JOURNAL OF MATERIALS SCIENCE **35** (2000) 1725– 1728

Preliminary data on compatibility between thick film perovskite electrodes and PLZT films

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The possible use of electrically conductive perovskites $SrRuO_3$, $La(Ni_{0.6}Co_{0.4})O_3$ and $(La_{0.5}Ca_{0.5})FeO_{3-y}$ as electrodes for PLZT ((Pb,La)(Ti,Zr)O_3 solid solutions) thick films was evaluated. As the ceramic electrode is placed between an alumina substrate and a PLZT thick film layer possible interactions between Al_2O_3 on one side and PLZT on the other and the chosen perovkites were studied. Both $SrRuO_3$ and $LaNi_{0.6}Co_{0.4}O_3$ reacted at 1000°C with Al_2O_3 forming $SrAl_2O_4$ and RuO_2 in the first case and $LaAlO_3$ and La_2NiO_4 in the second case. At higher firing temperatures reactions between $La_{0.5}Ca_{0.5}FeO_3$ and Al_2O_3 resulted in small quantities of an unknown phase or phases. The results of reactions of all three perovskites with PLZT were perovskite solid solutions incorporating ions from the conducting perovskites into the PLZT structure.

Today's piezoelectric ceramic materials are mainly based on Pb(Ti,Zr)O_3 (PZT) or modified solid solutions, for example (Pb,La)(Ti,Zr)O_3 (PLZT). These materials are easily polarised and, depending on composition, possess a wide range of suitable characteristics. For some applications, for example as sensors, PZT or PLZT thick films are screen printed and fired on Al_2O_3 substrates [1–5]. In most cases platinum is used for the electrodes due to its stability in an oxidising atmosphere during preparation of the piezoelectric layer.

Most piezoelectric materials have perovskite or perovskite-like structures. For some applications either conductive oxides (e.g. RuO_2) or conductive perovskite materials, e.g. $LaCoO_3$, $LaNiO_3$ or $SrRuO_3$, are used for electrodes, mainly in thin film structures [6–12].

In this work the possible use of the perovskites $SrRuO_3$, $La(Ni_{0.6}Co_{0.4})O_3$ and $(La_{0.5}Ca_{0.5})FeO_{3-y}$ as electrodes for PLZT thick film was evaluated. All three are good electrical conductors. The specific resistivity of $SrRuO_3$ is around 250 uohm·cm for single crystals and a few mohm·cm for thin films [13, 14]. The resistivity of $(La_{0.5}Ca_{0.5})FeO_{3-y}$ is, at 100 mohm·cm, nearly four orders of magnitude lower than the resistivity of unsubstituted $LaFeO_3$ [15]. The perovskite $LaNiO_3$ also has a low electric resistivity, around 10 mohm·cm at room temperature, and a metal-like type of conductivity [16]. However, it starts to decompose at temperatures above 860°C into $La_{n+1}Ni_nO_{3n+1}$, NiO and O_2 [17] and is therefore not stable at thick film firing temperatures. The partial exchange of Ni with Co stabilises the perovskite structure at temperatures up to or over 1200°C [18, 19].

Material with the nominal composition $LaNi_{0.6}Co_{0.4}O_3$ was prepared by coprecipitation of hydroxides. After washing and drying a calcination step at 850°C for 24 hours followed (for more details see [19]). SrRuO3 and $(La_{0.5}Ca_{0.5})FeO_{3-y}$ were synthesised from stoichiometric mixtures of $SrCO_3$ (Ventron, 99.9%) and RuO_2 (Ventron, 99.9%), and of $La(OH)_3$ (Ventron, 99.9%), $CaCO_3$ (Merck, 99.9%) and Fe_2O_3 (Alfa, 99.9%), respectively. Oxides and carbonates were mixed in isopropyl alcohol, pressed into pellets, calcined at 1000°C and fired at 1200°C ($SrRuO_3$) or 1300°C $(La_{0.5}Ca_{0.5})FeO_{3-y}$ for 50 hours with intermediate grinding. During firing pellets were placed on platinum foils. The formation of the perovskite structure for all three materials was confirmed by X-ray powder diffractometry (Philips PW 1710 X-ray diffractometer, Cu K_α radiation, range $2\Theta = 20°$ to 70°, steps 0.02°).

As the ceramic electrode is placed between an alumina substrate and a PLZT thick film layer possible interactions between Al_2O_3 on one side and PLZT on the other and the chosen perovkites were studied. Interactions between conducting perovskites and Al_2O_3 (Alcoa, A-16, +99%), and perovskites and PLZT ($Pb_{0.88}La_{0.08}Zr_{0.65}Ti_{0.35}O_3$) were preliminarily investigated by firing powder mixtures for 2 hours at 1000°C, 1100°C, and 1200°C. Results of X-ray powder diffraction analysis of fired mixtures are summarised in Table I.

All three conductive perovskites react with PLZT and Al_2O_3. The quantity of reacted products increases with increasing firing temperature. However, at 1000°C no reaction products could be detected only in the case of $La_{0.5}Ca_{0.5}FeO_3$ and Al_2O_3 or PLZT. Both $SrRuO_3$ and $LaNi_{0.6}Co_{0.4}O_3$ reacted at 1000°C with Al_2O_3 forming $SrAl_2O_4$ and RuO_2 in the first case and $LaAlO_3$ and La_2NiO_4 in the second case. At higher firing temperatures reactions between $La_{0.5}Ca_{0.5}FeO_3$ and Al_2O_3 resulted in small quantities of an unknown phase or phases. The results of reactions of all three perovskites

TABLE I X-ray powder diffraction analysis of powder mixtures, fired for 2 hours at 1000°C, 1100°C, and 1200°C

Powder mixture	Temp (°C)	Phases identified
$SrRuO_3 + Al_2O_3$	1000	$SrRuO_3$, Al_2O_3, RuO_2, $SrAl_2O_4$
	1100	$SrRuO_3$, Al_2O_3, RuO_2, $SrAl_2O_4$
	1200	$SrRuO_3$, Al_2O_3, RuO_2, $SrAl_2O_4$
$SrRuO_3$ + PLZT	1000	$SrRuO_3$, (La,Pb,Sr)(Zr,Ti,Ru)O_3 ss, $Pb_2Ru_2O_{6.5}$
	1100	$SrRuO_3$, (La,Pb,Sr)(Zr,Ti,Ru)O_3 ss, $Pb_2Ru_2O_{6.5}$
	1200	$SrRuO_3$, (La,Pb,Sr)(Zr,Ti,Ru)O_3 ss, $Pb_2Ru_2O_{6.5}$
$LaNi_{0.6}Co_{0.4}O_3 + Al_2O_3$	1000	$LaNi_{0.6}Co_{0.4}O_3$, Al_2O_3, $LaAlO_3$, La_2NiO_4
	1100	$LaNi_{0.6}Co_{0.4}O_3$, Al_2O_3, $LaAlO_3$, La_2NiO_4
	1200	$LaNi_{0.6}Co_{0.4}O_3$, Al_2O_3, $LaAlO_3$, La_2NiO_4
$LaNi_{0.6}Co_{0.4}O_3$ + PLZT	1000	$La_2Zr_2O_7$, (La,Pb)(Ni,Zr,Ti,Co)O_3 ss, PbO
	1100	$La_2Zr_2O_7$, (La,Pb)(Ni,Zr,Ti,Co)O_3 ss, PbO
	1200	$La_2Zr_2O_7$, (La,Pb)(Ni,Zr,Ti,Co)O_3 ss, PbO
$La_{0.5}Ca_{0.5}FeO_3 + Al_2O_3$	1000	$La_{0.5}Ca_{0.5}FeO_3$, Al_2O_3
	1100	$La_{0.5}Ca_{0.5}FeO_3$, Al_2O_3, unidentified peaks
	1200	$La_{0.5}Ca_{0.5}FeO_3$, Al_2O_3, unidentified peaks
$La_{0.5}Ca_{0.5}FeO_3$ + PLZT	1000	$La_{0.5}Ca_{0.5}FeO_3$, PLZT
	1100	$La_{0.5}Ca_{0.5}FeO_3$,$PbFe_4O_7$, $Pb_2Fe_2O_5$, (La,Ca)(Fe,Zr,Ti)O_3 ss
	1200	$PbFe_4O_7$, $Pb_2Fe_2O_5$, (La,Ca)(Fe,Zr,Ti)O_3 ss

ss-solid solution.

with PLZT were perovskite solid solutions incorporating ions from the conducting perovskites into the PLZT structure. In the case of $LaNi_{0.6}Co_{0.4}O_3$ even after firing at 1000°C the conductive perovskite "decomposed" completely resulting in $La_2Zr_2O_7$, PLZT solid solution and PbO. For $SrRuO_3$ $Pb_2Ru_2O_{6.5}$ was one of the reaction products and in the case of $La_{0.5}Ca_{0.5}FeO_3$ two compounds, $PbFe_4O_7$, and $Pb_2Fe_2O_5$, were detected.

Thick film pastes were prepared from an organic vehicle (ethyl cellulose and solvents) and $LaNi_{0.6}Co_{0.4}O_3$, $La_{0.5}$ $Ca_{0.5}FeO_3$, and $SrRuO_3$ powders. Pastes were deposited on alumina substrates and fired for 2 hours at 1200°C. To evaluate the adhesion between the fired films and the ceramic substrate a self adhesive tape was fixed on the film and then sharply peeled off (scotch tape method, as defined in [20]). The adhesion between the $SrRuO_3$ or $LaNi_{0.6}Co_{0.4}O_3$ layer and alumina was very low. On the other hand, the adhesion of $La_{0.5}Ca_{0.5}FeO_3$ was good-the layer could not be peeled off with scotch tape. The microstructure of $La_{0.5}Ca_{0.5}FeO_3$ on alumina, observed by SEM (scanning electron microscopy), is shown in Fig. 1. After firing a layer a few microns thick formed between $La_{0.5}Ca_{0.5}FeO_3$ (on the right) and Al_2O_3 substrate (on the left). EDS (Energy Dispersive X-ray Microanalysis) showed that this is (La,Ca)(Fe,Al)O_3 solid solution. This reacted layer could be the reason for the good adhesion between $La_{0.5}Ca_{0.5}FeO_3$ and alumina.

All presented results indicated that of the three tested conductive perovskites $La_{0.5}Ca_{0.5}FeO_3$ is a "better"

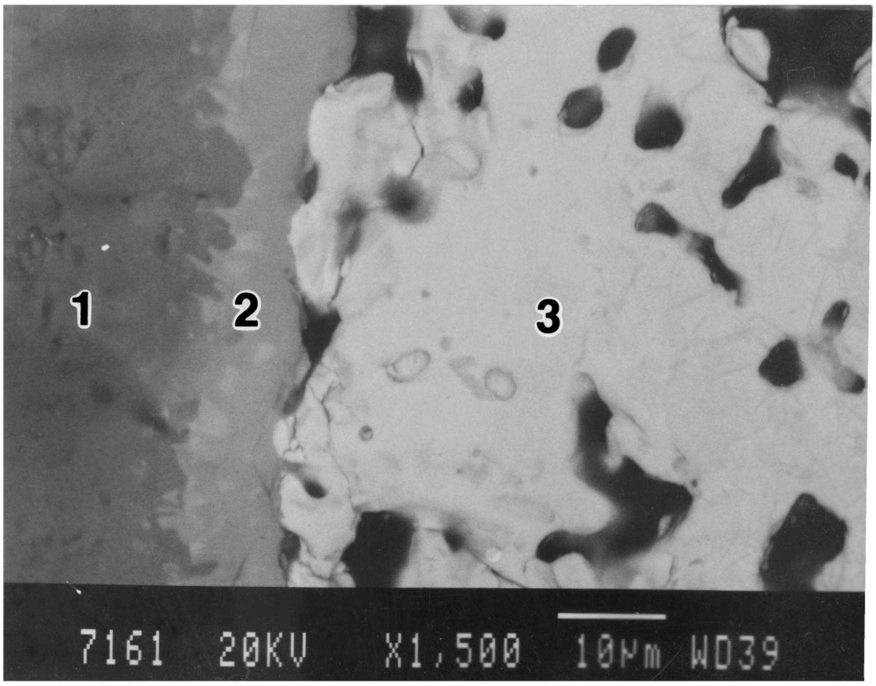


Figure 1 The microstructure of $La_{0.5}Ca_{0.5}FeO_3$ thick film, fired on alumina at 1200°C. The layer a few microns thick which formed between $La_{0.5}Ca_{0.5}FeO_3$ (on the right) and Al_2O_3 substrate (on the left) is (La,Ca)(Fe,Al)O_3 solid solution. (a) Alumina substrate; (b) (La,Ca)(Fe,Al)O_3 solid solution; (c) $La_{0.5}Ca_{0.5}FeO_3$.

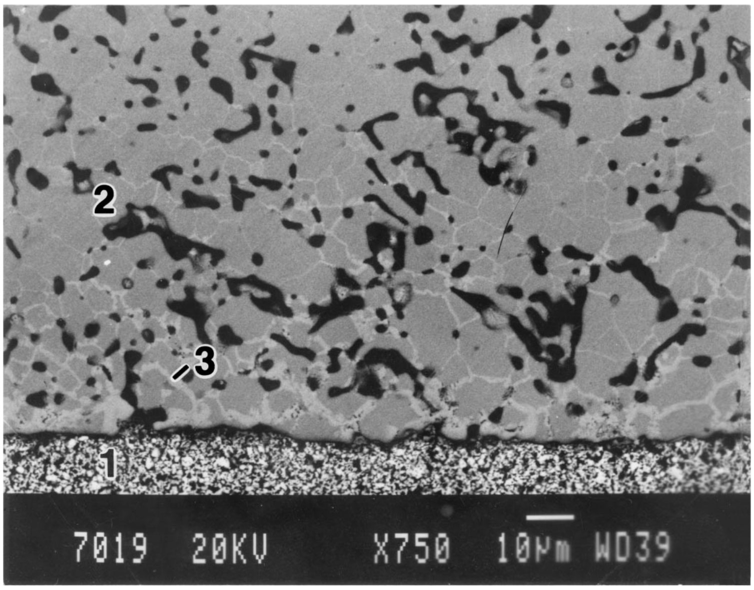
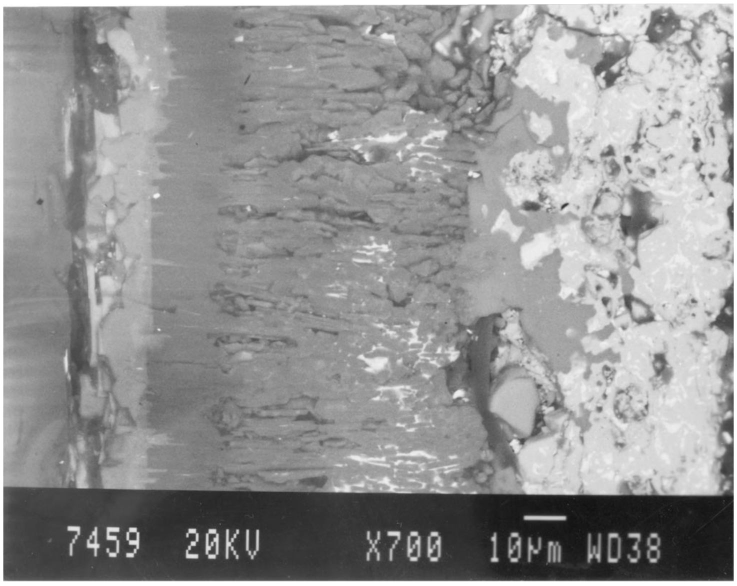
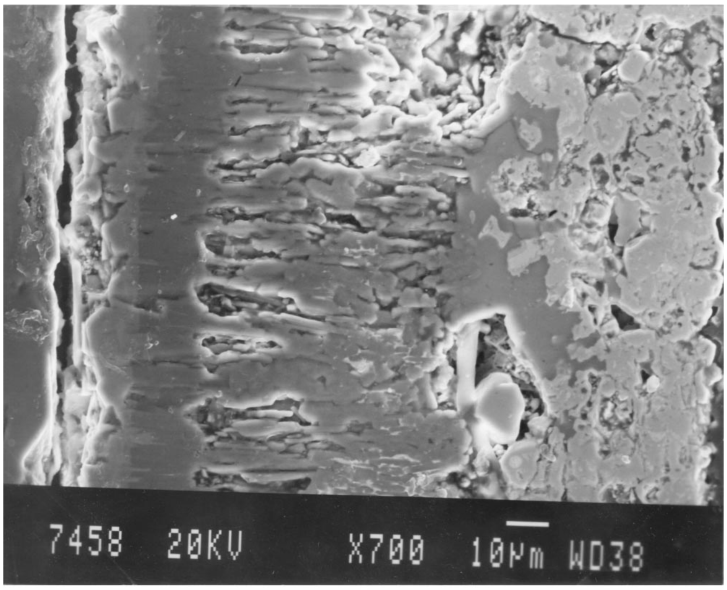


Figure 2 The diffusion couple of $La_{0.5}Ca_{0.5}FeO_3$ sintered pellet/thick film PLZT, fired at 1050°C for 2 hours. After firing intergranular liquid phase formed on the $La_{0.5}Ca_{0.5}FeO_3$ side. (a) PLZT; (b) $La_{0.5}Ca_{0.5}FeO_3$; (c) Intergranular liquid phase.



(a)



(b)

Figure 3 The microstructure of a "sandwich" of alumina/$La_{0.5}Ca_{0.5}FeO_3$ thick film electrode/PLZT thick film layer. The $La_{0.5}Ca_{0.5}FeO_3$ layer was sintered on alumina at 1200°C and the PLZT layer was then printed and fired at 1050°C. Al_2O_3 substrate is on the left. (a) Backscattered electrons; (b) Secondary electrons.

material for electrodes than other two, as higher reaction temperatures are needed to obtain observable quantities of reaction products both with alumina and PLZT. Also, the adhesion evaluation showed it to be more suitable. To evaluate the compatibility between $La_{0.5}Ca_{0.5}FeO_3$ and PLZT in a more "realistic" manner, i.e. between thick film PLZT and already sintered $La_{0.5}Ca_{0.5}FeO_3$, instead of reacting powder mixtures the $La_{0.5}Ca_{0.5}FeO_3$ pellet was sintered at 1200°C. A thick film paste, prepared from PLZT powder and an organic vehicle, was deposited on the sintered pellet and fired for 2 hours at 1050°C. The adhesion of the PLZT film on $La_{0.5}Ca_{0.5}FeO_3$, measured by the scotch tape method, was good. Small pieces of the PLZT layer broke away but the layer itself could not be peeled from the $La_{0.5}Ca_{0.5}FeO_3$ substrate. The diffusion couple of a $La_{0.5}Ca_{0.5}FeO_3$ sintered pellet and thick film PLZT, fired at 1050°C, is shown in Fig. 2. After firing an intergranular liquid phase formed on the $La_{0.5}Ca_{0.5}FeO_3$ side. The EDS microanalysis showed that the composition of this phase is basically $La_{0.5}Ca_{0.5}FeO_3$ with roughly 10% of Ca exchanged with Pb. It is interesting to note that elements in the thin darker layer between $La_{0.5}Ca_{0.5}FeO_3$ (on the top) and PLZT (on the bottom) are mainly Fe, Ca and Zr in roughly same quantities with traces of La, while PbO is not detected.

Finally, a structure consisting of alumina substrate/ $La_{0.5}Ca_{0.5}FeO_3$ thick film electrode/PLZT thick film layer was prepared. First a $La_{0.5}Ca_{0.5}FeO_3$ layer was sintered on alumina at 1200°C, after firing the layer was still a good conductor. Then the PLZT layer was printed and fired at 1050°C. The microstructure of this "sandwich" is shown in Fig. 3a (back scattered electrons) and b (secondary electrons). During firing presumably some low temperature eutectics resulted in formation of liquid phase all over the structure. Due to interdifusion of practically all the components, the microstructure is very complex. Starting from the left, cracks appeared between the alumina and thick film layers. The dark phase near alumina is mainly $(Fe,Al)O_3$ solid solution. In the formerly $La_{0.5}Ca_{0.5}FeO_3$ layer pores appeared. From the alumina substrate (on the left) Al_2O_3 diffused to the top of the "sandwich" and from the PLZT (mainly) PbO also diffused through the whole layer. On the PLZT side instead of single PLZT phase a number of phases appeared. These interactions spoiled desirable characteristics. The $La_{0.5}Ca_{0.5}FeO_3$ layer was no longer conducting and the PLZT layer lost its piezoelectric characteristics. These results indicate that the firing temperature of the PLZT thick film was too high. Further experiments are planned with fine grained PLZT powder with a sintering temperature of 800°C. It is hoped that lower firing temperatures will minimise the interactions and allow the use of conducting perovskites for electrodes.

Acknowledgement

The financial support of the Ministry of Science and Technology of Slovenia is gratefully acknowledged.

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Received 30 July 1998
and accepted 30 September 1999