the present study, we selected 3 wt.% excess PbO as a sintering aid. However, we found that at the firing temperature of 900°C (soaking time 30 min) the PMN powder of average particle size 5.8 μm gave rise to a little densification (Table 1) in the presence of PbO sintering aid which forms a liquid phase [19] at that temperature. The effect of 6 wt.% excess Nb_2O_5 (along with the same excess PbO) on the sintering behaviour of PMN powder was surprising in the sense that under identical firing conditions an appreciable expansion (upto 14%) instead of shrinkage was found (Table 1). Such behaviour remained the same whether the sample was directly introduced at 900°C or slowly heated to 900°C from room temperature; however, we followed the former procedure to minimize [20] lead loss during the heat treatment. However, at higher temperature, (as shown later, see Fig.2) as expected, shrinkage begins.

In our case, expansion due to grain growth and pore coalescence is ruled out as the heat treatment was carried out in the zone of initial stage of liquid phase sintering only. This is further supported by the fact (Table 1) that PMN + 3%PbO under identical condition did not show any expansion. Similarly, swelling due to any gas formation is ruled out in our case. Also any expansion owing to release of stored anelastic and plastic strain does not arise here because, under identical condition, PMN + 3%PbO did not show any expansion. To check any possibility of volume expansion due to the formation of larger molar volume pyrochlores (like P_3N_4 and P_2N_2 where P stands for PbO and N stands for Nb_2O_5) arising out of the reaction [12–14,21] between PbO and Nb_2O_5, the X-ray diffractogram (Fig. 1) of a crushed fired (900°C/30 min) pellet [PMN + 3 wt.%PbO + 6 wt.%Nb_2O_5] was taken. The diffractogram indicated some amount of pyrochlore formation. However, our observed expansion (upto 14%, see Table 1) cannot be explained by considering only the volume expansion due to the pyrochlore formation because a powder mixture consisting solely of PbO and Nb_2O_5 [in the ratio of 3:6 (i.e. 1:2) by weight, the ratio we maintained for the excess PbO and Nb_2O_5 additive for our PMN powder] after heat treatment under identical conditions gave rise to only 4.8% volume expansion. As shown in Fig. 2, (where volume changes of the samples were noted after heat treatment at particular temperatures for 30 min followed by cooling) the volume expansion due to such pyrochlore formation starts from around 650°C whereas, around the same temperature, the pellets without Nb_2O_5 show neither expansion nor shrinkage (Fig. 2). Interestingly, as depicted in Fig. 2 there is a sudden jump in volume expansion at around 900°C (above the melting point of PbO) where liquid phase starts forming and the major part of the volume expansion takes place in this region.

All these observations indicate that (1) such high volume expansion for pellets containing excess PbO and Nb_2O_5 cannot be solely attributed to volume changes due to formation of larger molar volume products during heat treatment and (2) to get such high expansion, the presence of a liquid phase (in our case molten PbO based liquid) seems to be a necessity.

To understand the expansion behaviour, we have to first consider the parameters controlling the early stage of liquid phase sintering. The early stage of liquid phase sintering is marked by a particle rearrangement [22] process in which surface tension forces act to bring about physical movement of the particles. The wetting of the solid by the liquid is a necessity for rearrangement and shrinkage. Based on the balance between surface tension and an intrinsic frictional force due to

Table 1
Green bulk densities and fired shrinkage/expansion of PMN samples containing excess PbO with or without excess Nb_2O_5

Composition	Pressure (MPa)	Green bulk density (% of theo. density)	Vol. expansion after firing at 900°C/30 min[a]
PMN + 3%PbO	25	60%	−3%
	50	61%	−2%
	75	63%	0%
PMN + 3%PbO + 6%Nb_2O_5	25	60%	12%
	50	61%	14%
	75	63%	14%

[a] Negative sign indicates shrinkage.

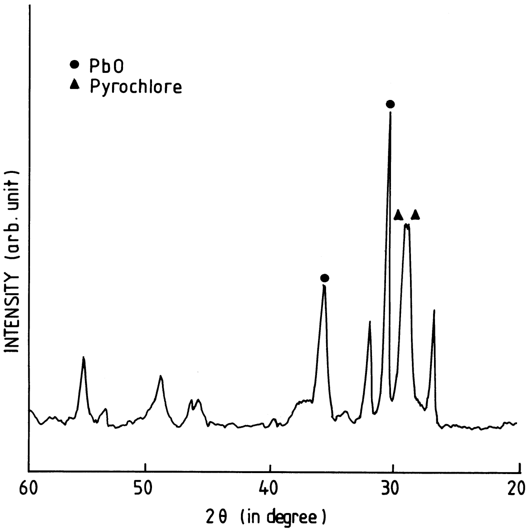


Fig. 1. X-ray diffractogram of a powdered pellet (PMN + 3%PbO + 6%Nb_2O_5) fired at 900°C for 30 min. (The two most intense peaks of PbO and pyrochlore have been marked.)

viscosity of the liquid, Kingery et al. [23] proposed a model for liquid phase sintering where they showed that the volume shrinkage ($\Delta V/V$) during the early stage is related to the time by the following relation:

$$\Delta V/V_o \sim t^y \tag{1}$$

where y is close to unity and generally lies between 1 and 1.5. Huppmann [11] considered rearrangement densification as a function of force existing between two solid particles which are connected by a melt bridge. He considered both rearrangement of initial particles and rearrangement of grains after particle disintegration. According to Huppmann, the rearrangement shrinkage $\Delta V/V$ is given by

$$\Delta V/V_o \sim (F - F_o) \tag{2}$$

where F is the interparticle force between two spheres connected by a liquid bridge. Only when F exceeds the weakest configuration intrinsic force F, particle rearrangement can take place. The interparticle force F per contact can be written as

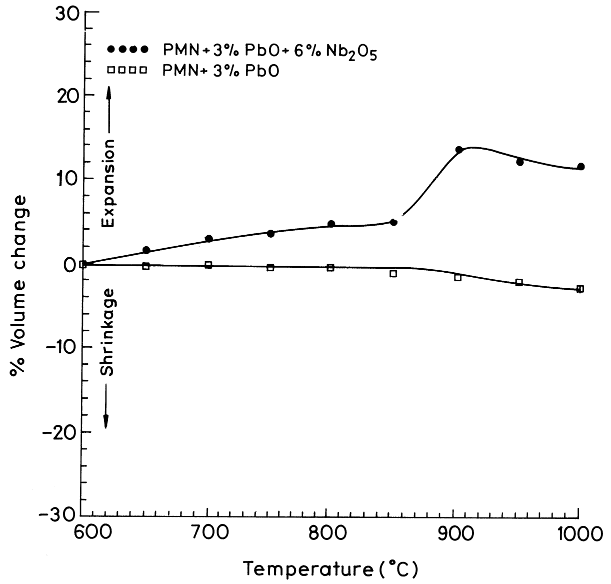


Fig. 2. Percentage of volume changes with firing temperatures for pellets of PMN containing 3 wt.% excess PbO with or without 6 wt.% excess Nb_2O_5.

$$F = 2\pi r \gamma_{LV} \cos\phi - \pi r^2 \gamma_{LV}(1/r_m + 1/r) \tag{3}$$

where (see Fig. 3) r is the radius of the ring, r_m is the radius of curvature of the liquid meniscus, γ_{LV} is the surface free energy of the liquid vapour interface. The angle ϑ is the wetting angle and the angle f has been shown in Fig. 3. The first term of Eq. (3) is due to the action of the surface tension forces along the perimeter of the liquid particle contact and the second term is due to the presence of a pressure difference across the liquid meniscus which gives rise to pulling of particles and hence densification. From the above equation [Eq. (3)], it is evident that the driving force for liquid phase sintering depends strongly on the radius of curvature of the liquid meniscus, the latter being dictated by the wetting angle and diameter of the capillary (effectively by the particle size). However, such an equation does not take care of the dilatancy effect [24]. For a long time it has been known that well-packed powders expand as shear occurs, a phenomenon called dilatancy by Reynolds [25] and this behaviour is a space-filling characteristic [26] of granular materials and occurs only in percolation [27] structures. All compact packings dilate when initially deformed but the phenomenon is often masked by subsequent collapse. Hence, during the particle rearrangement phase of early stage liquid phase sintering, the capillary pressure should give rise to dilatancy and the former must overcome the dilatancy pressure to show ultimate densification. Hence Eq. (3) should be rewritten as:

$$F = 2\pi r \gamma_{LV} \cos\phi - \pi r^2 \gamma_{LV}(1/r_m + 1/r) + F_D \qquad (4)$$

where, owing to dilatancy pressure on the powder compact, there is an equivalent of F_D dilatancy force per contact. In any system, it is obvious that if the capillary pressure generated is weak, there will be poor or no rearrangement of the particles. On the other hand, if the capillary pressure is strong, there will be rearrangement followed by collapse and ultimate shrinkage. However, if the capillary pressure is not strong enough for collapsing and shrinkage but sufficient for rearrangement and dilatancy, then instead of densification, expansion may be obtained as evident from Eq. (4). The possible reasons for such relatively weak/incomplete capillary pressure may be the higher wetting angle and/or the higher viscosity of the liquid melt. It is to be noted that in an ideal case, infiltration distance (x) of a melt into a capillary is parabolic with time (t) and can be described by Washburn model [28] as given below:

$$x^2/t = \gamma_{LV}\, d \cos\vartheta / 4\eta \qquad (5)$$

where d is the diameter of the capillary, ϑ is the wetting angle and η is the viscosity of the melt. It is also to be noted that for a viscous liquid, the liquid near the surface can not keep up with the advancing front so that a higher [29] dynamic contact angle develops. The higher the viscosity of the melt and wetting angle, the slower the liquid will penetrate the capillaries and the capillary pressure generated may be incomplete and relatively weak and conductive to dilatancy with consequent expansion. The possible reason why such expansions due to dilatancy is not frequently observed in different systems probably lies in the fact that in most of the cases of liquid phase sintering, the sintering aid forms a liquid phase (and hence generates capillary pressure) at high temperature where overlapping of rearrangement, solution reprecipitation and solid state sintering take place leading to an overall shrinkage.

As discussed earlier, a small part of the observed expansion at 900°C (Table 1 and Fig. 2) may be due to the formation of pyrochlore phases possessing larger molar volumes than the individual components. However,

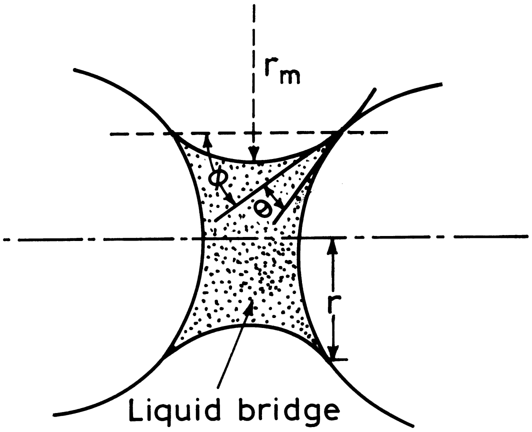


Fig. 3. Geometry of a particle contact region.

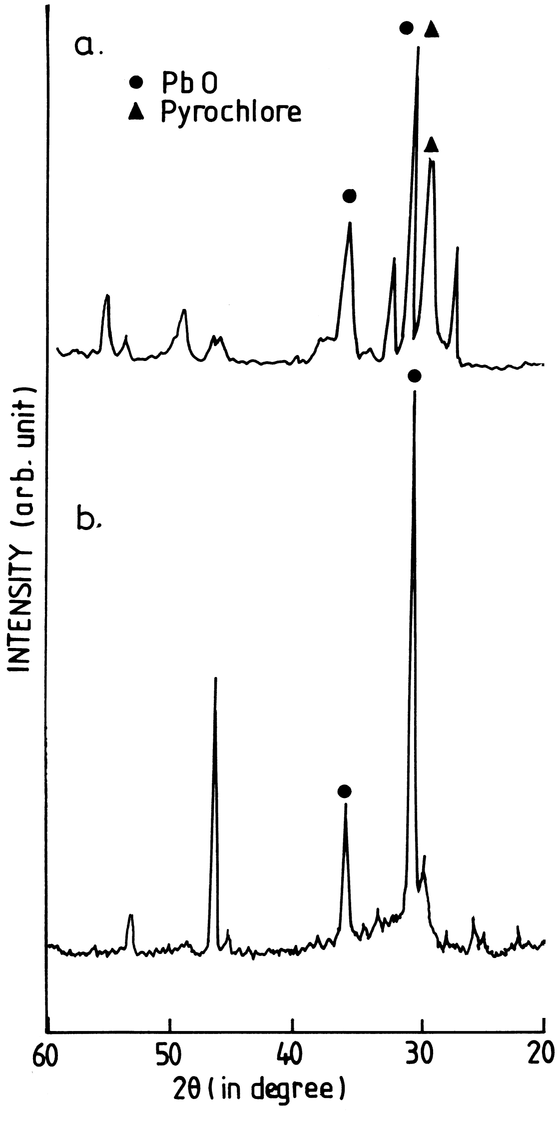
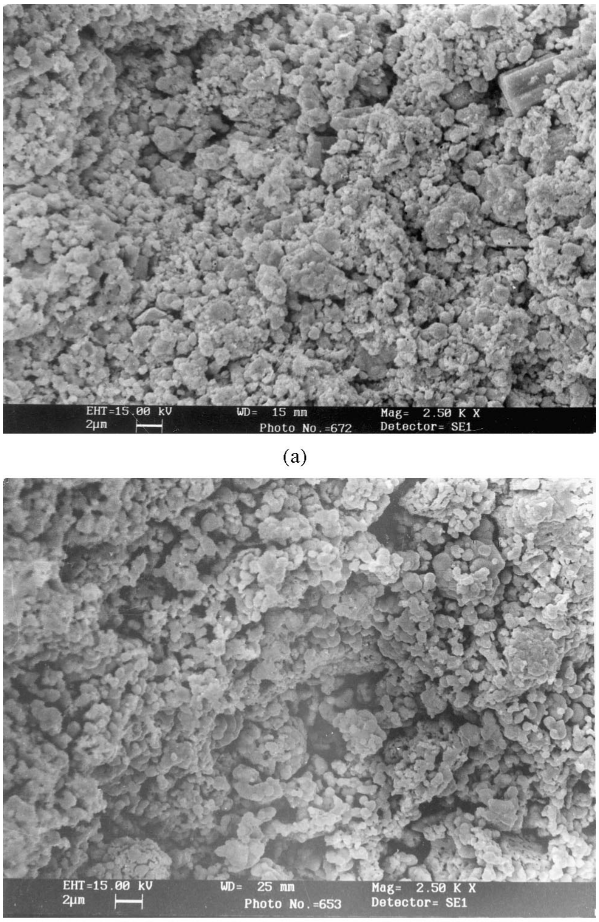


Fig. 4. X-ray diffractogram of powdered (a) PbO + 10 wt.%Nb_2O_5 melt and (b) pure PbO melt after quenching. (The two most intense peaks of PbO and pyrochlore have been marked.)

dilatancy seems to play the primary role in the aforesaid expansion as evident from the jump in expansion (Fig. 2) above the melting point of PbO when a liquid phase is formed. Incidentally, as expected, the overall expansion remained almost the same whether the samples were slowly heated to 900°C or directly introduced inside a furnace preheated to 900°C. It seems that the formation of a liquid phase followed by dilatancy primarily dictates the volume expansion. To understand the behaviour, we compared qualitatively the fluidity of pure PbO melt and a melt containing some Nb_2O_5 (~10 wt.%) along with PbO by pouring both the melts. We observed from the flow behaviour that the viscosity of the latter melt was more than that of the former probably owing to some dissolution of Nb_2O_5 in molten PbO. The latter was verified by XRD studies (Fig. 4) of powdered quenched melt of $PbO+Nb_2O_5$, where along with the presence of pyrochlore (P_2N_2 and/or P_3N_4) the characteristic peaks of PbO have been found to be slightly shifted to higher angles indicating some dissolution of Nb_2O_5 in PbO melt. The other role of dissolved Nb_2O_5 in PbO melt is to increase the wetting angle [30] of the melt. Hence the lower capillary pressure in case of $PbO+Nb_2O_5$ melt (in comparison to pure PbO melt) might be sufficient to show dilatancy but insufficient for collapsing of the structure and ultimate shrinkage. The comparison of the scanning electron micrographs of the fracture surfaces of green (pressed) and heat-treated pellets [Fig. 5(a) and (b)] of a typical composition [PMN + 3% PbO + 6%Nb_2O_5] shows more porosity and also enhanced nonuniformities in the distribution of pores after heat treatment which again supports [27] our conjecture about the role of dilatancy. Interestingly, higher forming pressure (leading to higher green bulk density, see Table 1) gives rise to more volume expansion after firing. This may be owing to more percolation in denser structure leading to higher dilatancy pressure with consequent higher volume expansion.



(a)

(b)

Fig. 5. Scanning electron micrographs of the fracture surfaces of (a) a green pellet [PMN + 3%PbO + 6%Nb_2O_5] and (b) the same pellet fired at 900°C for 30 min.

4. Conclusions

(a) Volume shrinkage, although little (~3%), takes place during firing (950°C/30 min) of pellets made from PMN powder (average particle size 5.8 μm) containing 3 wt.% excess PbO, whereas, an addition of Nb_2O_5 (6 wt.%) along with the same excess PbO leads to an appreciable expansion (up to 14%) instead of shrinkage.

(b) Such high expansion can be explained primarily by considering the generation of insufficient capillary pressure at the heat treatment temperature owing to the formation of a liquid phase (PbO melt containing some dissolved Nb_2O_5) at that temperature and the subsequent role of dilatancy which considers the expansion of well-packed powders during shear. A small part of the expansion can be accounted for by considering the formation of pyrochlore phases (during heat treatment) possessing larger molar volumes than the initial components.

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