RECEIVED
LAWRENCE
RADIATION LABORATORY

UCRL-20596
c.2

DOCUMENTS SECTION

SINTERING OF HIGH-PURITY SUBMICRON LEAD TITANATE CONTAINING NIOBIUM

John W. Sherohman
(M.S. Thesis)

June 1971

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

UCRL-20596 c.2

25

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

SINTERING OF HIGH-PURITY SUBMICRON LEAD TITANATE CONTAINING NIOBIUM

Contents

		Page
ABSTRACT		v
I.	INTRODUCTION	1
II.	EXPERIMENTAL	4
	A. Powder Characterization	4
	B. Powder Preparation	8
	C. Sintering Studies	9
III.	RESULTS	11
	A. Slow Heating Rate	11
	B. Fast Heating Rate	16
IV.	DISCUSSION	19
	A. Density Analysis	19
	B. Grain Growth Analysis	25
V.	CONCLUSION	27
ACKNOWLEDGMENTS		28
REFERENCES		29

SINTERING OF HIGH-PURITY SUBMICRON LEAD TITANATE CONTAINING NIOBIUM

John W. Sherohman

Inorganic Materials Research Division, Lawrence Radiation Laboratory, and Department of Materials Science and Engineering, College of Engineering, University of California, Berkeley, California

ABSTRACT

Chemically prepared lead titanate powders containing 1, 3, and 6 at.% Nb were obtained. From a characterization study of the as-received powders, an initial heat treatment before sintering was established. Sintering and grain growth results of the chemically prepared material were compared to laboratory $PbTiO_3$ produced by calcination of mixed oxides in the conventional processing method. The addition of niobium to lead titanate affects both the sintering and grain growth kinetics; densification and grain growth are both decreased with increasing niobium concentrations.

Differences in the sintering and grain growth characteristics were interpreted for the chemically prepared and laboratory materials. At a faster heating rate, the density at temperature of the as-received material increased with time. An increase in the compaction pressure of the chemically treated material led to an increase in the initial density at temperature. However, in the case of 3 at.% Nb, the density decreased. The changes in density and grain growth behavior were analyzed from photomicrographs of polished sintered specimens containing 3 at.% Nb.

I. INTRODUCTION

Lead titanate is a perovskite ferroelectric ceramic that has a Curie temperature of approximately 490°C. At this temperature there is a cubic to tetragonal phase transition leading to a corresponding c/a ratio of 1.063 at room temperature.[1]

Because of this high Curie temperature, $PbTiO_3$ ostensibly is an interesting material for high temperature applications. Furthermore, because it has a low dielectric constant,[1] implying a relatively high electrical impedance[2] and a very low dielectric constant rate of aging[3] as compared to other ferroelectrics, it is contemplated for use as a stable piezoelectric for high frequency utilization. Associated with the phase transformation is a large spontaneous strain. This strain is further intensified by an anisotropic thermal expansion on cooling from the Curie temperature to room temperature.[1] Consequently, the cooling of $PbTiO_3$ leads to the development of cracks in the polycrystalline ceramic. Thus, the fragile ceramic frequently disintegrates to a powder.

Other investigators have shown that by the addition of other oxides a relative dense and hard $PbTiO_3$ can be obtained.[4-7] Such techniques are used in ceramics to aid in sintering and to inhibit grain growth. The inhibition of grain growth generally affects densification by increasing the sintering rate. The increase in the rate of sintering is accomplished by impeding grain boundary mobility; thus, discontinuous grain growth is prevented and pores are maintained near grain boundaries where they can eventually be eliminated by vacancy diffusion to and along the grain boundaries.[8] If the addition forms a solid solution by forming a substitutional ion that has an incorrect valance, then an increase in the sintering rate may be achieved by the production of lattice vacancies that can increase the rate of volume diffusion.[9]

From thermogravimetric analysis (TGA) on lead zirconate titanate (PZT) doped with niobium,[10] it is believed that the addition of niobium to $PbTiO_3$ forms a solid solution by substitution of Nb^{+5} ion for Ti^{+4} ion. In this way one lead vacancy is produced for every two niobium ions creating an increased lead vacancy concentration. From thermodynamic considerations and work done on Al_2O_3 doped with MgO,[11] it is expected that the solid solution substitution segregates near the grain boundaries; hence, it reduces grain boundary mobility. Also, in the case of $PbTiO_3$ doped with niobium, the formation of a solid solution reduces the c/a ratio[4] which, therefore, decreases the induced strain and the fragility of the ceramic.

Recently the use of high-purity submicron powders have produced near theoretically dense ceramics with ultrafine grain sizes. It is known that the densification or the rate of decrease of porosity for spherical particles is inversely proportional to the cube of a dimension related to the grain size.[12] Assuming the above to hold true even for nonspherical particles, it is apparent that the use of a submicron powder has the potential to enhance the rate of sintering. Chemically treated powders of yttria-stabilized zirconia[13] and barium titanate[14] from decomposition of metal alcoholates have been produced having a particle size range of 50 to 150 Å. These powders, as prepared, were shown to be stoichiometric and homogeneous. Under optimum sintering conditions, densities approaching theoretical were obtained with fine grain sizes.[15]

Taking into consideration the factors mentioned to augment the densification of $PbTiO_3$, a high-purity submicron lead titanate powder was obtained containing niobium as an additive. A processing technique for the synthesis of high-purity submicron $PbTiO_3$ powders has been

developed by Robert Dosch of the Sandia Corporation in Albuquerque, New Mexico. The $PbTiO_3$ powder received from Sandia is basically prepared from alkoxides in an aqueous solution. A precipitate can be formed having the desired molar ratio with niobium concentrations of 1, 3, and 6 at.%. The precipitate is freeze dried to remove most of the water and organic residue and then allowed to come to ambient temperature. The impurity content of the S powders was analyzed by Dosch and was found to be in the 200 ppm range of which half was Si picked up from the glassware in the synthesis steps.

The purpose of this work was to investigate the sintering characteristics and the grain growth behavior of this chemically prepared lead titanate powder. The results are compared to material produced by calcination of mixed oxides in the conventional method of producing lead titanate powders for ceramic processing.

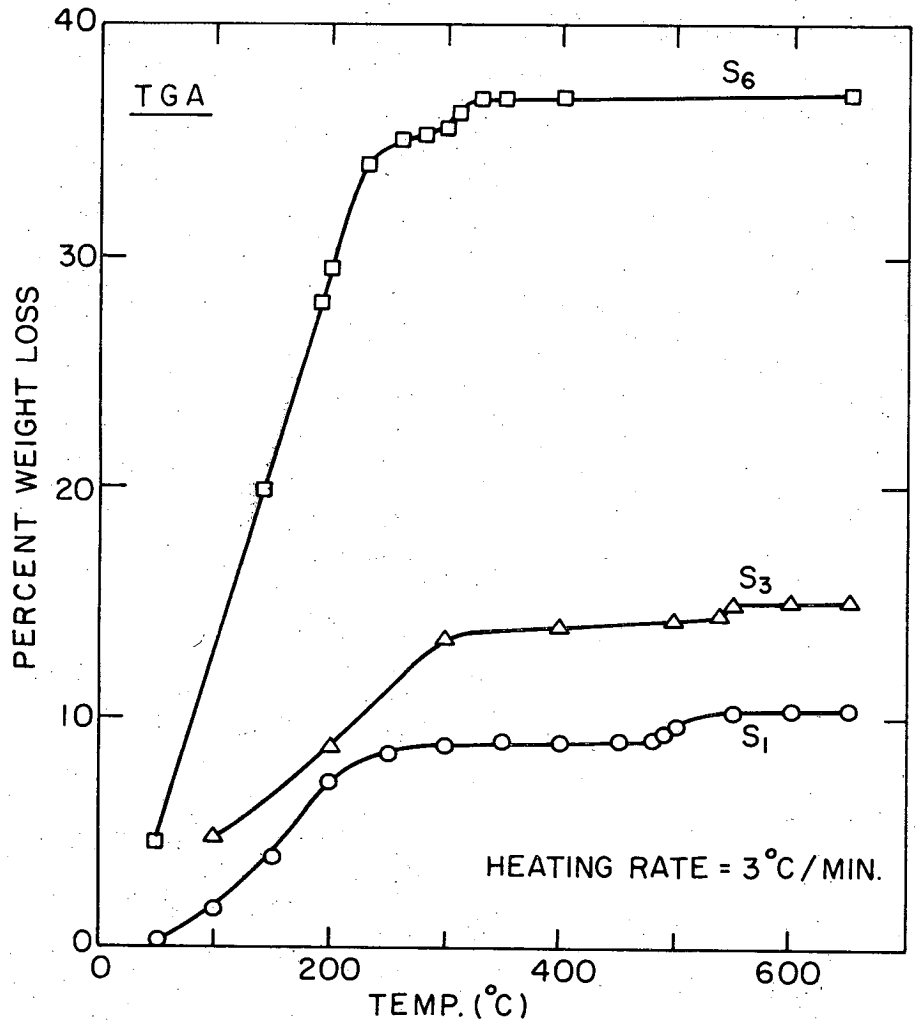
II. EXPERIMENTAL

A. Powder Characterization

The characterization of the as-received Sandia powder was necessary to understand the nature of the starting material. Hence thermogravimetric analysis (TGA), differential thermal analysis (DTA), X-ray diffraction, and specific surface area measurements were conducted.

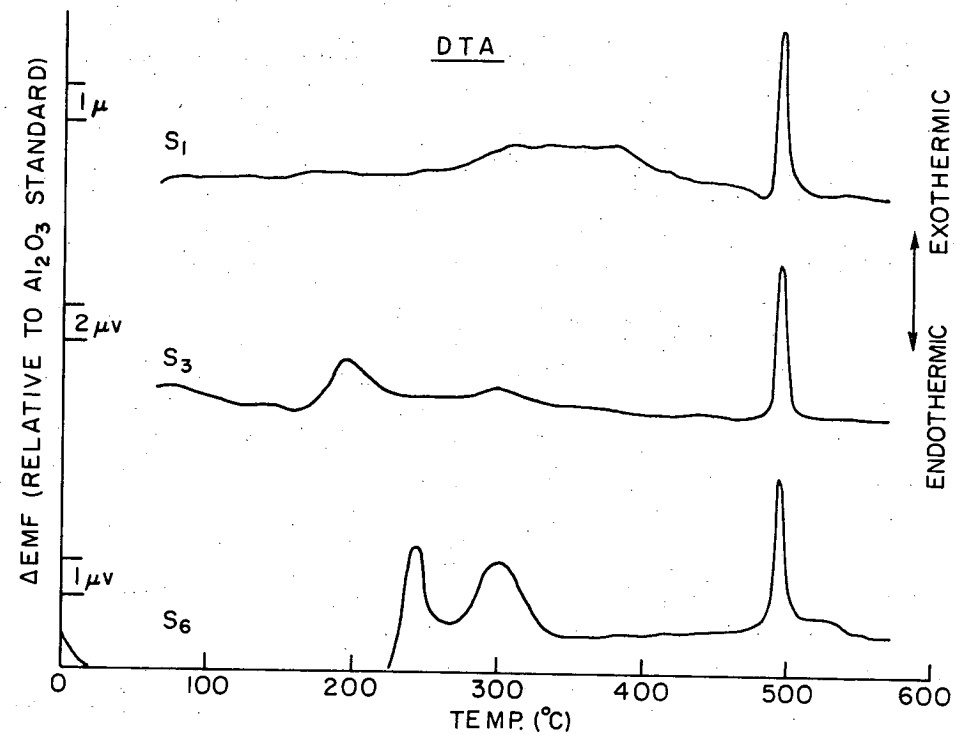
A TGA on the as-received Sandia powders was made to determine the amount of weight loss due to water and carbonaceous impurities. The results are shown in Fig. 1 where S_1, S_3 and S_6 correspond to the niobium concentrations of 1, 3 and 6 at.%, respectively. It is observed that the increase in the concentration of niobium tends to produce a higher percentage of weight loss. Also in each of the weight loss curves, two distinct temperature regions of weight loss are observed. The second temperature region has been verified by Dosch[16] to be water vapor thought to be associated with the last remaining hydroxyls leaving the system.

In the DTA experiments a large exothermic peak slightly below 500°C was observed for each powder as shown in Fig. 2. The samples of powder were heated at 12°C per minute. The exothermic peaks occurred at a temperature which is interestingly at the Curie temperature. Upon heating, because the formation of a compound is almost always exothermic, it was assumed that the peak is related to the crystallization of $PbTiO_3$. X-ray examination of powders heated below the exothermic temperature, even when held for long times, showed a very broad halo characteristic of an amorphous structure. Yet when the powder is heated above the exothermic temperature and then cooled to room temperature, a tetragonal perovskite lead titanate pattern is observed by X-ray diffraction. Therefore, it is concluded that the Sandia powder



XBL 7010-6733

Fig. 1. Thermogravimetric analysis on the as-received Sandia powders.



XBL 7010-6734

Fig. 2. Differential thermal analysis on the as-received Sandia powders.

crystallized as $PbTiO_3$ at a temperature of 490°C. It is also observed in the DTA curve for S_6 that there exists a large endothermic peak. This result is thought to be associated with the higher percentage of weight loss as shown for S_6 in Fig. 1.

From the results of the TGA and DTA, it is seen that an apparent heat treatment would be to calcine the Sandia powders above 500°C to both remove all the water and organic material and to form the lead titanate compound. To retain an active powder and still remove a significant amount of the impurities, a heat treatment of 300°C for one hour was used on the S powders. As a consequence, disks pressed for sintering were of an amorphous powder containing some hydroxyls.

The specific surface area measurements were conducted by a single point BET method* using the continuous flow technique. Before determination of the surface area the sample was baked out in flowing helium. Because it is of interest to know the specific surface area of the powder before sintering, it was necessary to bake out the as-received powder at 300°C for one hour corresponding to the weight loss heat treatment. In this way only an apparent specific surface area measurement is obtained because of the remaining hydroxyls. Material made from mixed oxides of lead, titanium, and niobium in the conventional method is referred to as the laboratory powder, hence, designated as L. These powders were also given the same bake-out treatment for specific surface analysis. In Table I, the specific surface areas are given for both the S and L powders. It shows that there is still a high surface activity in the S powders compared to the $PbTiO_3$ made in the laboratory. Consequently, the powder is of high purity and also submicron as shown

*Perkin-Elmer Shell Model 212 Sorptometer.

by the apparent specific surface area measurements.

Table I.

Sample	Specific surface area(m^2/g)	Relative green density in % of theoretical density of $PbTiO_3$	
		25,000 psi	63,000 psi
S_1	24.3	38.5	45.2
S_3	18.4	38.8	45.6
S_6	105.5	33.7	43.8
L_1	1.04	62.8	
L_3	5.96	54.6	
L_6	2.51	53.1	

B. Powder Preparation

The powder preparation for the S powders was a heat treatment of 300°C for one hour as discussed in Section A. In the case of the laboratory $PbTiO_3$ the oxides of lead, titanium, and niobium of reagent grade powders were used to form compounds having the same compositions as the S powders as shown in Table II. For the L material the oxides were mixed with isopropyl alcohol in a neoprene lined ball mill using teflon cylinders as a mixing media. After a mixing treatment for 50 hours, the alcohol was evaporated at 80°C. The material was prepared for the calcination by forming 1 in. dia. 4 in. long slugs by isostatically pressing at 25,000 psi. The slugs were placed in a covered platinum crucible and calcined for 3 hours at 750°C. To promote grinding after calcination, the slug was quenched in an ice bath. Further grinding was done by a lucite mortar and pestal and any lucite contamination was completely removed by air oxidation at 400°C. The L and S

Table II.

Niobium content at.%	Compound formula
1	$Pb_{.995}\ \square_{.005}\ (Ti_{.99}\ Nb_{.01})\ O_3$
3	$Pb_{.985}\ \square_{.015}\ (Ti_{.97}\ Nb_{.03})\ O_3$
6	$Pb_{.97}\ \square_{.03}\ (Ti_{.94}\ Nb_{.06})\ O_3$

$\square$ indicates lead vacancy

powders were pressed into disks by a 1/2 inch steel die at 25,000 psi. An isopropyl alcohol binder was used in the case of the L material; therefore, these disks were oven dried at 80°C. Table I gives the values of the green densities in terms of percent theoretical after pressing. Since the S powders are amorphous, the values given are apparent green densities for purpose of comparison. The low green density shown by the S powders is characteristic for submicron powders and is an important factor that must be considered in sintering.

C. Sintering Studies

Both S and L disks were placed into a platinum crucible and covered by a niobium free $PbTiO_3$ packing powder. Because of the high vapor pressure of lead oxide, the use of the packing powder established a PbO atmosphere to prevent lead loss from the samples. The crucible was covered with a platinum lid and placed in a kanthal wound furnace and heated at 200°C per hour in one atmosphere of oxygen. The disks were sintered at 1200°C up to 4 hours and then furnace cooled. Density measurements were determined by mercury displacement and as-fired surfaces were examined with a scanning electron microscope. As-fired

surface grain sizes were measured from photomicrographs using the line intercept methods and multiplying the average cord length by 1.5. Density and grain size versus time curves were plotted.

Investigation of a faster heating rate of 750°C per hour on density and grain growth behavior was conducted on the S disks. Related density and grain size versus time curves were also plotted. A study on the sintering behavior of the S disks having a higher green density obtained by pressing at 63,000 psi was performed. Microstructures of polished sintered S_3 specimens were examined by the scanning electron microscope.

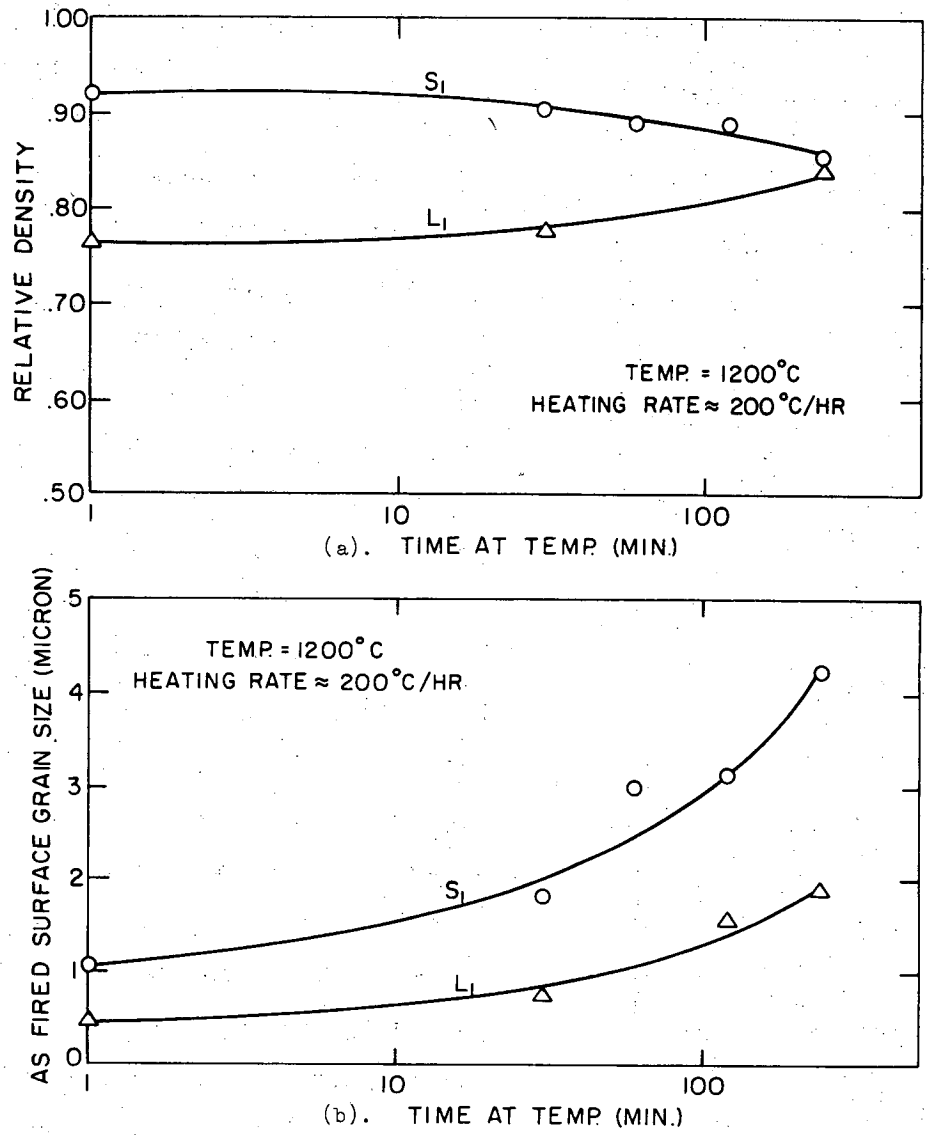
III. RESULTS

A. Slow Heating Rate

The density versus time curves of the S and L materials containing 1 at.% niobium are shown in Fig. 3a for a heating rate of 200°C per hour. It is observed that S_1 has reached a higher density than L_1 in heating to temperature. Although S_1 has the higher initial densification, its density decreased with time at temperature. Fine radial and internal cracks developed in the S_1 disks after sintering. It was noticed that the internal cracking was more severe with an increase in grain size. For the L_1 material, the density curve gradually increased with time. Figure 3b shows a comparison of grain size on the as-fired surface of S_1 and L_1. The grain growth for S_1 is shown to be greater.

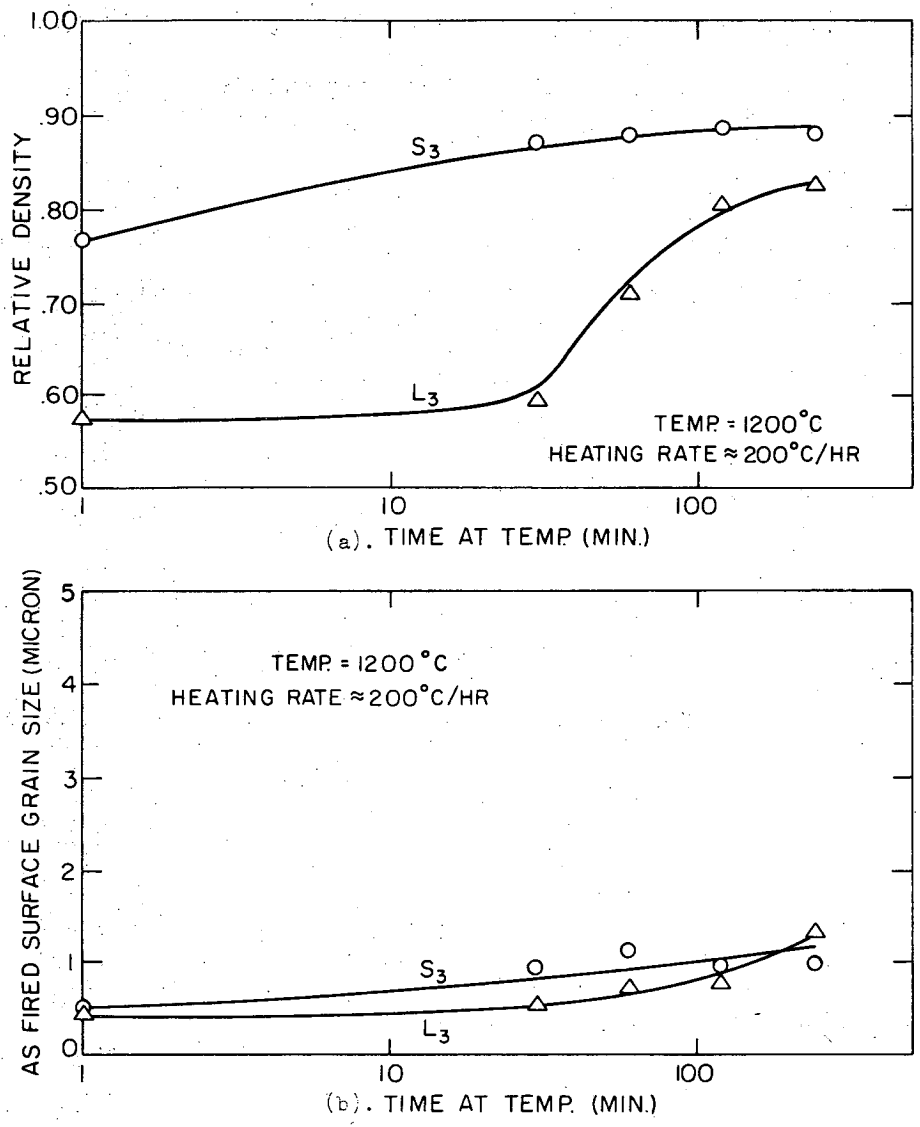
For 3 at.% niobium, the density versus time curves for the S and L materials are present in Fig. 4a. The density of S_3 is greater than L_3 for one minute at temperature. It is further observed, by comparison of Fig. 3a, that this initial density at one minute, ρ_1, is suppressed by the addition of 3 at.% niobium. The density curve for S_3 increases with time and appears to approach a limiting density. For the L_3 material, the density curve exhibits an incubation region with no appreciable densification; however, after a period of time at temperature the density increases. In Fig. 4b the grain size of the as-fired surface is compared to S_3 and L_3. It is noted that 3 at.% niobium impedes the grain growth.

Figure 5a shows the density relationship of S and L with time at temperature for 6 at.% niobium. The initial density ρ_1 of S_6 is shown to be greater than L_6. As was indicated for 3 at.% niobium, ρ_1 is suppressed even more by the larger niobium addition. This effect is summarized for S and L in Fig. 6 as a plot of ρ_1 versus at.% niobium.



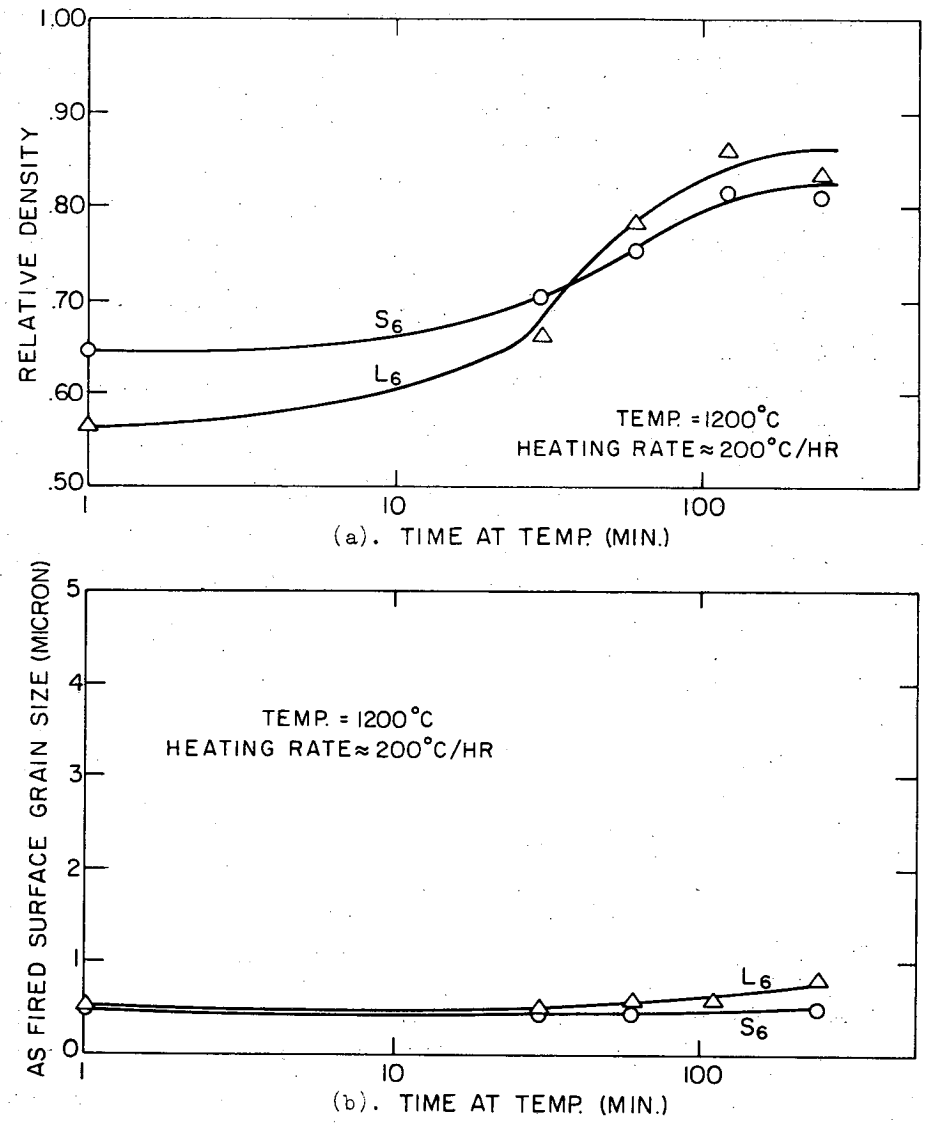
XBL 7010-6736

Fig. 3. The sintering and grain growth behavior for 1 at.% niobium.



XBL 7010-6735

Fig. 4. The sintering and grain growth behavior for 3 at.% niobium.



XBL 7010-6737

Fig. 5. The sintering and grain growth behavior for 6 at.% niobium.

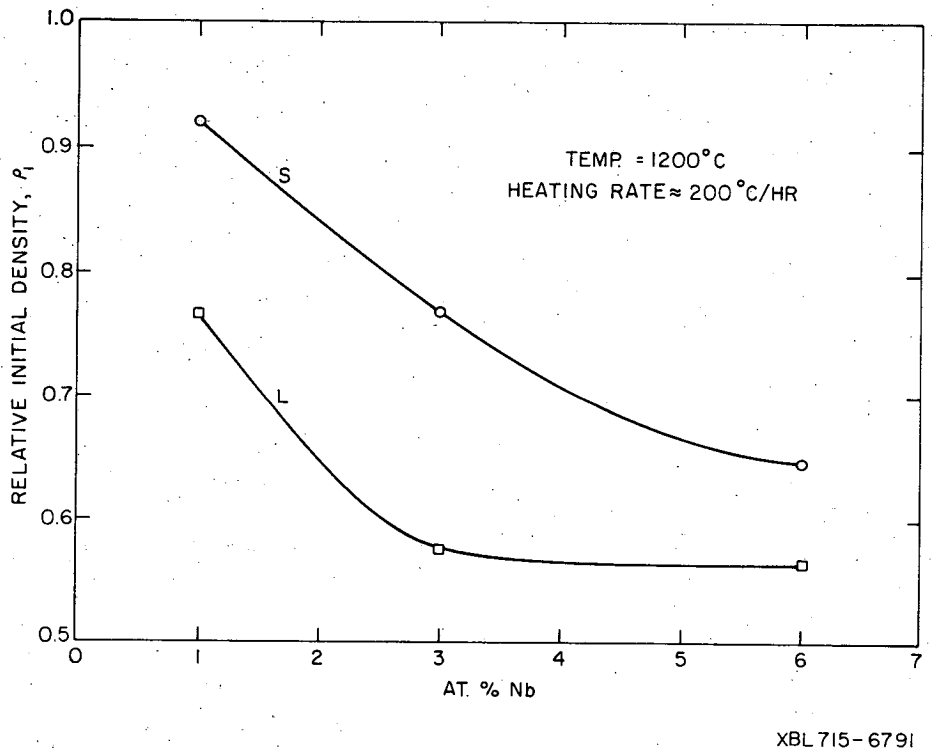


Fig. 6. The effect of niobium additions on the initial density at temperature.

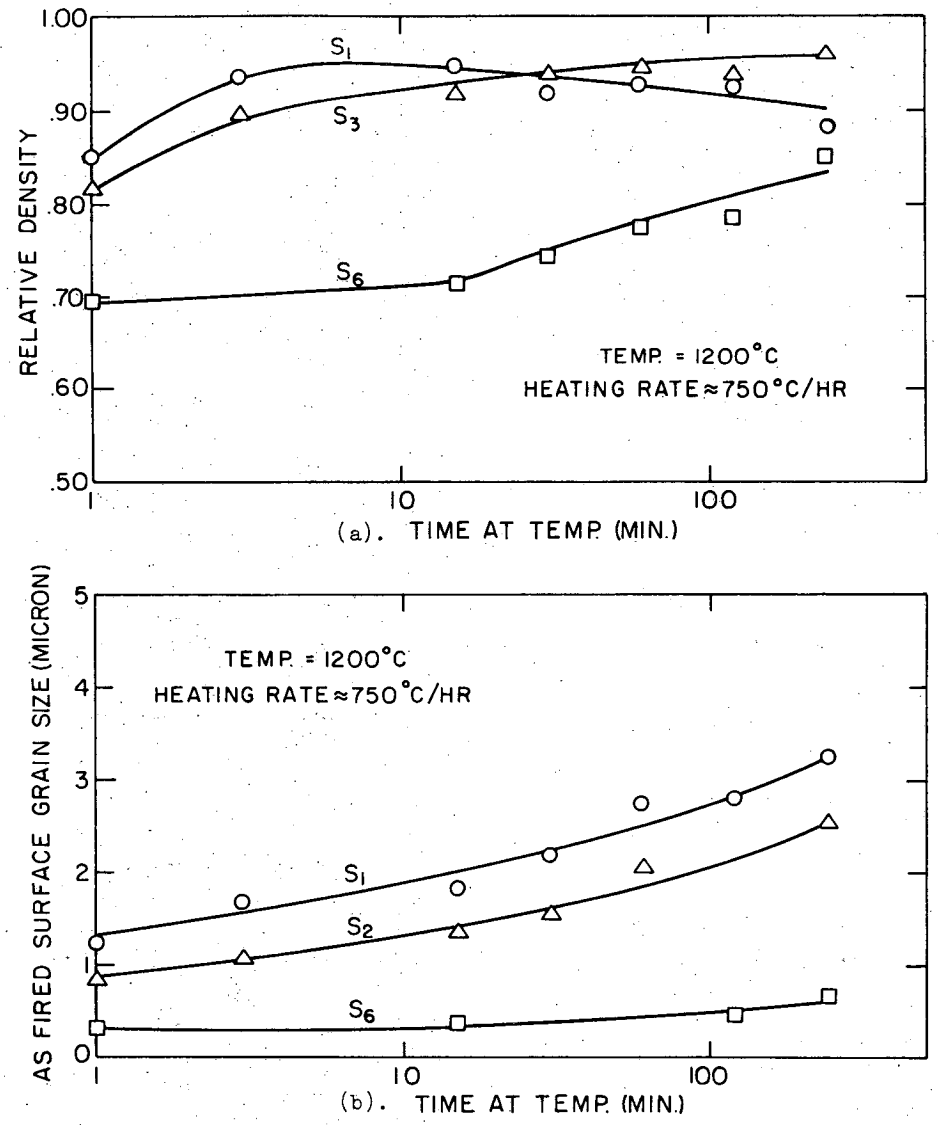
It is assumed that ρ_1 is a reasonable measure of the sinterability of the powders.

A density incubation region, as described for the density curve of L_3, exists for both S_6 and L_6. Also, the grain growth, represented in Fig. 5b, is inhibited more with 6 at.% niobium.

B. Fast Heating Rate

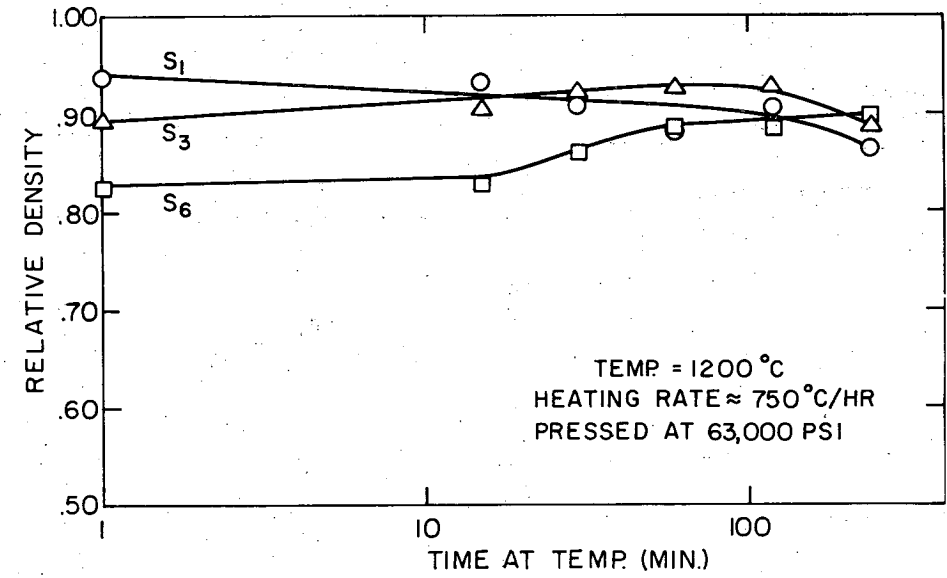
The sinterability of the S material under a faster heating rate of 750°C per hour was examined. An increase in ρ_1 for S_3 and S_6 is shown in Fig. 7a, as compared to the slower rate of heating. Although ρ_1 for S_1 decreased, it is still observed that ρ_1 decreases for greater concentrations of niobium. In the S_1 material, the disks still showed radial and internal cracks, but for the fast heating rate a higher density was obtained. Similarly, S_3 and apparently S_6 achieved a higher density. At the higher densities of S_3 some internal cracks were observed. Also, it is noted that the density curve for S_6 maintained an incubation region. An as-fired surface grain size versus time curve for the fast heating rate is presented in Fig. 7b. There is a noticeable grain growth difference as compared to the slow rate of heating.

To alleviate the density limitation due to low green density, the S material was pressed at 63,000 psi. The apparent green densities at this pressure are shown in Table I. All cases exhibited a higher ρ_1 as shown in Fig. 8. The S_1 disks again contained internal cracks, but because the shrinkage was reduced, the radial cracking was eliminated. The density curves for both S_3 and S_6 still showed a density limit, and in the case of S_3 the density decreased with time.



XBL 7010-6738

Fig. 7. The sintering and grain growth behavior of the Sandia materials at the fast heating rate.



XBL715-6734

Fig. 8. The sintering behavior of the Sandia materials cold pressed at a higher pressure.

IV. DISCUSSION

A. Density Analysis

In comparing the L materials, it is shown that a greater concentration of niobium decreases the initial density ρ_1. It is suggested, from the observed incubation regions of L_3 and L_6, that this decrease in ρ_1 may be due to an incomplete reaction of niobium to form a solid solution. Therefore, for the larger additions of niobium, the $PbTiO_3$ particles may retain a niobium rich surface layer that impedes sintering.

The S materials also show a reduction in ρ_1 for a greater concentration of niobium. The chemically treated S material has very fine intimately mixed particles that makes for a very active powder. Consequently, the niobium has a greater tendency to go into solution than for the relative coarse particles made from mixed oxides. In this way, as shown for all related cases, ρ_1 for the S material is greater than that of the L. Figure 4a tends to support this idea by showing that the density curve of S_3 does not have an incubation region as compared to L_3. Because a region of incubation is now shown for S_3, it is believed that niobium completely forms a solid solution. The decrease in ρ_1 for S_3 as compared to S_1 may be explained by the segregation of the solid solution substitution of niobium to the grain boundaries. Jorgensen[17] demonstrated that the addition of 0.1 wt.% MgO to Al_2O_3 initially caused a decreased sintering rate. The segregation MgO to the grain boundaries was predicted to decrease the diffusion coefficient of the rate controlling species and the solid-vapor surface energy. It is proposed that niobium behaves in a similar manner as MgO, but showing a greater influence because of the increased concentration.

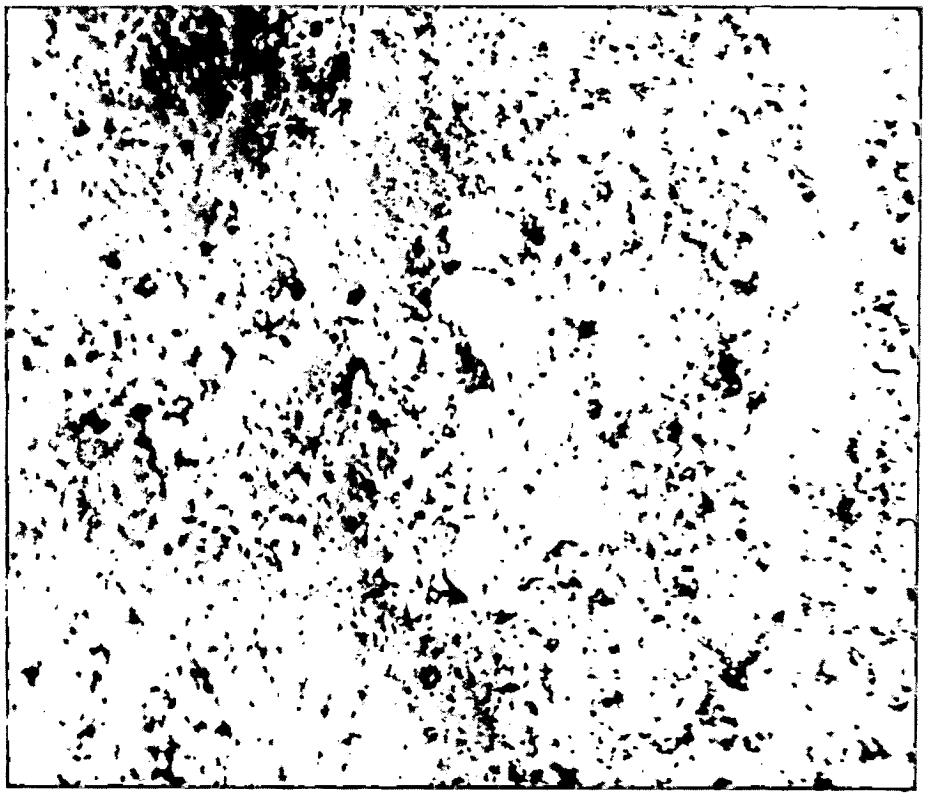
In Fig. 5a it is observed that the density curve of S_6 does exhibit a region of incubation along with L_6. Because of the larger addition of

niobium, the S_6 material (and L_6) may have a nonhomogeneous niobium concentration as a result of exceeding the solubility limit. Subbaro[4] predicted that the solubility limit for niobium in lead titanate lies within the range of 2 to 5 at.%. X-ray examination of the materials containing 6 at.% niobium could not detect the presence of a second phase.

Figure 3a shows that the density curve for S_1 decreased in density. It is assumed that this decrease is related to the cracking detected after sintering. The cracking behavior may be the result of both a high rate of shrinkage, due to the low green density, and the induced strain associated with the phase transition. Hence, the greater the extent of cracking, the lower the density of a disk as determined by mercury displacement.

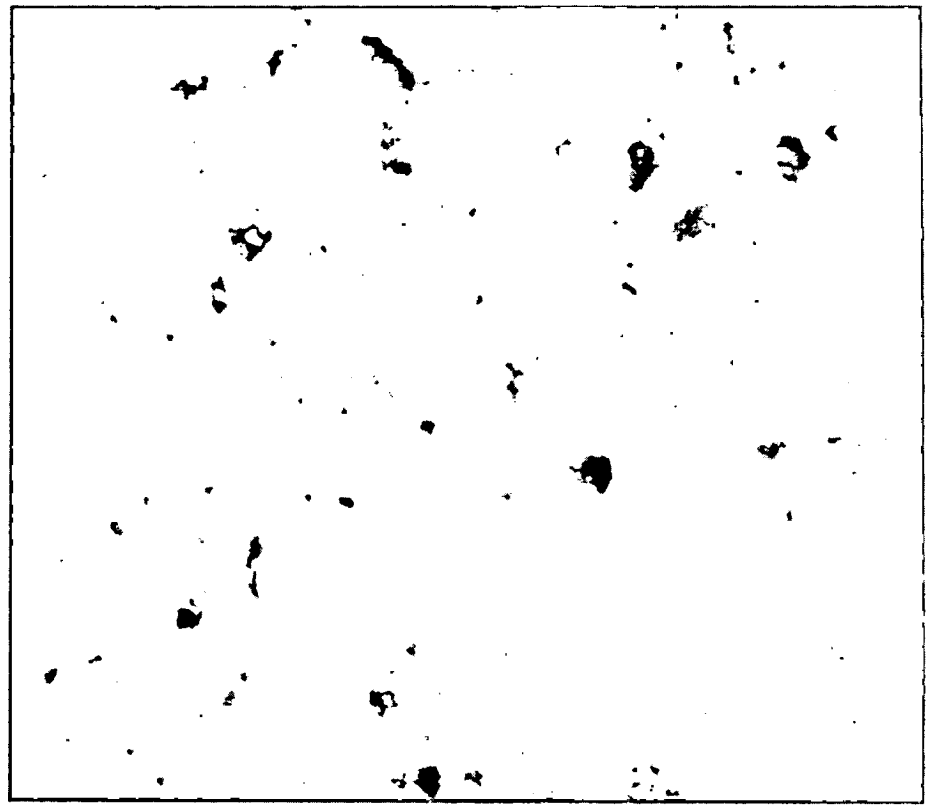
Figure 4a shows for S_3 and apparent density limitation. The density limit could be the result of pore coalescence which tends to develop from low green densities. Pore coalescence is the ability of local concentrations of pores to consolidate into larger pores. Bruch,[18] working with Al_2O_3 doped with MgO, demonstrated that pore coalescence or pore growth develops from a low green density. Another result of a low green density that leads to a density limitation is the development of fissures. Mansour and White[19] in their work on UO_2 showed that fissures can evolve from internal shrinkage in the compact. It may well be that both types of phenomenons are involved. However, from photomicrographs it is believed that pore growth is the dominate mechanism from a comparison of Figs. 9 and 10.

At the fast heating rate the S materials are noted to have obtained a higher density. This may be the result of a pore growth mechanism; the time involved for pores to coalesce was reduced during the heating



XBB 716-2243

Fig. 9. A polished surface of S_3 after sintering for one hour at 1200°C with a slow heating rate. (1500X, tilt 45°)



XBB 716-2347

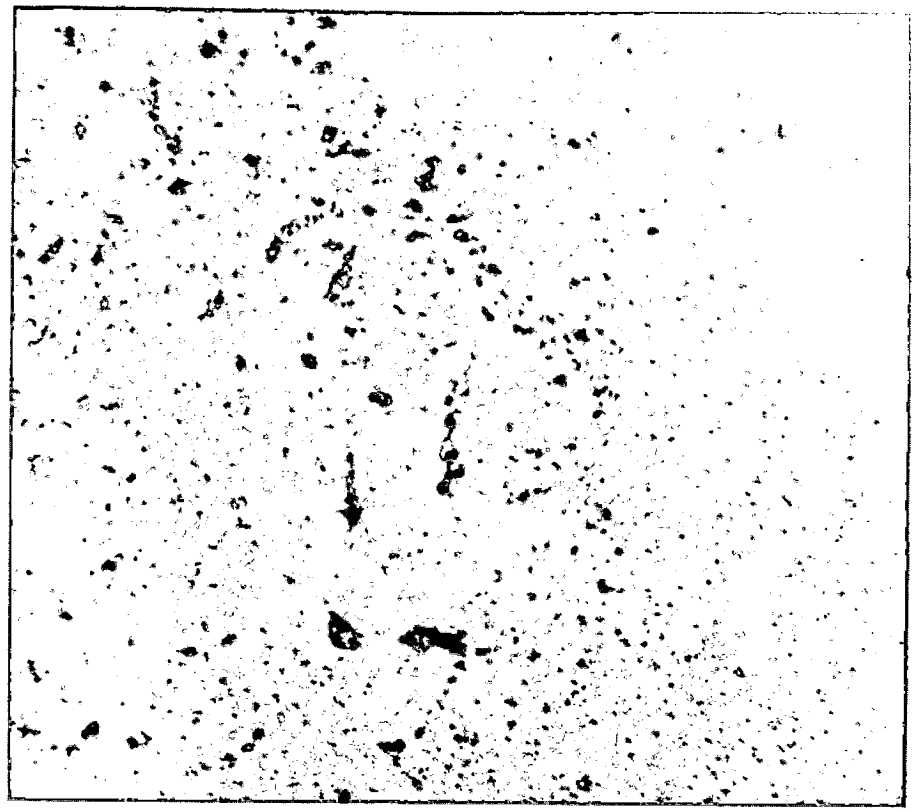
Fig. 10. A polished surface of S_3 after sintering for one hour at 1200°C with a fast heating rate. (1500X, tilt 45°)

cycle. Thus, the extent of pore growth is diminished, allowing more densification to occur. Figure 10 is a photomicrograph of the S_3 material at the same temperature and time as in Fig. 9. The comparison of the two figures shows that at the fast heating rate more of the pores are removed.

At the higher densities of S_3, some internal cracks were noticed. Consequently, there seems to be a correlation of internal cracking to the degree of densification. It is believed, therefore, that the density of S_1 at temperature is much higher than S_3. A possible explanation for the cracking effect may be due to a nonhomogeneous distribution of niobium that results in localized exaggerated grain growth. Thus, at the higher densities, the strain associated with the phase transformation at the Curie temperature develops stress gradients that lead to internal cracks.* If this is the case, then it follows that the homogeneity of S_3 is greater than S_1.

Figure 8 shows that a decrease in density with time is noted for S_3 which was pressed at 63,000 psi. A reason for this behavior may be the result of the remaining impurities in the powder after compaction. It is proposed, that while heating to temperature, the surface of a disk is at a higher temperature than the bulk. Hence, with the higher green density and the S material being an active powder, the sinterability of the surface was greater than the bulk. The open pore channels were first closed off at the surface; hence, the impurity gas in the bulk was essentially trapped. As the density limitation is reached, continued pore growth results in a density decrease from pore

* Preliminary experiments on cooling the S_1 disks through the Curie temperature within an electric field have eliminated all observable cracks.



XBB 716-2349

Fig. 11. A polished surface near the edge (right side of photomicrograph) of S_3 after sintering for one hour at 1200°C with a fast heating rate. The sample was pressed at 63,000 psi. (1500X)

expansion due to the gas exchange between pores.[20]

Figure 11 gives evidence of this assumption by showing that near the edge of the S_3 disk there is a region of low porosity that separates the very porous bulk region. Consequently, to achieve a high sintered density by increasing the green density, the heat treatment for the S powder at 300°C for one hour is not adequate.

B. Grain Growth Analysis

It is observed in both the S and L materials that the grain growth is decreased with increasing additions of niobium. The differences in the grain sizes of S and L for each niobium concentration is assumed to be the result of the incomplete solubility of niobium. As proposed in section A, the L particles may have a niobium rich surface layer; therefore, the surface layer can act as a limiting grain size inclusion. When inclusions are located on a grain boundary, the curvature of the boundary becomes insufficient for continued grain growth. The grains cannot grow until a limiting grain size is obtained given by the approximate equation:[21]

$$D_\ell \, \alpha \, \frac{d}{f}$$

D_ℓ = limiting grain size.

d = particle size of the inclusion.

f = volume fraction of the inclusions.

The grain growth curves for L_3 and L_6 tend to support this effect in that the grain size initially remains constant.

The grain growth curves for the S materials at the faster heating rate were noticeably different from those at the slower rate of heating. It is known that the presence of a solute can affect the grain boundary

mobility by different mechanisms. It has been shown by theoretical treatments[22-25] that the controlling mechanism in a given instant of time will depend on (a) the solute concentration, (b) the rate of boundary motion, and (c) the solute-boundary interaction energy.[11] The assumption is made that the heat rate may change the factors (b) and (c). Therefore, it is suggested that the observed differences in grain growth may lie in the switching from one controlling mechanism to another.

V. CONCLUSION

The densification, during the early stages of sintering, and grain growth of lead titanate are sensitive to the additions of niobium. The density and grain growth are both decreased with increasing niobium concentrations. Furthermore, because of the density decrease from the higher pressing pressure, the initial heat treatment of the chemically treated powder is insufficient. Further research on a favorable powder treatment before pressing is therefore necessary. Nevertheless, it is believed that the Sandia material has the potential as a high-purity submicron powder to produce a near theoretically dense sintered $PbTiO_3$ if optimum powder preparation techniques are used.

ACKNOWLEDGMENTS

The author wishes to thank Professor Richard M. Fulrath for his guidance in this work. Appreciation is expressed for helpful comments and criticism to Professor Thomas S. Mika, Dr. Robert Atkin, Robert Holman and Gautam Bandyopadhyay. Although Bob Powell had nothing to do with this work, I still would like to thank him for his interest.

I am also very grateful to Kelly Radmilovic, Bill Bullis, Neal Houlding, Jack Wodei, and George Georgakopoulos for their experimental assistance. Finally, I want to especially thank my wife, Karen, for her understanding and encouragements.

This work was done under the auspices of the United States Atomic Energy Commission.

REFERENCES

1. Gen Shirane and Sadao Hoshino, "On the Phase Transition in Lead Titanate," J. Phys. Soc. Japan, 6 [4] 265-70 (1951).
2. H. Jaffe and D. A. Berlincourt, "Piezoelectric Transducer Materials," Proc. IEEE, 53 [10] 1372-86 (1965).
3. Seiji Ikegami and Ichiro Ueda, "Mechanism of Aging in Polycrystalline $BaTiO_3$," J. Phys. Soc. Japan, 22 [3] 725-34 (1967).
4. E. D. Subbarao, "Studies on Lead Titanate Ceramics Containing Niobium or Tantalum," J. Am. Ceram. Soc., 43 [3] 119-22 (1960).
5. T.Y. Tien and W. G. Carlson, "Effect of Additives on Properties of Lead Titanate," J. Am. Ceram. Soc., 45 [12] 567-71 (1962).
6. Yoshihiro Matsuo, Masanori Fujimura, and Hiromu Sasaki, "Lead Titanate Ceramics Deoped with Manganese Oxide," J. Am. Ceram. Soc., Discussions and Notes, 48 [2] 111-12 (1965).
7. Ichiro Ueda and Seiji Ikegami, "Piezoelectric Properties of Modified $PbTiO_3$ Ceramics," Jap. J. App. Phys., 7 [3] 236-42 (1968).
8. J. E. Burke, "Role of Grain Boundaries in Sintering," J. Am. Ceram. Soc., 40 [3] 80-5 (1957).
9. W. A. Weyl, "Atomistic Interpretation of Mechanism of Solid State Reactions and of Sintering," Ceram. Age, 60 [5] 28-38 (1952).
10. R. B. Atkin, R. L. Holman, and Richard M. Fulrath, "Substitution of Bi and Nb Ions in Lead Zirconate-Titanate," J. Am. Ceram. Soc., 54 [2] 113-15 (1971).
11. P. J. Jorgensen and J. H. Westbrook, "Role of Solute Segregation at Grain Boundaries During Final-STage Sintering of Alumina," J. Am. Ceram. Soc., 47 [7] 332-38 (1964).
12. R. L. Coble, "Sintering Crystalline Solids: I, Intermediate and Final State Diffusion Models," J. Appl. Phys., 32 [5] 787-92 (1961).

13. K. S. Mazdiyasni, C. T. Lynch, and J. S. Smith, "Cublic Phase Stabilization of Translucent Yttria-Zirconia at Very Low Temperatures," J. Am. Ceram. Soc., 50 [10] 532-37 (1967).
14. K. S. Mazdiyasni, R. T. Dolloff, and J. S. Smith, "Preparation of High-Purity Submicron Barium Titanate Powders," J. Am. Ceram. Soc., 52 [10] 523-26 (1969).
15. H. C. Graham, N. M. Tallen, and K. S. Mazdiyasni, "Electrical Properties of High-Purity Polycrystalline Barium Titanate," Am. Ceram. Soc. Bull., 48 [4] 509 (1969).
16. R. Dosch, private communication.
17. P. J. Jorgensen, "Modification of Sintering Kinetics by Solute Segregation in Al_2O_3," J. Am. Ceram. Soc., 48 [4] 207-10 (1965).
18. C. A. Bruch, "Sintering Kinetics for the High Density Alumina Process," Am. Ceram. Soc. Bull., 41 [12] 799-806 (1962).
19. Nayla A. L. Mansour and J. White, "Causes of Residual Porosity in Sintered Uranium Dioxide," Powder Metallurgy, [12] 108-21 (1963).
20. R. L. Coble, "Sintering Alumina: Effect of Atmospheres," J. Am. Ceram. Soc., 45 [3] 123-27 (1962).
21. C. S. Smith, "Grains, Phases, and Interfaces: An Interpretation of Microstructure," Trans. AIME, 175, 15-51 (1948).
22. K. Lücke and K. Detert, "Quantitative Theory of Grain-Boundary Motion and Recrystallization in Metals in Presence of Impurities," Acta Met., 5 [11] 628-37 (1957).
23. E. S. Machlin, "Theory of Solute Atom Limited Grain Boundary Migration," Trans. AIME, 224 [11] 1153-67 (1962).
24. J. W. Cahn, "Impurity Drag Effect in Grain Boundary Motion," Acta Met., 10 [9] 789-98 (1962).

25. Paul Gordon and R. A. Wandermeer, "Mechanism of Boundary Migration in Recrystallization," Trans. AIME, 224 [9] 917-28 (1962).

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720