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Interactions between RuO_2 and PZT material

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Abstract

The compatibility between RuO_2 based electrodes and PZT films was investigated by firing mixtures of RuO_2 and PZT. The reaction resulted in the formation of $Pb_2Ru_2O_{6.5}$ pyrochlore. Subsolidus equilibria in air in the RuO_2–PbO–ZrO_2 systems were studied with the aim of obtaining some information on interactions between the RuO_2 and PZT materials. No ternary compound was found in the system. The tie lines are between $Pb_2Ru_2O_{6.5}$ and ZrO_2, and between $Pb_2Ru_2O_{6.5}$ and $PbZrO_3$. The obtained results confirmed that RuO_2 reacts with PZT forming $Pb_2Ru_2O_{6.5}$.

Keywords: Electron microscopy; Phase equilibria; Powders: solid state reaction; PZT; X-ray methods

1. Introduction

Ferroelectric ceramic materials based on solid solutions of Pb(Zr,Ti)O_3 (PZT) are used in the electronics industry for sensors and actuators and for electromechanical transducers, to name just a few examples. The characteristics of these solid solutions depend on chemical composition, processing parameters, microstructure, etc. Significant part of the research in this field is aimed at the development and characterisation of PZT thin films. Thin films may be deposited on substrates by various techniques, for example sputtering, evaporation, sol–gel process, etc. In most cases, platinum is used for the electrodes, due to its stability in an oxidising atmosphere during the preparation of the piezoelectric layer. Data in the literature indicate that some characteristics of PZT films can be improved with the use of RuO_2-based electrodes instead of Pt electrodes.[1,2] The published results are reported mainly for thin-film structures, where the highest annealing temperatures are limited to relatively low values, 600–700°C, and the possible interactions on the RuO_2/PZT interface do not proceed significantly. However, the high leakage current, observed in some cases with RuO_2 electrodes, was attributed to the possible formation of conducting pyrochlores, e.g. $Pb_2Ru_2O_{7-x}$ or $Pb_2(Ru,Zr,Ti)O_{7-x}$.[3]

For some applications, for example as sensors or electrophoretic printing, PZT based thick films are screen printed and fired on Al_2O_3 substrates.[4–8] Thick-film technology, i.e. the deposition of thick-film pastes by screen printing, is a relatively simple and convenient method for producing thicker layers with thicknesses up to 100 μm. The characteristics of thick-film ferroelectrics are similar to the characteristics of bulk materials. In addition, thick films are fired at higher temperatures than thin films, i.e. around or over 1000°C, thus increasing the possibility of interactions either with the electrodes or substrates and the consequent degradation of properties.

In this work, some results on the compatibility of RuO_2 and PZT will be given. Phase equilibria in the PbO–ZrO_2–RuO_2 system, which suggest some of the possible interactions between RuO_2 and PZT, will be presented. The results would confirm possible interactions between a RuO_2-based electrode and either ZrO_2 or PbO from PZT materials.

Phase equilibria in the RuO_2–PbO and RuO_2–ZrO_2 systems have been studied by Hrovat et al.[9,10] The pyrochlore $Pb_2Ru_2O_{6.5}$ compound exists in the RuO_2–PbO system.[11] The eutectic composition is around 95 % PbO and the eutectic temperature is 875°C. The RuO_2–ZrO_2 system is "empty"; there is no binary compound and no liquid phase (eutectic) at temperatures up to 1405°C, the temperature at which RuO_2 decomposes (in air) to metallic ruthenium and oxygen. The binary compound $PbZrO_3$ in the PbO–ZrO_2 system melts incongruently at 1570°C. The melting point of the eutectic is at 838°C.[12]

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2. Experimental

For the experimental work, RuO_2 (Ventron, 99.9%), PbO (Merck, 99.9%), ZrO_2 (Ventron, 99.9%) and TiO_2 (Fluka, 99%) were used. Oxides were mixed in isopropyl alcohol, pressed into pellets, and fired. During firing the pellets were placed on platinum foils. Compositions were repeatedly fired at the highest temperature with intermediate grinding. PZT with the composition $Pb(Ti_{0.5}Zr_{0.5})O_3$, perovskite $PbZrO_3$ and pyrochlore $Pb_2Ru_2O_{6.5}$ were synthesised by prefiring the mixtures of oxides at 850°C and by repeated firing at 900°C (PZT and $PbZrO_3$) and 950°C ($Pb_2Ru_2O_{6.5}$). Compositions in the RuO_2–PbO–ZrO_2 system were prefired at 850°C and fired up to five times in air at 950°C with intermediate grinding. The exceptions were compositions in the PbO-rich part of system which were fired at 850°C. The compositions of the relevant samples in the RuO_2–PbO–ZrO_2 system are shown in Fig. 5. Some samples were also prepared from pre-reacted $Pb_2Ru_2O_{6.5}$ and/or $PbZrO_3$, and oxides.

The fired materials were characterised by X-ray powder diffraction analysis (XRD) using a Philips PW 1710 X-ray diffractometer with CuK_α radiation. X-ray spectra were measured from $2\Theta = 20°$ to $2\Theta = 70°$ in steps of 0.02°. A JEOL 5800 scanning electron microscope (SEM) equipped with a ISIS 300 energy-dispersive X-ray analyser (EDX) was used for overall microstructural and compositional analysis. Samples prepared for the SEM were mounted in epoxy in a cross-sectional orientation and then polished using standard metallographic techniques. Prior to analysis in the SEM, the samples were coated with carbon to provide electrical conductivity and avoid charging effects.

3. Results and discussion

The XRD spectrum of the mixture of prereacted PZT and RuO_2, fired at 950°C, is presented in Fig. 1. Besides the peaks of unreacted PZT and RuO_2, new peaks appeared. These peaks can be attributed to the $Pb_2Ru_2O_{6.5}$ pyrochlore. The formation of $Pb_2Ru_2O_{6.5}$ was also confirmed with SEM and EDX analyses of the sample, which is shown in Fig. 2. The large white grains are $Pb_2Ru_2O_{6.5}$ while the matrix is a mixture of unreacted RuO_2 and PZT. The results indicate a reaction between RuO_2 and PZT.

The results of the X-ray powder analysis of the relevant samples in the RuO_2–PbO–ZrO_2 system, fired in air, are summarised in Table 1. The numbers of the samples in Table 1 correspond to the numbers marked in the phase diagram in Fig. 5. Nominal compositions of the samples and the phases identified after firing are provided.

The microstructures of materials with nominal compositions $RuO_2 + PbO + ZrO_2$ and $2\ RuO_2 + PbO + 2\ ZrO_2$, fired at 950°C, are shown in Figs. 3 and 4,

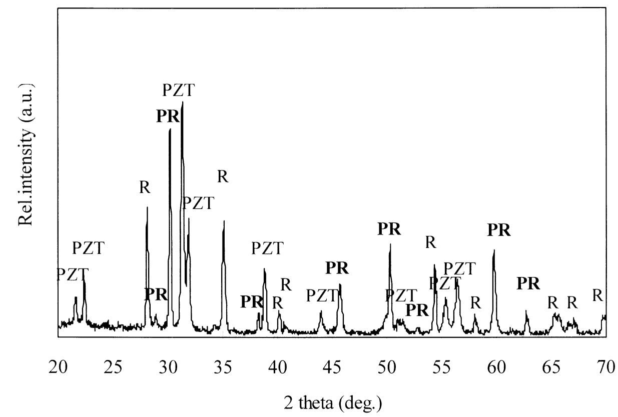

Fig. 1. XRD spectrum of the mixture of RuO_2 and prereacted PZT, fired at 950°C. Peaks of $Pb_2Ru_2O_{6.5}$, RuO_2 and PZT are denoted "PR", "R" and "PZT", respectively.

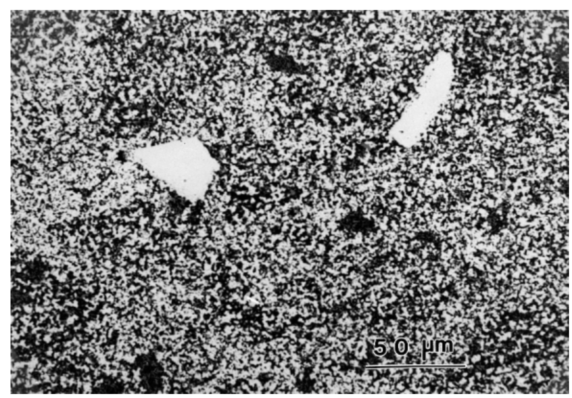

Fig. 2. The microstructure of the mixture of RuO_2 and prereacted PZT, fired at 950°C. Larger white grains are $Pb_2Ru_2O_{6.5}$ and the matrix is a mixture of unreacted RuO_2 and PZT.

Table 1
Results of X-ray diffraction analyses of some compositions in the RuO_2–PbO–ZrO_2 system

No.	Nominal composition	Phases identified
1	$2\ PbO + RuO_2 + ZrO_2$	$Pb_2Ru_2O_{6.5} + PbZrO_3$
1′ [a]	$2\ PbO + RuO_2 + ZrO_2$	$Pb_2Ru_2O_{6.5} + PbZrO_3$
2	$PbO + RuO_2 + ZrO_2$	$Pb_2Ru_2O_{6.5} + ZrO_2$
2′ [b]	$PbO + RuO_2 + ZrO_2$	$Pb_2Ru_2O_{6.5} + ZrO_2$
2″ [b]	$PbO + RuO_2 + ZrO_2$	$Pb_2Ru_2O_{6.5} + ZrO_2$
3	$42.5\ PbO + 15\ RuO_2 + 42.5\ ZrO_2$	$Pb_2Ru_2O_{6.5} + PbZrO_3 + ZrO_2$
4	$PbO + 2\ RuO_2 + 2\ ZrO_2$	$Pb_2Ru_2O_{6.5} + RuO_2 + ZrO_2$
5	$PbO + 3\ RuO_2 + ZrO_2$	$Pb_2Ru_2O_{6.5} + RuO_2 + ZrO_2$
6	$14\ PbO + 3\ RuO_2 + 3\ ZrO_2$	$Pb_2Ru_2O_{6.5} + PbZrO_3 + PbO$

[a] Composition 1′ was prepared from prereacted $Pb_2Ru_2O_{6.5}$ and $PbZrO_3$

[b] Compositions 2′ and 2″ were prepared from a prereacted $Pb_2Ru_2O_{6.5}$ compound and ZrO_2, and from a prereacted $PbZrO_3$ compound and RuO_2, respectively.

respectively. The sample with nominal composition $RuO_2 + PbO + ZrO_2$ is a two-phase mixture of $Pb_2Ru_2O_{6.5}$ (light grains) and ZrO_2 (darker phase). The sample with the nominal composition $2\ RuO_2 + PbO + 2\ ZrO_2$

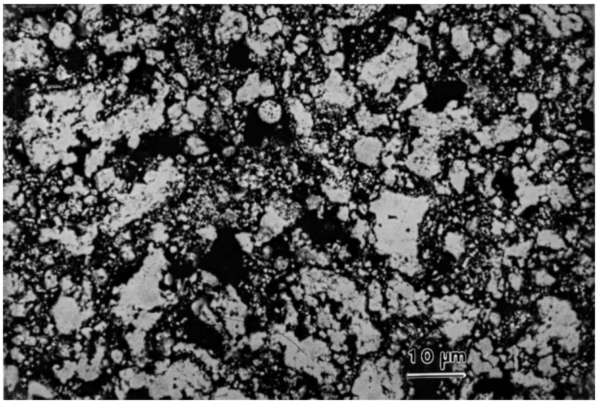

Fig. 3. The microstructure of the sample with nominal composition $RuO_2 + PbO + ZrO_2$, fired at 950°C. The material is a two-phase mixture of $Pb_2Ru_2O_{6.5}$ (light grains) and ZrO_2 (darker phase).

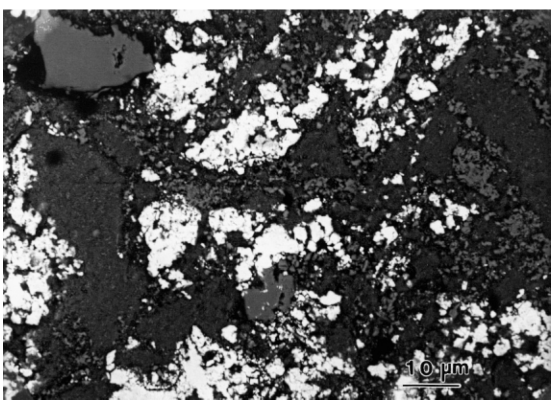

Fig. 4. The microstructure of the sample with nominal composition 2 $RuO_2 + PbO + 2\ ZrO_2$, fired at 950°C. The material is a three-phase mixture of light grey RuO_2 grains, light $Pb_2Ru_2O_{6.5}$ phase and dark ZrO_2.

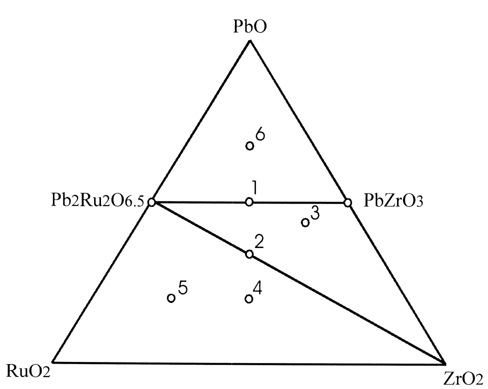

Fig. 5. The proposed subsolidus ternary phase diagram of the RuO_2–PbO–ZrO_2 system in air. The tie lines are between $Pb_2Ru_2O_{6.5}$ and ZrO_2, and between $Pb_2Ru_2O_{6.5}$ and $PbZrO_3$.

is a three-phase mixture of light grey RuO_2 grains, light $Pb_2Ru_2O_{6.5}$ grains and dark-fine grained ZrO_2. EDX micro-analysis showed around 3% of solid solubility of PbO in ZrO_2.

Based on the results obtained by XRD and EDX, a subsolidus RuO_2–PbO–ZrO_2 diagram, shown in Fig. 5, was constructed. The solid solution of around 3% of PbO in ZrO_2 is not shown in the diagram. No ternary compound was found. The tie lines are between $Pb_2Ru_2O_{6.5}$ and ZrO_2, and between $Pb_2Ru_2O_{6.5}$ and $PbZrO_3$.

4. Conclusions

The preliminary data on compatibility between RuO_2 and PZT material were obtained by firing mixtures of RuO_2 and PZT in air. Results of XRD, SEM and EDX analyses showed the formation of $Pb_2Ru_2O_{6.5}$. Subsolidus phase equilibria (in air) in the RuO_2–PbO–ZrO_2 system were studied. No ternary compound was found in the system. The tie lines are between $Pb_2Ru_2O_{6.5}$ and ZrO_2, and between $Pb_2Ru_2O_{6.5}$ and $PbZrO_3$. The obtained results confirmed that the RuO_2 reacts with PZT forming the $Pb_2Ru_2O_{6.5}$ pyrochlore. These reactions could lead to the decomposition of PZT material at the electrode/PZT film interface.

Acknowledgements

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