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PHASE COMPOSITION OF PIEZOCERAMICS BASED ON MANGANESE—DOPED SOLID SOLUTIONS $Pb(Mg_{1/3}Nb_{2/3})TiZrO_3$

KAREL NEJEZCHLEB, MIROSLAV BOUDYŠ

Research Institute of Electrotechnical Ceramics, Pospíšilova 281, 500 64 Hradec Králové

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X-ray structural analysis and X-ray spectral microanalysis have proved a heterogeneous phase structure of piezoceramics based on MnO_2 *doped solid solutions* $Pb(Mg_{1/3}Nb_{2/3})TiZrO_3$. *According to the sintering conditions, the ceramics contains, beside the perovskite phase, also the pyrochloric phase* ($Pb_2Nb_2O_7$) *and phases in which the* Mg, Mn *and* Ti *elements are concentrated. A lower* PbO *content in sintered samples leads to a greater inhomogeneity of compostition, but also to a higher density of the sintered specimens. Relationships are pointed out between the mutual distribution of the perovskite and pyrochloric phases, apparent density and temperature and time stability of the properties of the system in question.*

INTRODUCTION

Most of the commercial piezoceramics are based on $PbTiO_3—PbZrO_3$ solid solutions. For the preparation of piezoceramic transducers with desired properties it is possible to choose a solid solution composition within a wide range, or to dope this solid solution with suitable admixtures, in particular oxides of transient metals [1].

The possibilities for the preparation of new types of piezoceramics were further expanded on the basis of the studies by Smolenskij [2] who has synthetized a series of perovskite lead compounds, in which the tetravalent Ti^{4+} or Zr^{4+} ions are substituted by couples of ions, of which one has its valency lower and the other higher than four. In the formulas of these compounds, Pb $(Me_i^u Me_j^w)O_3$, Me_i is a mono, bi or trivalent cation, Me_j is a pentavalent or hexavalent cation. The stoichiometric coefficients u and w comply with the condition of electroneutrality. Compounds of this type form solid solutions with $PbTiO_3$ and $PbZrO_3$.

Ouchi [3, 4] utilized the advantageous properties of solid solutions $Pb(Mg_{\frac{1}{3}}Nb_{\frac{2}{3}})\,O_3$ $—PbTiO_3—PbZrO_3$ for the preparation of new types of piezoceramics. By doping the solid solutions in this system with manganese oxide he prepared piezoceramic transducers with a high temperature and time resonance frequency stability, and high mechanical quality factor values. These transducers have found wide application in electronics in the construction of frequency filters.

In contrast to the materials based on $PbTiO_3—PbZrO_3$ solid solutions, for which the real phase composition of sintered specimens was carefully studied in terms of the sintering conditions [5, 6, 7], the phase composition of materials based on the system $Pb(Mg_{1/3}Nb_{2/3})TiZrO_3$ has not so far been investigated in greater detail. Ouchi [8] just states that synthesis of these materials from a mixture of oxides involves, as an intermediate stage, formation of the compound $Pb_2Nb_2O_7$ having a pyrochloric structure. This compound arises at 600 to 650 °C and may also be contained in sintered samples. The following reaction is probably taking place during the preparation of materials from the given system:

$$Pb_2Nb_2O_7 + PbO + MgO \rightleftharpoons Pb(Mg_{1/3}Nb_{2/3})O_3 \qquad (1)$$

The present work has the aim to determine the phase composition in the sintered samples of the very significant manganese oxide-doped system $Pb(Mg_{1/3}Nb_{2/3})O_3$—$PbTiO_3$—$PbZrO_3$. Another task was to establish the relationship between phase composition and the conditions of sintering for this system. In addition to this, the study deals with the relationship between phase composition and the attainable densification of specimens on sintering firing. In connection with the phase composition established, the discussion presents a possible explanation for the improved temperature and time stability of the materials in the system $Pb(Mg_{1/3}Nb_{2/3})O_3$—$PbTiO_3$—$PbZrO_3$ doped with manganese oxide.

EXPERIMENTAL

The properties of a material having the composition $Pb(Mg_{\frac{1}{3}}Nb_{\frac{2}{3}})_{0.44}Ti_{0.44}Zr_{0.12}O_3$, doped suprastoichiometrically with 1.0 wt. % MnO_2 were studied. The composition of the material, which is suitable for the preparation of stable piezoceramics, is indicated by point *F* in the phase diagram of the system x mole % $Pb\,Mg_{1/3}Nb_{2/3}\,O_3$ + y mole % $PbTiO_3$ + z mole % $PbZrO_3$ [8] in Fig. 1.

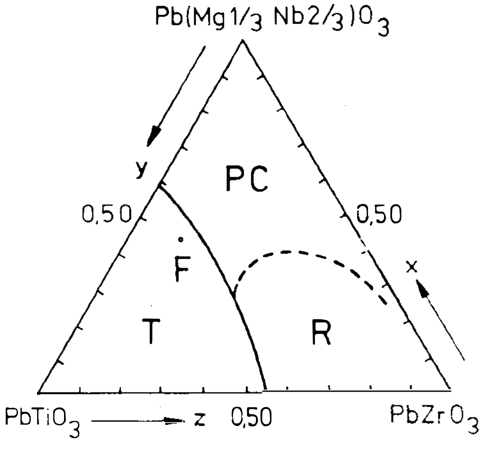

Fig. 1. Phase diagram of the system $Pb(Mg_{1/3}Nb_{2/3})O_3$—$PbTiO_3$—$PbZrO_3$; *T — tetragonal phase, R — rhombohedral phase, PC — pseudocubic phase (The composition studied is marked by point F).*

The material was prepared by standard ceramic technology from a mixture of PbO, MgO, Nb_2O_5, TiO_2 and ZrO_2 of stoichiometric composition and using the addition of MnO_2 mentioned. The procedure of the preparation was described in the authors' previous papers [6, 7].

The sintering at 1280 °C for the period of one hour was carried out at various vapour pressures of PbO. This has been adjusted by means of compacts having the composition $PbTi_{1-u}Zr_uO_3$ with excess ZrO_2, which had been added to the sintering case. (In the system the pressure of PbO vapours decreases with increasing Ti content.) In the instance that the pressure of PbO vapours in the sintering case was higher than the equilibral partial pressure of PbO above the sample, the lead oxide diffused into the specimens being sintered, and vice versa. These changes in composition can be assessed from the changes in weight of the sintered specimens. In this way it was possible to obtain samples with an increased, a decreased or an unchanged their weight because of sintering.

The X-ray structural analysis was performed on powdered samples using the Kristallflex 4 apparatus by Siemens with K_α radiation of the copper anticathode. The mutual distributin of phases in sintered specimens was studied by X-ray spectral microanalysis using the JXA-5A Jeol microanalyser. The method employed in the X-ray analysis was described in the previous papers [6, 7].

RESULTS AND THEIR EVALUATION

The initial proportions of the mixture of oxides, PbO, MgO, Nb_2O_5, TiO and ZrO_2 corresponds to the stoichiometric composition of the solid solution $Pb(Mg_{1/3}Nb_{2/3})_{0.44}Ti_{0.44}Zr_{0.12}O_3$. At high temperatures, during calcination and sintering, a solid solution should be formed and the doping Mn ion should be built up into its crystal lattice. The considerable variability of the valency of manganese in its oxides at high temperatures was one of the reasons why the mechanism of its dissolution in solid solutions of perovskite lead compounds has not been explicitly explained [9, 10]. Manganese may probably dissolve in these solutions as Mn^{2+}, Mn^{3+} and possibly also Mn^{4+}, while the radii of these ions lead to an assumption of the substitution of Ti^{4+} or Zr^{4+} by manganese ions. For the simplest case of $PbTiO_3$, these substitutions can be expressed by equations, for instance

$$PbTiO_3 + x\,MnO + x\,PbO \rightleftharpoons Pb_{1+x}TiMn''_xO_{3+2x}V''_x \qquad (2)$$

$$PbTiO_3 + x\,MnO_2 + x\,PbO \rightleftharpoons Pb_{1+x}TiMn_xO_{3+3x} \qquad (3)$$

According to these equations, the doping addition of manganese oxides should be compensated for by a PbO addition at the molar ratio of 1 : 1, otherwise the solid solution would partially dissociate and a new phase would form. The material being sintered, of course, may take the required amount of PbO from the atmosphere of PbO vapours which surrounds the specimen. When the required amount of PbO has not been introduced directly into the reaction mixture and when neglecting the changes in weight due to transition of MnO_2 to lower manganese oxides, the dissolving of an addition of 1 wt. % MnO_2 should involve an increase in weight of sintered specimens by 2.7 % (in terms of their initial weight).

The possibilities for substitution of manganese ions in $Pb(Mg_{1/3}Nb_{2/3})O_3$ are still greater; however, it should likewise be assumed that the doping addition of MnO_2 is compensated by lead oxide during dissolution.

As mentioned above the superstoichiometric addition of MnO_2 in the given mixture of oxides was not compensated and its reactions at high temperatures may be assumed to produce further phases. For this purpose, in the way described in the experimental section, specimens were prepared in which sintering resulted in an increase in the weight (sample 2), a decrease in weight (sample 3) and a specimen whose weight remained constant (sample 1).

Figs. 2a through 2f show the pattern of reflected electron intensity distribution

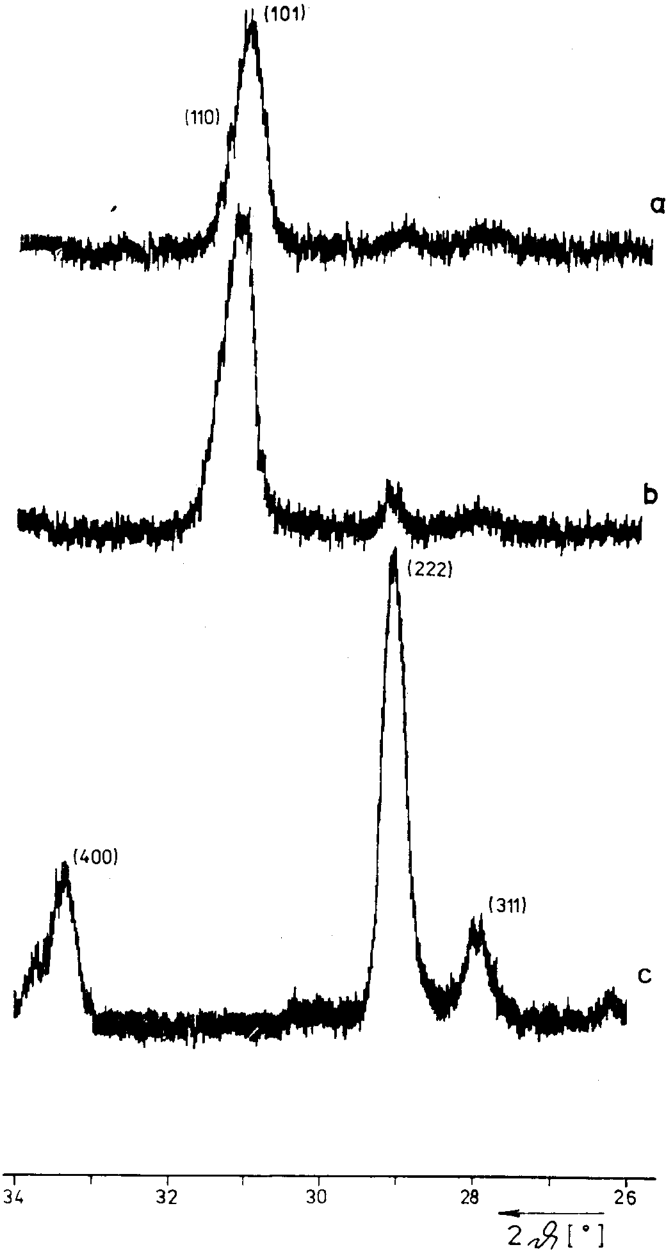

Fig. 3. X-ray patterns of samples 1 (a), 3 (b) and X-ray pattern of the compound $Pb_2Nb_2O_7$ *(c).*

from sample 1 and the distribution of X-ray fluorescence radiation distribution (Mg_{K_α}, Mn_{K_α}, Ti_{K_α}, Zr_{L_α}, Nb_{L_α}) over the same sample area. Since no change in weight has taken place during the sintering of sample 1, it may be assumed that the PbO content is equal to its content in the initial mixture.

The prevailing type of phase, which appears as a light-shaded area in Fig. 2a, contains Pb and may be assumed to be solid solution with the perovskite structure. In addition to this the specimen comprises a phase which, according to Figs. 2b, c, d, contains Mg, Mn and Ti, or Mg only (the particles at the left top edge of the micrograph) and does not contain Nb nor Zr (Figs. 2e, 2f) and likewiese does not contain Pb, because the phase appears to be dark in micrograph 2a. Similarly to Mg, Nb, Ti, Zr, the doping Mn is also present in the prevailing perovskite phase.

The presence of Mg-containing grains indicates that according to equation (1) the specimens studied should contain the compound $Pb_2Nb_2O_7$ with a pyrochloric structure. Fig. 3a, c shows a comparison of the X-ray patterns of sample 1 and of the compound $Pb_2Nb_2O_7$. The line of $Pb_2Nb_2O_7$ of the highest intensity (222) is situated at $d = 3.0727$. Although there is a certain indication of a line on the X-ray pattern of sample 1 at this d value, the presence of $Pb_2Nb_2O_7$ cannot be proved explicitly. The content of this compound is obviously under the sensitivity limit of the X-ray structural analysis employed.

Figs. 4a, b, c and d show the patterns of intensity distribution of electrons reflected from the surface of sample 2 characterized by an increase in weight by 2.0 % due to sintering; the intensity distribution of X-ray fluorescence radiation (Mg_{K_α}, Mn_{K_α}, and Ti_{K_α}) over this area is also shown. Fig. 4d allows to assume that an increase in PbO content was responsible for a decrease in Ti content in the phase, which with specimen 1 contains Mg, Mn and Ti. Manganese is concentrated in some of the grains of this phase only. A considerable proportion of grains in this phase are probably composed of magnesium oxide.

The increase in weight of sample 2 by 2.0 % due to sintering is close to the increase in weight required according to equations (2, 3) for the formation of the solid solution and complete dissolution of manganese. Complete suppression of the phase containing Mg, Mn and Ti would obviously require sintering at a high pressure of PbO vapours which would diffuse into the specimens being sintered in amounts greater to those contained in sample 2. The presence of grains containing solely Mg in sample 2 then indicates that the reacting of MgO in the initial oxide mixtures, according to equation (1), is the most difficult one and obviously requires the highest temperatures.

According to equations (2), (3), an increase in the PbO content leads to a decrease in the content of minority phases, but simultaneously has a negative effect on the course of sintering. Whereas at sample 1 the apparent density $\varrho = 7.65$ g/cm^3, at sample 2 this density reached only 7.21 g/cm^3.

The maximum apparent density values have been achieved with samples from which PbO had partially volatilized in the course of sintering, and which have lost their weight at sintering. However, in these instances the heterogeneous composition has also become markedly more distinct.

Fig. 3b shows the X-ray pattern of sample 3, whose weight decreased by 3.1 % by sintering ($\varrho = 7.73$ g/cm^3). According to Fig. 3b, the sample contains the pyrochloric phase in a distinct concentration. As a result of PbO volatilization, there increased the content of a phase in which Mg, Mn and Ti are concentrated, as shown by Figs. 5a, b, c, d and e.

However, the Pb-containing phase shown in Fig. 5a, b is not quite homogeneous. Micrograph 5a shows the presence of light-shaded grains. The surroundings of the grains are somewhat darker, thus containg Pb in lower concentrations. These inhomogeneities are more distinctly shown in pattern 5f, taken at a greater contrast. Two phases are therefore in fact involved. Fig. 6a indicates that the phase appearing dark in the high contrast micrograph contains higher amounts of Ti and lower amounts of Nb than the „light-shaded“ grains. A confrontation of the result of X-ray analysis (Figs. 3b, c) indicates that these grains can be assumed to be the perivskite phase. This phase is surrounded by the pyrochloric phase. According to semiquantitative analysis, the doping Mn is present both in the perovskite and in the pyrochloric phase. However, its content is about 1.5 times higher in the former.

Notice:

A geometrical distortion results from high-contrast taking of X-ray spectral microanalysis micrographs. According to Birks [11] the high contrast may result in an apparent increase in the sizes of small specimen grains. For example, the sizes of grains in Fig. 5f are considerably distorted compared to Fig. 5a. For this reason the grain sizes in Figs. 5f, 6a, b cannot be regarded as actual.

The results of X-ray structural analysis and X-ray spectral microanalysis indicate that the piezoceramics based on MnO_2-doped solid solutions $Pb(Mg_{1/3}Nb_{2/3})TiZrO_3$ has a heterogeneous structure and generally contains three phases. In dependence on PbO content, the ceramics contains, apart from a perovskite phase, also a pyrochloric phase consisting of the compound $Pb_2Nb_2O_7$, and an additional phase, in which the elements Mg, Mn and Ti are concentrated. The last phase is probably composed of magnesium oxide or compounds containing MgO, MnO_2 and TiO_2. The content of Mn and Ti in this phase increases when the total PbO content is decreased.

A lower pressure of PbO vapours on sintering and the resulting lower PbO content in sintered specimens leads to a greater inhomogeneity of composition; however, the apparent density of the sintered specimens increases.

According to the phase diagram of the system $PbO-Nb_2O_5$ [12] the melting point of $Pb_2Nb_2O_7$ is at 1230 °C, that is within the sintering interval of these materials. It may therefore be assumed that the sintering proceeds in the presence of the liquid phase of $Pb_2Nb_2O_7$, which assists in the attainment of a high apparent density.

The X-ray spectral micrograms indicate that the pyrochloric phase, uniformly surrounding the grains of the perivskite phase, can be regarded as an intergranular phase. As assumed by Heywang [13] and by Okazaki [14], the presence of an intergranular phase in piezoceramics (ferroelectric) materials, which include the system in question, has a profound effect on their properties. According to Heywang, the spontaneous polarization of the individual grains of the perovskite phase is compensated by charges trapped in the intergranular phase. As a result of this charge compensation and the consequent stabilization of the existing state, the properties of peizoceramics are then more stable in terms of both temperature and time [13, 14].

In view of the ideas expressed by Heywang and Okazaki, the siutable mutual distribution of the peroskite and pyrochloric phases established in the present study, and the differring contents of doping manganese in these phases are the cause of the high temperature and time stability of the properties of these materials.

CONCLUSION

The results of the present work have shown that piezoceramics based on MnO_2—doped solid solutions $Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3-PbZrO_3$ have a heterogeneous structure. Sintered specimens may contain three phases: the majority perovskite phase, the minority pyrochloric phase consisting of the compound $Pb_2Nb_2O_7$, and an additional minority phase, in which the elements Mg, Mn and Ti are concentrated. The mutual ratio of these phases can be controlled by adjusting the pressure of PbO vapours in the course of sintering. A lower pressure of PbO vapours on sintering leads to an increased content of the minority phases and to an increase in apparent density of the sintered specimens.

The sintering processes and the improved stability of properties of the solid and an additional minority phase, in which the elements Mg, Mn and Ti are concentrated. The mutual ratio of these phases can be controlled by adjusting the pressure of PbO vapours in the course of sintering. A lower pressure of PbO vapours on sintering leads to an increased content of the minority phases and to an increase in apparent density of the sintered specimens.

The sintering processes and the improved stability of properties of the solid solution in terms of time and temperature can be considered to be most significantly influenced by the mutual distribution of the perovskite and the pyrochloric phases. Since the pyrochloric phase is regarded as an intergranular one which is in liquid state at the sintering temperatures, it may be assumed to facilitate sintering and promote attainment of a high apparent density of sintered specimens. It may also be assumed that this advantageous distribution of the perovskite and pyrochloric phases creates conditions for charge compensation of the spontaneous polarization of the ferroelectric perovskite phase, and in this way, according to Heywang's and Okazaki's ideas, it improves the time and temperature stability of properties of the material being studied.

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K. Nejezchleb, M. Boudyš:

FÁZOVÉ SLOŽENÍ PIEZOKERAMIKY NA BÁZI PEVNÝCH ROZTOKŮ $Pb(Mg_{1/3}Nb_{2/3})$ $TiZrO_3$ DOTOVANÉ MANGANEM

Karel Nejezchleb, Miroslav Boudyš

Výzkumný ústav elektrotechnické keramiky, 500 64 Hradec Králové

V práci je sledováno fázové složení piezokeramiky na bázi pevných roztoků $Pb(Mn_{1/3}Nb_{2/3})$ O_3—$PbTiO_3$—$PbZrO_3$ dotovaných MnO_2. Tato piezokeramika díky vysoké teplotní a časové stabilitě svých vlastností a vysokým hodnotám činitele mechanické jakosti nalezla široké uplatnění v elektronice při konstrukci frekvenčních filtrů. Metodou rtg. strukturní analýzy a rtg. spektrální mikroanalýzy bylo zjištěno, že studovaná piezokeramika má heterogenní strukturu a může obsahovat tři fáze: majoritní perovskitovou, minoritní pyrochlorovou tvořenou sloučeninou $Pb_2Nb_2O_7$ a další minoritní fázi, v níž jsou koncentrovány prvky Mg, Mn a Ti (obr. 2, 3, 4). Bylo ukázáno, že vzájemný poměr těchto fází je možno ovládat tenzí par PbO při slinování. Nižší tenze par PbO při slinování se projevuje zvýšením obsahu minoritních fází (obr. 3). Zvýšení obsahu pyrochlorové fáze je spojeno se zvýšením objemové hmotnosti slinutých vzorků.

Pro vysvětlení slinovacích procesů a zvýšení časové a teplotní stability vlastností studovaného pevného roztoku se jeví jako nejzávažnější zjištěné vzájemné rozložení perovskitové a pyrochlorové fáze. Snímky rtg. spektrální mikroanalýzy ukázaly, že feroelektrickou perovskitovou fázi rovnoměrně obklopuje fáze pyrochlorová (obr. 5, 6), kterou tak můžeme považovat za fázi integranulární. Vzhledem k tomu, že pyrochlorová fáze je při slinovacích teplotách v kapalném stavu, je možno předpokládat, že přítomnost minoritní pyrochlorové fáze usnadňuje slinování a umožňuje tak dosažení vysoké objemové hmotnosti slinutých vzorků.

Zvýšení časové a teplotní stability vlastností studovaného systému je spojeno rovněž s existencí intergranulární fáze. Spontánní polarizace jednotlivých zrn perovskitové fáze je kompenzována náboji zachycenými v integranulární fázi; v důsledku této nábojové kompenzace, a tedy v důsledku stabilizace existujícího stavu, jsou pak vlastnosti piezokeramiky teplotně a časově stabilní.

Obr. 1. Stavový diagram systému $Pb(Mg_{1/3}Nb_{2/3})O_3$—$PbTiO_3$—$PbZrO_3$; *T — tetragonální fáze R — romboedrická fáze, PC — pseudokubická fáze. (Sledované složení je vyznačeno bodem F).*

Obr. 2. Rozložení intenzity odražených elektronů od plochy vzorku 1 (a). Rozložení intenzity rtg. fluorescenčního záření $Mg_{K\alpha}$ *(b);* $Mn_{K\alpha}$ *(c);* $Ti_{K\alpha}$ *(d);* $Zr_{L\alpha}$*(e);* $Nb_{L\alpha}$ *(f) na ploše vzorku 1. (Zvětšení 600×).*

Obr. 3. Rentgenogramy vzorků 1 (a), 3 (b) a rentgenogram sloučeniny $Pb_2Nb_2O_7$ *(c).*

Obr. 4. Rozložení intenzity odražených elektronů od plochy vzorku 2 (a). Rozložení intenzity rtg. fluorescenčního záření $Mg_{K\alpha}$ *(b);* $Mn_{K\alpha}$ *(c);* $Ti_{K\alpha}$ *(d); na ploše vzorku 2. (Zvětšeno 600×).*

Obr. 5. Rozložení intenzity odražených elektronů od plochy vzorku 3; zvětšeno 300× (a); zvětšeno 600× (b). Rozložení intenzity rtg. fluorescenčního záření $Mg_{K\alpha}$ *(c),* $Mn_{K\alpha}$ *(d),* $Ti_{K\alpha}$ *(e). Zvětšení 600×. Rozložení intenzity odražených elektronů od plochy vzorku 3 (f). Kontrastní zobrazení. Zvětšení 300×.*

Obr. 6. Rozložení intenzity rtg. fluorescenčního záření $Nb_{L\alpha}$ *(a),* $Ti_{K\alpha}$ *(b) podél vyznačené přímky. (Zvětšeno 1200×, kontrastní zobrazení).*

СОСТАВ ФАЗ ПИЕЗОКЕРАМИКИ НА БАЗЕ ТВЕРДЫХ РАСТВОРОВ $Pb(Mg_{1/3}Nb_{2/3})TiZrO_3$ С ДОБАВКОЙ МАРГАНЦА

Карел Неезхлеб, Мирослав Боудыш
Научно-исследовательский институт электротехнической керамики,
500 64 Градец-Кралове

В работе исследуется фазовый состав пиезокерамики на базе твердых растворов $Pb(Mg_{1/3}Nb_{2/3})O_3 — PbTiO_3 — PbZrO_3$ с добавкой MnO_2. Данная пиезокерамика благодаря высокой температурной и временной стойкости своих свойств и высоким величинам коэффициента механического качества находит широкое применение в электронике при конструкции частотных фильтров. С помощью рентгенографического структурного анализа и рентгенографического спектрального микроанализа установили, что исследуемая пиезокерамика имеет гетерогенную структуру и может содержать три фазы: мажоритарную перовскитовую, миноритную пирохлоровую, состоящую из соединений $Pb_2Nb_2O_7$ и дальнейшую миноритную фазу, в которой концентрируются элементы Mg, Mn и Ti (рис. 2, 3, 4). Было доказано, что взаимным отношением данных фаз можно управлять при помощи давления паров PbO при спекании. Более низкое давление паров PbO при спекании проявляется повышением содержания миноритных фаз (рис. 3). Повышение содержания пирохлоровой фазы связано с повышением объемного веса спекшихся образцов.

Для объяснения процессов спекания и повышения временной и температурной устойчивости свойств исследуемого твердого раствора оказывается наиболее важным установленное взаимное распределение перовскитовой и пирохлоровой фаз. Съемки рентгеновского спектрального микроанализа показывают, что фероэлектрическую перовскитовую фазу равномерно окружает пирохлоровая фаза (рис. 5, 6), которую таким образом можно считать интергранулярной фазой. В виду того, что пирохлоровая фаза при температурах спекания находится в жидком состоянии, можно предполагать, что присутствие миноритной пирохлоровой фазы помогает спеканию и таким образом можно получать высокий объемный вес спекшихся образцов.

Повышение временной и температурной стойкости свойств исследуемой системы связано также со существованием интегранулярной фазы — спонтанная поляризация отдельных зерен перовскитовой фазы компенсируется зарядами, задерживаемыми в интергранулярной фазе; в результате приводимой компенсации заряда, а следовательно стабилизации существующего состояния становятся свойства пиезокерамики по отношению к температуре и времени стойкими.

Рис. 1. Фазовая диаграмма системы $Pb(Mg_{1/3}Nb_{2/3})O_3 — PbTO_3 — PbZrO_3$; *T — тетрагональная фаза, R — ромбоэдрическая фаза, PC — псевдокубическая фаза (Исследуемый состав обозначен через F).*

Рис. 2. Распределение интенсивности отраженных электронов от поверхности образца 1 (a). Распределение интенсивности ренгеновской флуоресценции $Mg_{K\alpha}$ *(b);* $Mn_{K\alpha}$ *(c);* $Ti_{K\alpha}$ *(d);* $Zr_{L\alpha}$ *(e);* $Nb_{L\alpha}$ *(f) на поверхности образца 1. Увеличение 600 раз.*

Рис. 3. Рентгенограммы образцов 1 (a), 3 (b) и рентгенограмма соединения $Pb_2Nb_2O_7$ *(c).*

Рис. 4. Распределение интенсивности отраженных электронов от поверхности образца 2 (a). Распределение интенсивности рентгеновской флуоресценции $Mg_{K\alpha}$ *(b);* $Mn_{K\alpha}$ *(c);* $Ti_{K\alpha}$ *(d); на поверхности образца 2. Увеличение 600 раз.*

Рис. 5. Распределение интенсивности отраженный электронов от поверхности образца 3; увеличение 300 раз (a); увеличение 600 раз (b). Распределение интенсивности рентгеновской флуоресценции $Mg_{K\alpha}$ *(c),* $Mn_{K\alpha}$ *(d),* $Ti_{K\alpha}$ *(e). Увеличение 600 раз. Распределение интенсивности отраженных электронов от поверхности образца 3 (f). Контрастное изображение. Увеличение 300 раз.*

Рис. 6. Распределение интенсивности рентгеновской флуоресценции $Nb_{L\alpha}$ *(a),* $Ti_{K\alpha}$ *(b) вдоль обозначенной прямой. Увеличение 1200 раз, контрастное изображение.*

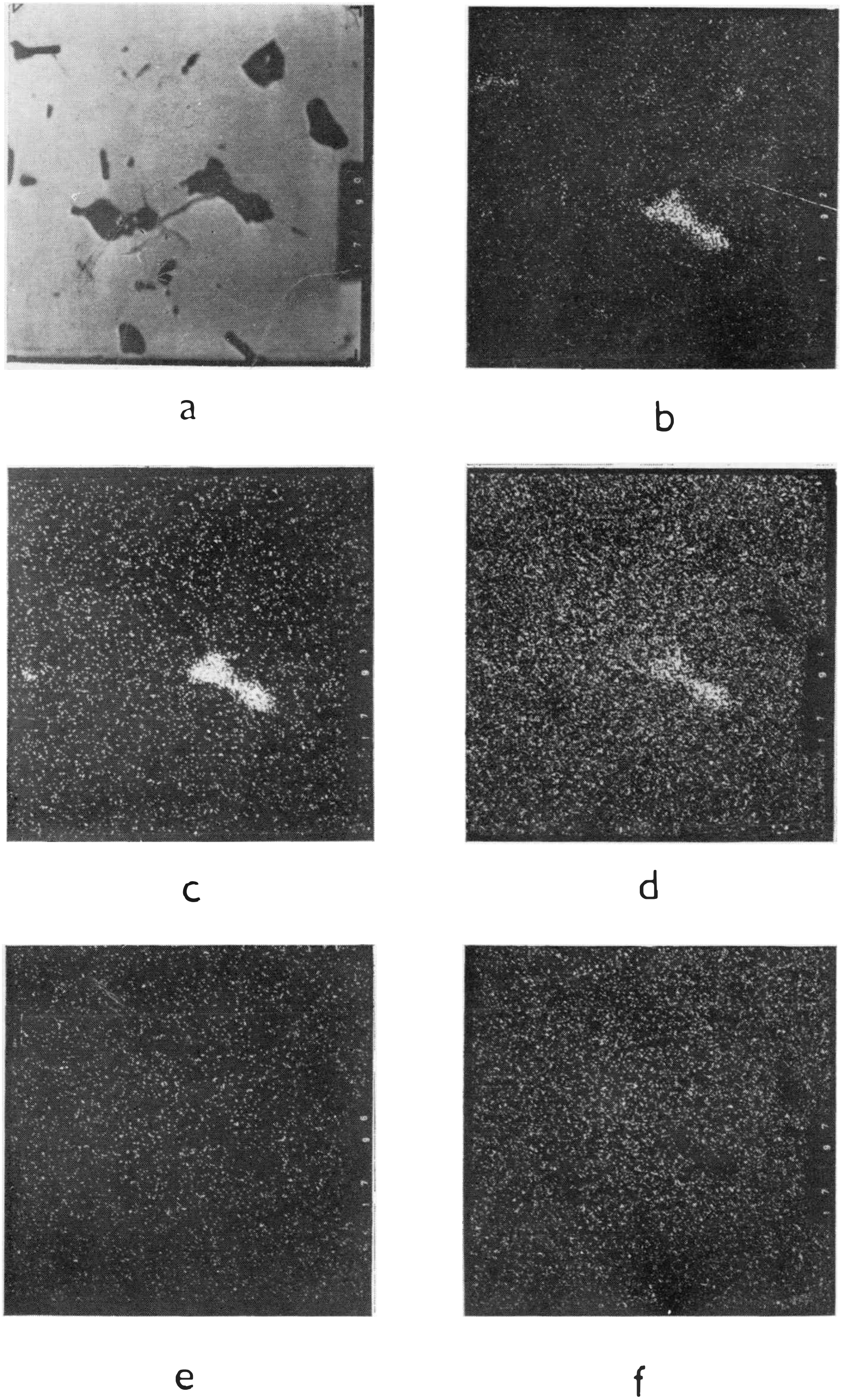
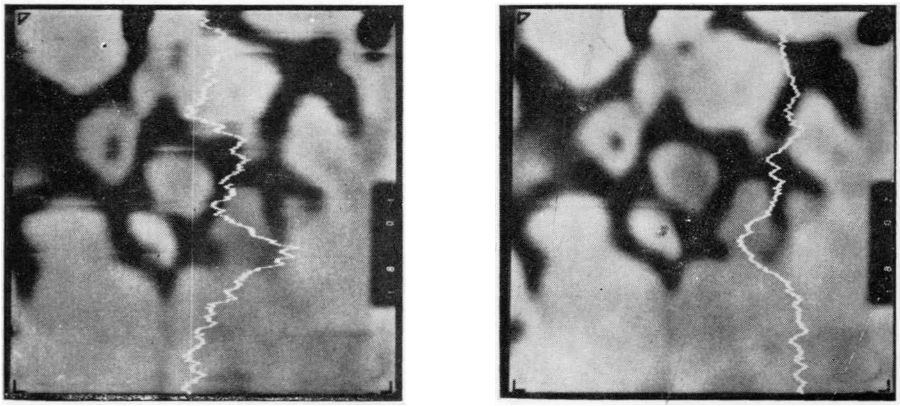


Fig. 2. Intensity distribution of electrons reflected from an area of sample 1 (a).



a

b

Fig. 6. Intensity distribution of X-ray fluorescence radiation $\mathrm{Nb}_{L\alpha}$ *(a),* $\mathrm{Ti}_{K\alpha}$ *(b) along the indicated line. (Magn. 1200×, high-contrast exposure).*