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Původní práce

THE EFFECT OF MnO_2 AND La_2O_3 ADDITIONS ON THE SINTERING OF $Pb(Zr, Ti)O_3$ SOLID SOLUTIONS

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The study revealed a substantial effect of non-compensated charged defects, resulting from the presence of heterovalent admixtures of MnO_2 *and* La_2O_3 *oxides, on the final microstructure following the sintering of solid solutions based on* $Pb(Zr, Ti)O_3$.

Solid solutions of $Pb(Zr, Ti)O_3$ *containing excess of charged point defects were found to be capable of sintering up to about 98 % of theoretical density. On the other hand, solid solutions based on* $Pb(Zr, Ti)O_3$ *free from heterovalent admixtures, or with electrically compensated admixtures of acceptor or donor type, showed extensive grain growth at sintering and were virtually uncapable of being sintered to an apparent density exceeding 95 % of theoretical density.*

INTRODUCTION

Sintering is one of the decisive technological processes which significantly influence the final physical properties of polycrystalline materials. This is also the case of ferroelectric solid solutions based on lead zirconate and lead titanate (briefly designated $Pb(Zr, Ti)O_3$) [1]—[3]. In spite of this fact, relatively little attention has so far been paid to the description of sintering of these materials in the literature. It may be due to a somewhat complex chemical composition of these materials and to the unclear principle of mass transfer during their sintering, which practically excludes the use of the generally known theoretical models and mathematical relations for describing the mechanism and kinetics of their sintering [4]—[7].

The present study was aimed at studying one of the important aspects influencing the sintering of $Pb(Zr, Ti)O_3$, namely to determining the effect of small amounts of manganese and lanthanium oxides on the development of microstructure of these solid solutions at sintering.

SAMPLE PREPARATION AND EXPERIMENTAL CONDITIONS

The following raw materials were used in the preparation of samples: lead oxide PbO A.R., zirconium dioxide containing 98.35 % ZrO_2 (by wt.), titanium dioxide containing 99.60 % TiO_2; the MnO_2 and La_2O_3 oxides were of A.R. purity and chemically pure, respectively.

The individual oxides were weighed in stoichiometric ratios listed in Table I with an accuracy better than 0.01 %, at total charges of about 150 g each. The stoichiometric mixtures of oxides were then homogenized by grinding for two hours in an agate planetary mill with agate grinding elements in an aqueous medium. After drying at 100 °C, the homogenized mixtures were heat treated ("calcined") in an electrical chamber furnace at 1000 °C for one hour. The reaction degree was checked by X-ray analysis. The resulting calcinates were ground for 5 hours in the same agate mill in an aqueous medium. The grain sizes of the ground calcinates varied in the range from 0.1 to 2 μm. The ground calcinates were then pressed into pellets of 14.3 mm in diameter and 3 mm in height. The pellets were sintered at 1280 °C with a dwelling time of 1 hour. In the course of sintering, the samples were placed in two platinum boxes (in one of which the specimens with MnO_2 were placed separately). To suppress volatilization of lead oxide from the specimens being sintered, the remaining space in the boxes was filled up with a powdered material having the composition $Pb(Zr_{0.60}Ti_{0.40})O_3$. Some other specimens were sintered under external pressure. This pressure sintering was carried out in a device of the author's own design at 1100 °C with a hold of 3 hours and under a pressure of 10 MPa on the faces of the specimens.

Apparent density of the sintered specimens was determined by the double weighing method or in the case of excessively porous specimens by calculation from the geometrical dimensions of the individual specimens and their weight. Some specimens were then broken up and their fracture surfaces were examined with the BS 300 electron scanning microscope (TESLA) at magnifications 500×, 2000× and 5000×.

RESULTS AND THEIR DISCUSSION

The compositions listed in Table I were chosen for studying the effect of MnO_2 and La_2O_3 additions on the sintering of solid solutions $Pb(Zr, Ti)O_3$. These oxides and their concentrations were intently chosen to include additions of the acceptor type, MnO_2, as well as of the donor type, La_2O_3. As it was indicated in [8]—[10], interaction of these additions with the lattice of $Pb(Zr, Ti)O_3$ can namely be schematically described by equations of the type:

Table I

The composition of the studied specimens and the apparent density values ϱ achieved at sintering

Specimen composition	ϱ, kg m^{-3}
$Pb(Zr_{0.60}Ti_{0.40})O_3$	7 178
$Pb(Zr_{0.60}Ti_{0.40})O_3 + 0.015\ MnO_2$	7 825
$Pb(Zr_{0.60}Ti_{0.40})O_3 + 0.015\ MnO_2 + 0.0025\ LaO_{1.5}$	7 726
$Pb(Zr_{0.60}Ti_{0.40})O_3 + 0.015\ MnO_2 + 0.0050\ LaO_{1.5}$	7 242
$Pb(Zr_{0.60}Ti_{0.40})O_3 + 0.015\ MnO_2 + 0.0075\ LaO_{1.5}$	6 687
$Pb(Zr_{0.60}Ti_{0.40})O_3 + 0.015\ MnO_2 + 0.015\ LaO_{1.5}$	6 600
$Pb(Zr_{0.60}Ti_{0.40})O_3 + 0.015\ MnO_2 + 0.030\ LaO_{1.5}$	7 225
$Pb(Zr_{0.60}Ti_{0.40})O_3 + 0.015\ MnO_2 + 0.045\ LaO_{1.5}$	7 821
$Pb(Zr_{0.60}Ti_{0.40})O_3 + 0.02\ LaO_{1.5}$	7 623

1. $Pb(Zr, Ti)O_3 + MnO_2 + PbO \rightarrow Pb(Zr, Ti, Mn^{+4})O_3$
2. $Pb(Zr, Ti)O_3 + MnO_2 + PbO \rightarrow Pb(Zr, Ti, Mn^{+3})O_3V_0 + O_2$
3. $Pb(Zr, Ti)O_3 + MnO_2 + PbO \rightarrow Pb(Zr, Ti, Mn^{+2})O_3V_0 + O_2$

4. $Pb(Zr, Ti)O_3 + LaO_{1.5} \rightarrow PbLaV_{Pb}(Zr, Ti)O_3 + PbO$, or even
5. $Pb(Zr, Ti)O_3 + LaO_{1.5} \rightarrow PbLaV_{Pb}(Zr, Ti, V_{Zr, Ti})O_3 + PbO$
6. $V_0 + 2\,h^+ \rightarrow V_0^{+2}$
7. $V_0 \rightarrow V_0^{+2} + 2\,e^-$
8. $V_{Pb} + 2\,e^- \rightarrow V_{Pb}^{-2}$
9. $V_{Pb} \rightarrow V_{Pb}^{-2} + 2\,h^+$

Figs. 1 through 5 show the micrographs of the fracture surfaces of $Pb(Zr_{0.60}Ti_{0.40})O_3$ with additions of 0.015 MnO_2 and y of $LaO_{1.5}$, where $y \in \langle 0; 0.045 \rangle$.

The given values of apparent density and the fracture surface micrographs imply that specimens with separate additions of both acceptor and donor-type admixtures, or those with an excess of one type of additions have grain sizes of about $2 \div 5$ μm. These specimens exhibit relatively high apparent densities (96 to 98 % of the density calculated from X-ray data, which amounts to 7992 kg m^{-3}) and a merely discontinuous residual porosity.

In contrast, those specimens of $Pb(Zr, Ti)O_3$, which had an approximately equal molar content of the two admixtures, showed a low apparent density after sintering (lower than 93 % of the calculated density), contained relatively large grains (up to 30 μm) and continuous porosity (their water absorption did exceed 1 %). The latter specimens show analogous microstructural properties as the specimens of $Pb(Zr, Ti)O_3$ free from any admixtures (cf. Fig. 6 and Table I). Both Table I and Fig. 7 indicate that even these specimens can be prepared with a high apparent density ($\geqq$ 99 % of calculated density), but solely by pressure sintering.

On the basis of the results obtained it may be assumed that as a result of introducing of additions of heterovalent impurities to $Pb(Zr, Ti)O_3$, which does imply to increas concentration of charged point defects, the mobility of the grain boundaries, is substantially suppressed at the sintering. Such phenomenon was studied in great detail at heterovalently doped polycrystalline aluminium oxide [13, 14] and the phenomenon was supposed to be involved in the sintering of $Pb(Zr, Ti)O_3$ doped with Al and Nb [15], too.

A comparison between the microstructural properties of $Pb(Zr, Ti)O_3$ specimens free from admixtures and the specimens which had an approximately equal molar content of both types of admixtures on one hand, and the microstructural properties of $Pb(Zr, Ti)O_3$ specimens with an excess of heterovalent admixtures on the other hand shows a dominant significance of the charged point defects relatively to the influence of the atomary aspects alone (such as geometrical conditions, electronegativity, etc.) in governing mass transport in the course of sintering of $Pb(Zr, Ti)O_3$ [11], [12].

The results of this experimental work have their important technical consequences. It has been namely found that the solid solutions of $Pb(Zr, Ti)O_3$ free from admixtures or those with "electrically compensated" admixtures of acceptor and donor type cannot be prepared with the required apparent density by sintering under normal pressure ($\geqq$ 95 % of theoretical density). However, sintering of such solid solutions is being very positively affected by pressure applied in the course of sintering, which allows to achieve the maximum apparent density also with these materials ($\geqq$ 99 % of theoretical density). It was further found that by proper adjusting the technological conditions at the preparation of the materials containing an excess of donor or acceptor admixtures (grinding, grain-size such as distribution, compacting, etc.) it is possible to achieve relatively readily apparent densities corresponding to about 98 % of theoretical density without applying pressure sintering.

However, even with these materials, pressure sintering markedly suppresses the dependence of microstructure quality on the other technological steps, and particularly reduces the occurrence of accidental pores and voids in the sintered materials.

CONCLUSION

It has been established that sintering and the resulting recrystallization and densification of Pb(Zr, Ti)O_3 compacts are strongly affected by an excess of acceptor or donor admixtures. This excess of one or the other type of admixture results in the suppression of the crystallization of Pb(Zr, Ti)O_3 in the course of sintering, while the sintered specimens exhibit high apparent densities (approx. 96—98 % of theoretical density) and the residual porosity is of the "non-communicating" type.

The effect of an excess of one type of admixture can be compensated by introducing admixtures of the opposite type (i.e. an excess of donors by an addition of acceptor, and vice versa). Sintered specimens of Pb(Zr, Ti)O_3 with "electrically compensated" additions of acceptor and donor types create relatively large grains (up to 30 μm), do achieve only low apparent density values ($>$ 90 %) and contain communicating porosity.

The studies also indicate the significance of pressure sintering in the preparation of materials based on Pb(Zr, Ti)O_3, in particular of those which do not contain any admixtures nor contain admixtures of acceptor or donor type in equal molar ratios.

The relationships established also apply to the introduction of acceptor admixtures of the type Fe_2O_3 and Cr_2O_3, and that of donor admixtures of the type Nb_2O_5 and Sb_2O_3, and their mutual combinations, to Pb(Zr, Ti)O_3. This will be the subject of further studies.

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VLIV PŘÍDAVKŮ MnO_2 A La_2O_3 NA SLINOVÁNÍ PEVNÝCH ROZTOKŮ $Pb(Zr, Ti)O_3$

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Práce je zaměřena na prostudování vlivu malých množství přídavků oxidů manganičitého a lanthanitého na výslednou mikrostrukturu pevných roztoků na bázi $PbZrO_3$—$PbTiO_3$ po slinování.

Studované vzorky, jejichž složení je uvedeno v tabulce I, byly připraveny běžnou keramickou technologií z oxidů PbO, ZrO_2, TiO_2, MnO_2 a La_2O_3.

Na základě studia snímků mikrostruktury lomových ploch připravených vzorků (viz obr. 1—8) a měření jejich objemové hmotnosti (tabulka I) a za předpokladů, uvedených v citovaných pracích, bylo zjištěno, že slinování a s tím spojená rekrystalizace a zhutnění kompaktů z $Pb(Zr, Ti)O_3$ jsou silně ovlivněny nadbytkem akceptorových anebo donorových příměsí. Tento nadbytek jedněch či druhých příměsí se projevuje potlačením rekrystalizace $Pb(Zr, Ti)O_3$ v průběhu slinování, přičemž slinuté vzorky vykazují vysoké objemové hmotnosti (přibližně 96—98 % teoretické hustoty) a pouze jen „nekomunikující“ zbytkovou pórovitost.

Vliv nadbytku příměsí jednoho typu lze vykompenzovat přídavkem příměsi opačného typu (tj. nadbytek donorů přídavkem akceptorů a naopak). Slinuté vzorky $Pb(Zr, Ti)O_3$ s „elektricky vykompenzovanými“ příměsemi akceptorového a donorového typu obsahují relativně velká zrna (až 30 μm), dosahují jen nízkých hodnot objemových hmotností (více jak 90 %) a obsahují komunikující pórovitost.

Z provedených prací vyplynul i význam tlakového slinování pro přípravu materiálů na bázi $Pb(Zr, Ti)O_3$, zejména těch, které neobsahují žádné příměsi anebo obsahují příměsi akceptorového a donorového typu ve stejném molárním poměru.

Pozorované zákonitosti platí i při zavádění akceptorových příměsí typu Fe_2O_3 a Cr_2O_3 a donorových příměsí typu Nb_2O_5 a Sb_2O_3 a jejich vzájemných kombinací do $Pb(Zr, Ti)O_3$.

Obr. 1. Snímek mikrostruktury lomové plochy vzorku se složením $Pb(Zr_{0,60}\,Ti_{0,40})O_3 + 0{,}015\,MnO_2$.

Obr. 2. Snímek mikrostruktury lomové plochy vzorku se složením $Pb(Zr_{0,60}\,Ti_{0,40})O_3 + 0{,}015\,MnO_2 + 0{,}0050\,LaO_{1,5}$.

Obr. 3. Snímek mikrostruktury lomové plochy vzorku se složením $Pb(Zr_{0,60}\,Ti_{0,40})O_3 + 0{,}015\,MnO_2 + 0{,}015\,LaO_{1,5}$.

Obr. 4. Snímek mikrostruktury lomové plochy vzorku se složením $Pb(Zr_{0,60}\,Ti_{0,40})O_3 + 0{,}015\,MnO_2 + 0{,}030\,LaO_{1,5}$.

Obr. 5. Snímek mikrostruktury lomové plochy vzorku se složením $Pb(Zr_{0,60}\,Ti_{0,40})O_3 + 0{,}015\,MnO_2 + 0{,}045\,LaO_{1,5}$.

Obr. 6. Snímek mikrostruktury lomové plochy vzorku $Pb(Zr_{0,60}\,Ti_{0,40})O_3$ *bez příměsí* MnO_2 *a* La_2O_3.

Obr. 7. Snímek mikrostruktury lomové plochy tlakově slinovaného vzorku se složením $Pb(Zr_{0,60}Ti_{0,40}) + 0{,}015\,MnO_2 + 0{,}015\,LaO_{1,5}$. *Tlakové slinování tohoto vzorku bylo provedeno při teplotě 1100 °C po dobu 1 hodiny při tlaku 10 MPa s následující temperací při 1000 °C po dobu 2 hodin.*

ВЛИЯНИЕ ДОБАВОК MnO_2 И La_2O_3 НА СПЕКАНИЕ ТВЕРДЫХ РАСТВОРОВ $Pb(Zr, Ti)O_3$

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Автор в работе сосредоточил свое внимание на рассмотрение влияния небольших количеств добавок оксидов четырехвалентного марганца и трехвалентного лантана на окончательную микроструктуру твердых растворов на базе $PbZrO_3$—$PbTiO_3$ после спекания.

Исследуемые образцы, состав которых приводится в таблице I, были приготовлены обыкновенной керамической технологией из оксидов PbO, ZrO_2, TiO_2, MnO_2 и La_2O_3.

На основании исследования съемок микроструктуры поверхностей излома приготовленных образцов (см. рис. 1—8) и измерения их объемного веса (табл. I) и при предположениях, приводимых в цитируемых работах, было установлено, что на спекание и с ним связанную рекристаллизацию и уплотнение компактов из Pb/Zr, Ti/O_3 сильное влияние оказывает избыток акцепторных или донорных примесей. Данный избыток тех или других примесей проявляется подавлением рекристаллизации Pb(Zr, Ti)O_3 во время спекания, причем спекшиеся образцы имеют высокий объемный вес (приблизительно 96—98 % теоретической плотности) и только „некомуникирующую" избыточную пористость.

Влияние избытка примесей одного типа можно компенсировать добавкой примесей другого типа (т. е. избыток доноров добавкой акцепторов и наоборот). Спекшиеся образцы Pb(Zr, Ti)O_3 с „электрически компенсированными" примесями акцепторного и донорного типов содержат относительно большие зерна (до 30 μм), достигают только низких величин объемного веса (больше чем 90 %) и содержат комуникирующую пористость.

Из проведенных работ вытекает также и значение спекания под давлением для приготовления материалов на базе Pb(Zr, Ti)O_3, именно тех, которые не содержат никаких примесей или содержат примеси акцепторного и донорного типов в одинаковом молярном отношении.

Наблюдаемые закономерности справедливы также при введении акцепторных примесей типа Fe_2O_3 и Cr_2O_3 и донорных примесей типа Nb_2O_5 и Sb_2O_3 и их взаимных комбинаций в Pb(Zr, Ti)O_3.

Рис. 1. Съемка микроструктуры поверхности излома образца составом $Pb(Zr_{0,60}Ti_{0,40})O_3 + 0,015\ MnO_2$.

Рис. 3. Съемка микроструктуры поверхности излома образца составом $Po(Zr_{0,60}Ti_{0,40})O_3 + 0,015\ MnO_2 + 0,0050\ LaO_{1,5}$.

Рис. 4. Съемка микроструктуры поверхности излома образца составом $Pb(Zr_{0,60}Ti_{0,40})O_3 + 0,015\ MnO_2 + 0,030\ LaO_{1,5}$.

Рис. 5. Съемка микроструктуры поверхности излома образца составом $Pb(Zr_{0,60}Ti_{0,40})O_3 + 0,015\ MnO_2 + 0,045\ LaO_{1,5}$.

Рис. 6. Съемка микроструктуры поверхности излома образца составом $Pb(Zr_{0,60}Ti_{0,40})O_3$ *ьез примесей* MnO_2 *и* La_2O_3.

Рис. 7. Съемка микроструктуры поверхности излома спекаемого под давлением образца составом $Pb(Zr_{0,60}Ti_{0,40}) + 0,015\ MnO_2 + 0,015\ LaO_{1,5}$.

Спекание под давлением данного образца проводили при температуре 1 100 °C во время 1 часа под давлением 10 МПа с последующим темперированием при 1 000 °C во время 2 часов.

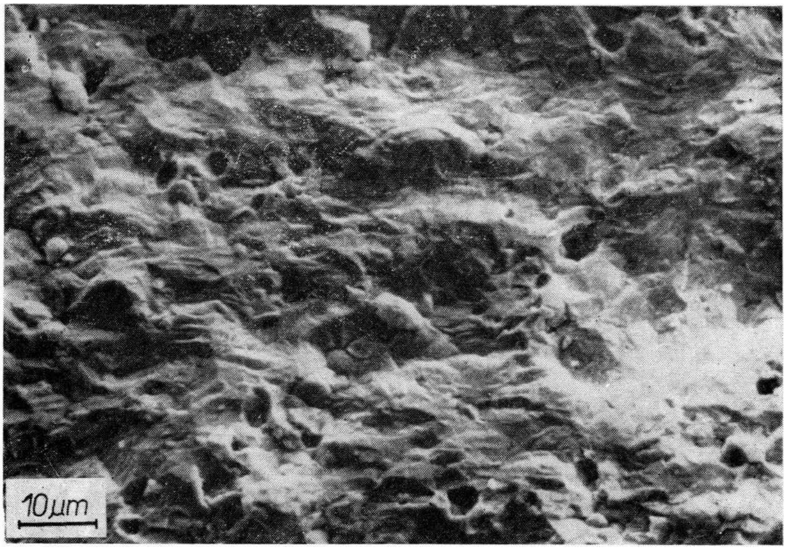

Fig. 1. Microstructure of the fracture surface of a specimen having the composition $Pb(Zr_{0.60}Ti_{0.40})O_3 + 0.015\ MnO_2$.

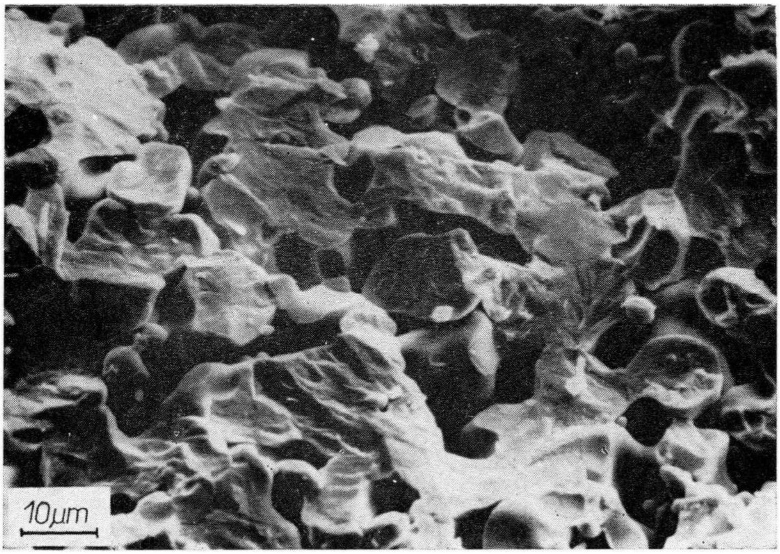

Fig. 2. Microstructure of the fracture surface of a specimen having the composition $Pb(Zr_{0.60}Ti_{0.40})O_3 + 0.015\ MnO_2 + 0.005\ LaO_{1.5}$.

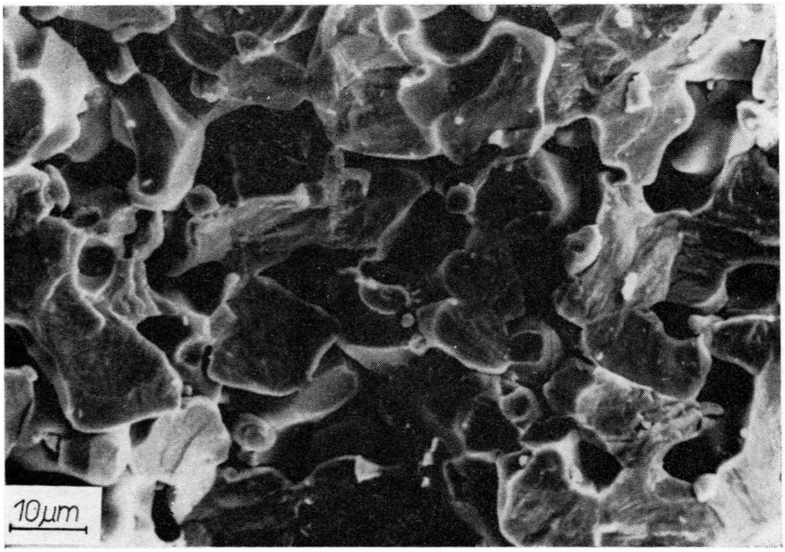

Fig. 3. Microstructure of the fracture surface of a specimen having the composition $Pb(Zr_{0.60}Ti_{0.40})O_3 + 0.015\ MnO_2 + 0.015\ LaO_{1.5}$.

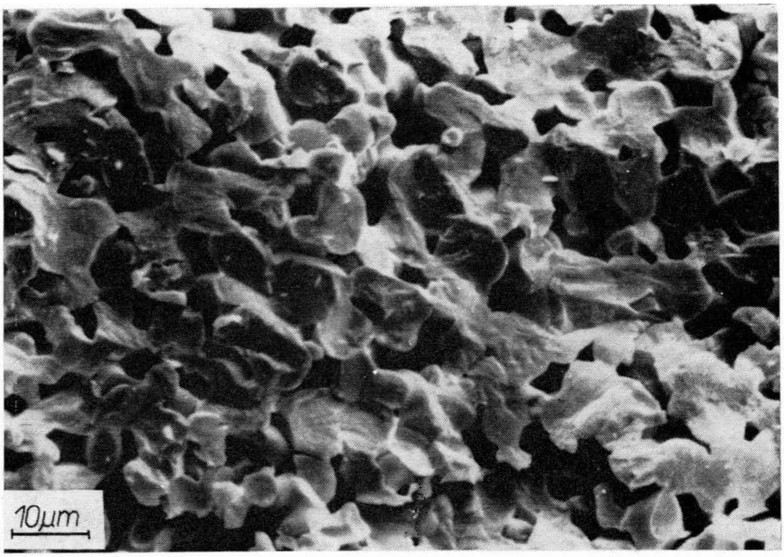

Fig. 4. Microstructure of the fracture surface of a specimen having the composition $Pb(Zr_{0.60}Ti_{0.40})O_3 + 0.015\ MnO_2 + 0.030\ LaO_{1.5}$.

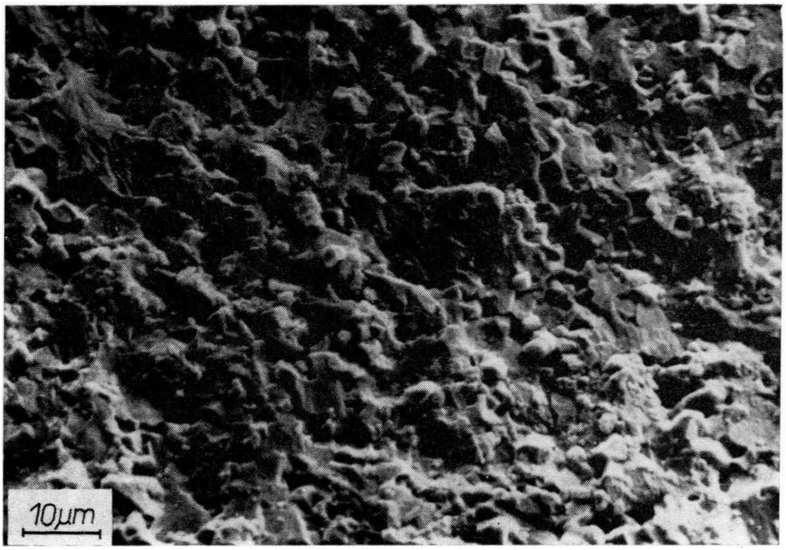

Fig. 5. Microstructure of the fracture surface of a specimen having the composition $Pb(Zr_{0.60}Ti_{0.40})O_3 + 0.015\ InO_2 + 0.045\ LaO_{1.5}$.

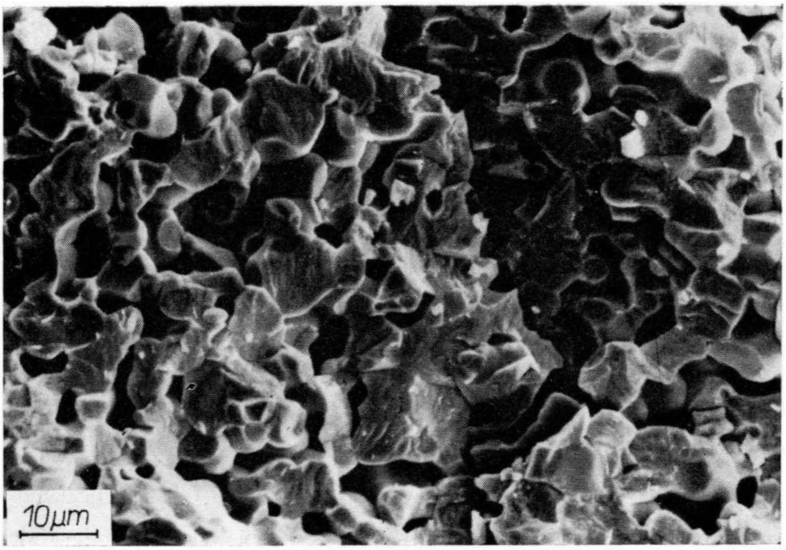

Fig. 6. Microstructure of the fracture surface of a specimen having the composition $Pb(Zr_{0.60}Ti_{0.40})O_3$ *free from* MnO_2 *and* La_2O_3 *admixtures.*

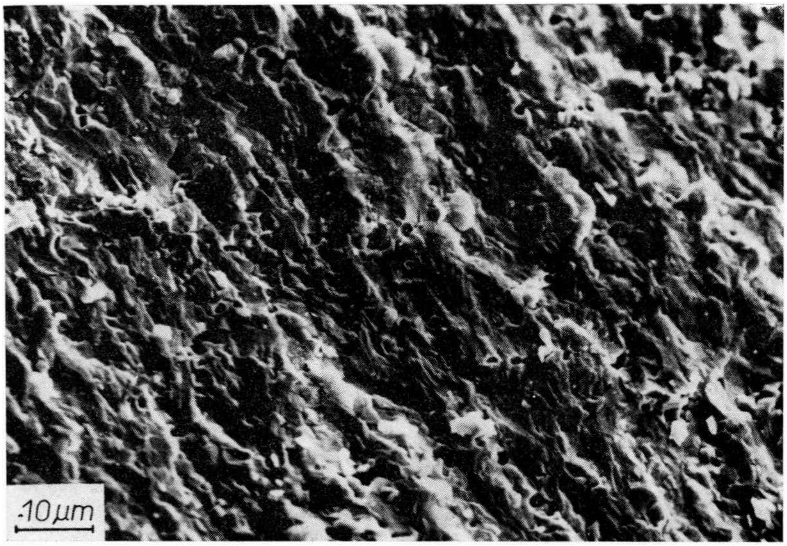

Fig. 7. Microstructure of the fracture surface of a pressure-sintered specimen having the composition $Pb(Zr_{0.60}Ti_{0.40})O_3 + 0.015\ MnO_2 + 0.015\ LaO_{1.5}$. *Pressure-sintered at 1100 °C for 1 hour under a pressure of 10 MPa with subsequent tempering at 1000 °C for 2 hours.*