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Ceramics International 27 (2001) 85–89

CERAMICS INTERNATIONAL

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Interfacial reaction of Ag/Pd metals with Pb-based relaxor ferroelectrics including additives

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Received 14 January 2000; received in revised form 18 January 2000; accepted 8 March 2000

Abstract

In order to effectively control the interfacial reactions during co-firing a multilayer ceramic device (MLCD), different effects of silver/palladium on Pb-based relaxor ferroelectric ceramics were investigated by means of a series of powder X-ray diffraction (XRD) spectra and chemical reaction thermodynamics. It is found that the reaction kinetics of palladium and Pb-based relaxor ceramics lies in the activity of palladium and the structural stability of relaxor ferroelectric ceramics. In this respect, silver can decrease the activity of palladium so that a less serious interfacial problem exists in a MLCD with 30Pd/70Ag electrodes. Moreover, $BaTiO_3$ and $SrTiO_3$ ceramic additives were found to effectively suppress Pd-PNN reactions because of increasing the structural stability of PNN. It is pointed out that the addition of $BaTiO_3$ or $SrTiO_3$ ceramic powders into the dielectric layers and particularly into the inner electrode pastes may play dual roles, including modifying the densification mismatch and preventing the interfacial reactions between the electrodes and the dielectric layers.

Keywords: Interfacial reaction; Pb-based relaxor ferroelectric; MLCD; Additive

1. Introduction

In the past few years, multilayer ceramic chip devices with a monolithic structure have been widely applied in the information industry and pressed for the reduction of cost and the improvement of reliability. Pb-based relaxor ferroelectric ceramics, which were used in multilayer piezoelectric or dielectric ceramic devices, can make an inner electrode rich-in silver possibly used and the properties improved. However, during the co-firing of the ceramic layers and silver/palladium internal electrodes, a potential for the chemical reaction and the inter-diffusion at the interfaces, and their influence on the co-firing behaviors of relaxor-based MLCDs must be considered. The interaction and inter-diffusion may change the sintering behavior and the final properties of MLCDs [1–3]. Therefore, research into the effects of silver/palladium electrodes on the co-firing behaviors is apparently interesting for preparing a satisfactory device. Even though in the past there was a few reports about the incompatibility between the ceramics and the electrodes [4,5], such as delaminations, cracks, chemical interaction and silver migration into the ceramics, the reaction mechanism of silver and palladium metals with Pb-based relaxors have been poorly investigated. Moreover, other research into the measures of suppressing Pd-$Pb(B_1B_2)O_3$ reaction is also very essential. The aim of this paper has been to analyze the different roles of silver and palladium co-fired with relaxor ceramics, respectively. A further knowledge about the effects of the inner electrodes on the co-firing behaviors can be obtained; above all, the effects of some additives on Pd-based interfacial reactions were also investigated.

2. Experimental procedure

$Pb(Ni_{1/3}Nb_{2/3})O_3$ (PNN) was chosen as a candidate because of its good piezoelectric or dielectric properties and a sensitive structural stability. The columbite method was used to synthesize PNN ceramic powder by using reagent-grade starting material (PbO, NiO, Nb_2O_5). Nearly complete perovskite phases in the as-calcined powder were confirmed by XRD. The calcined PNN powder was mixed with 40 mol% pure silver (pure

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PII: S0272-8842(00)00046-8

palladium or a 70:30 mol% mixture of silver and palladium), respectively; and then blended with 10 mol% $BaTiO_3$ or $SrTiO_3$ ceramic powder. Finally, these mixtures were ball-mixed for 24 h with ethyl alcohol medium. The mixed powders were uniaxially pressed into 10-mm-diameter disks. The samples were sintered for 2 h at the temperature ranging from 800 to 1100°C in a closed Al_2O_3 crucible using a protective Pb atmosphere. The powder XRD using CuK_a radiation was used to identify the phases existed in the specimens as sintered. The microstructure evolution was observed by SEM. Differential thermal analysis (DTA) was performed to examine the reactions existed in the mixtures.

3. Results and discussion

As Fig. 1 showed, no evident chemical reactions happen between pure silver and PNN. Ag–Pb compounds or other products are not observed even at a higher temperature than 1000°C. However, at about 1100°C, silver seems to be incorporated into the lattice of growing PNN ceramic grains. This can be confirmed with an XRD spectrum of the samples sintered at 1100°C. The main diffraction peaks of PNN perovskite phase appear to split, as indicated in Fig. 1. Because silver migrating into PNN lattice substitutes for A-site cations and then produces $V_O^{\cdot\cdot}$ in view of non-equivalent replacement, the distortion or contraction of partial cells will exist ($2Ag^+ + 2Pb^{2+} \rightarrow 2Ag'_{Pb} + V_O^{\cdot\cdot}$). Thus, when preparing MLCDs, silver migrating into the ceramic layers will influence the insulation resistance, dielectric properties and reliability of MLCDs, which has been previously reported. Fig. 2 shows the SEM picture of silver-doped PNN ceramic sintered at 950°C. It is evident that silver particles were inlaid in the matrix of PNN ceramic. This may be because a poor wetting ability of silver and PNN ceramic and no chemical reaction cause the formation of granular particles. Furthermore, silver can effectively promote the sintering of ceramics at higher temperature because of its low melting point(≈960°C). The effects of silver dopant on the grain size or density were reported elsewhere [6].

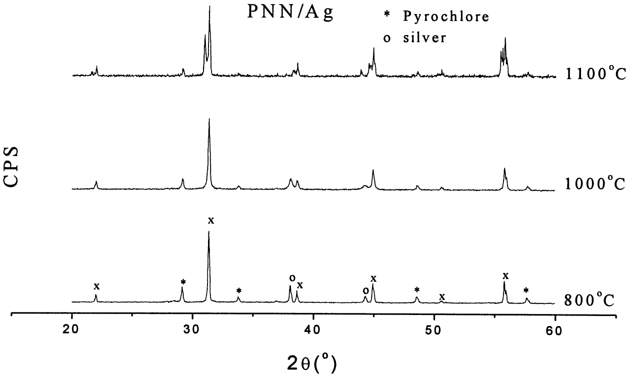

Fig. 1. XRD spectra of the mixtures of pure silver and PNN at different sintering temperature.

On the other hand, during the co-firing of MLCDs, Pd-based interface reactions, mainly including Pd–Bi or Pd–Pb reaction, will happen at the interface [7,8]. But it is found in this paper that the degree of chemical reactions to a large extent depends on the properties of a perovskite ceramic itself, such as its structural stabilization. This can be confirmed by the following presentation about Pd–PNN reaction kinetics. Moreover, because of the kind of ceramic materials and the different sintering processes, different reaction products are formed at the interfaces. Fig. 3 shows that the Pd–Pb compounds such as $PbPdO_2$, and the intermetallics with low melting point will begin to form even though they can disappear at high temperature. These reactions will result in the electrode discontinuities, microcracks and voids. Secondly, because of the addition of palladium, the amount of pyrochlore phase in the samples is greatly increased. This process can be presented as follows:

$$Pb\left(Ni_{\frac{1}{3}}Nb_{\frac{2}{3}}\right)O_3 \Longleftrightarrow \frac{1}{6}Pb_3Nb_4O_{13} + \frac{1}{2}PbO + \frac{1}{3}NiO \tag{1}$$

$$PdO + PbO \rightarrow PbPdO_2 \rightarrow PdO + PbO \rightarrow Pd(Pb) \tag{2}$$

We can see that with this process palladium or its oxide deprives Pb of the lattice of PNN ceramic grains, considering no free PbO in the original mixtures. Fig. 4 indicates that the reaction of PbO and $NiNb_2O_6$ is at 200°C higher temperature than that of PbO and Pd and more heat was given out by the latter. From thermodynamic analysis, the reaction of Pd and Pb in PNN is

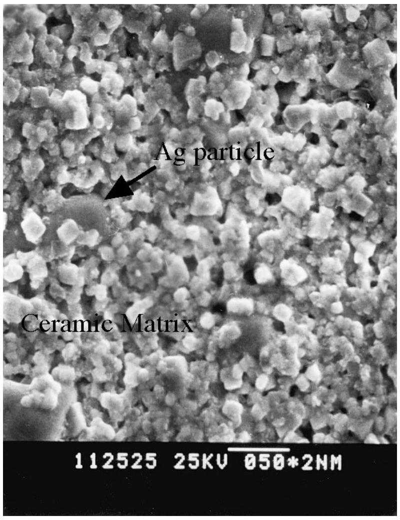

Fig. 2. SEM picture of silver-doped samples sintered at 950°C.

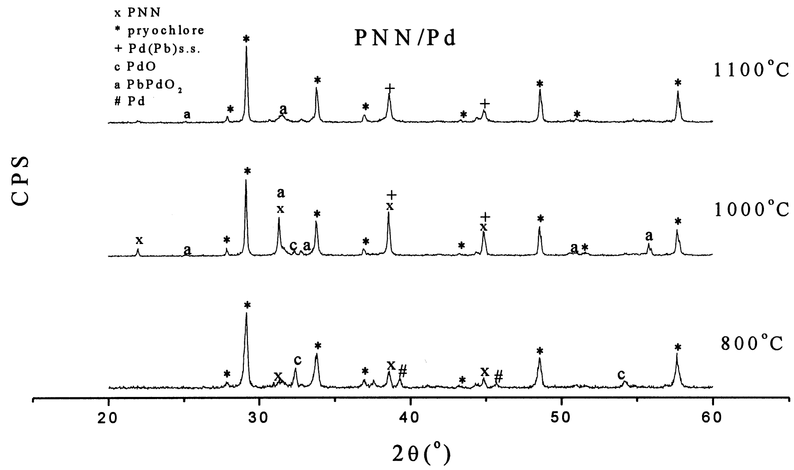

Fig. 3. Powder XRD spectra of the mixtures of pure Pd and PNN ceramic sintered at different temperature.

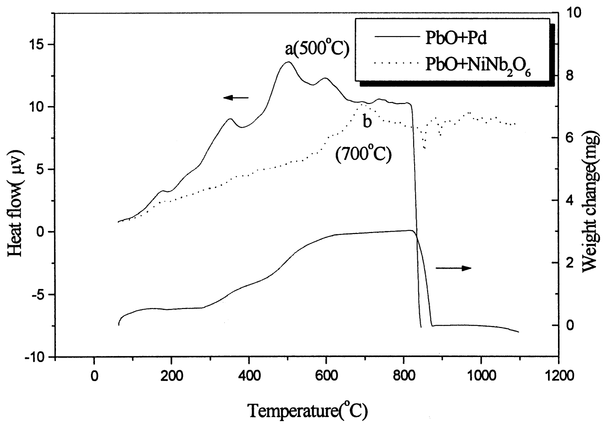

Fig. 4. DTA/TGA curves of 1:1 mol mixtures (10°C/min, in air).

favorable. Furthermore, Eq. (1) stands for a reversible process, like many other Pb-based relaxors, such as PMN, PZN, etc. So the calcined PNN ceramic powders with perovskite structures may become unstable and decompose into the pyrochlore phases under the condition of PbO loss or high temperature, like many other Pb-based relaxors. In the samples, including palladium, palladium or its oxide may capture Pb from PNN ceramic grains to form kinds of Pd–Pb products with relatively stable structures at different temperature, which would make the direction of Eq. (1) move to the right. In comparison, $PbTiO_3$ or $Pb(TiZr)O_3$ has a better stability with Pd, as reported elsewhere [8]. Even if Pd–Pb products do exist, it still remains a perovskite structure. Moreover, Pd-based interfacial reactions are also influenced by the activity of Pd metal. Fig. 5 shows that the addition of silver can suppress the reaction. The amount of pyrochlore phase visibly decreased. The percentage of pyrochlore phase can be approximately calculated from the intensity of the (110) perovskite peak and the (222) pyrochlore peak. It is likely that the lower activity of palladium will greatly diminish the reactivity of palladium and PNN dielectric on account of silver addition [9]. So, the 70Ag/30Pd electrode may have less serious interfacial reactions with Pb-based relaxors. Figs. 5 and 6 indicate how the addition of $BaTiO_3$ and $SrTiO_3$ powder into the mixture of Pd metal and PNN ceramics affects the formation of phases in the samples. It is found that they have different roles with the change of sintering temperature, even though both of them can suppress the Pd–PNN reaction to a certain extent. It is well known that $BaTiO_3$ and $SrTiO_3$ are very often used to stabilize the perovskite formation during the preparation of Pb-based complex relaxors. This is due to their larger tolerance factor and electronegativity than PNN ceramic [10,11]. That is to say, the intensity or ionic characteristic of Pb–O, Nb–O and Ni–O bonds in the lattice of PNN grains seems to be increased because of the additives. So at this time the PNN ceramic becomes more stable even if palladium exists, so that the diffraction peaks of palladium metal appear in the powder XRD spectra. In contrast, in the as-sintered samples without additives nearly all the palladium reacted with PNN ceramic to form kinds of Pd–Pb products at 1000°C. But it is very interesting that at 900°C the effect of $BaTiO_3$ seems more marked than $SrTiO_3$ and at 1000°C there is little difference between them. Except that $BaTiO_3$ is a more effective stabilizer than $SrTiO_3$, $BaTiO_3$ seems to more easily form into a solid solution with PNN ceramic at a lower temperature. Moreover, with the increasing of the sintering temperature, the influence of temperature on the Pd–PNN reaction becomes more important than the perovskite stabilizer in view of the direction of the reaction. So in the samples sintered above 1100°C, the suppressing role of $BaTiO_3$ or $SrTiO_3$ for Pd–PNN reaction becomes very weak. Thus, the addition of a suitable amount of these stabilizers into the dielectric ceramic layers when preparing the tape-casting paste, and particularly into the silver/palladium electrode paste may be thought of as an

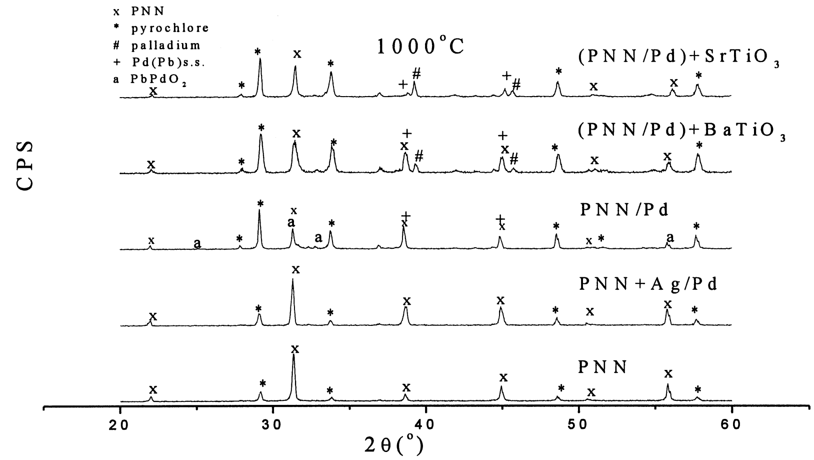

Fig. 5. Comparison of powder XRD spectra of Pd–PNN mixtures with additives as sintered at 1000°C.

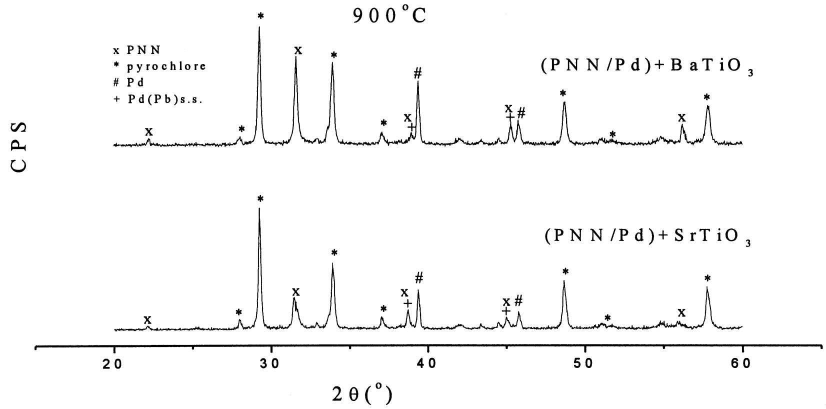

Fig. 6. Powder XRD spectra of Pd–PNN mixture with additives as sintered at 900°C.

effective approach for suppressing the detrimental Pd-based interfacial reactions. Furthermore, the densification mismatch of silver/palladium electrodes with the dielectrics is all along a serious problem for MLCDs [12]. So a fire-resistant ceramic oxide was hoped to tailor the sintering behavior of electrodes. In this regard, the doping of $BaTiO_3$ and $SrTiO_3$ ceramic powders may play dual roles. About this, further studies are in progress.

4. Conclusions

Different chemical stability of silver and palladium with the PNN ceramic was confirmed in the paper. There is no visible reaction between pure silver and the PNN ceramic except that silver can effectively promote the sintering of ceramics. Palladium can deprive Pb of the PNN ceramic to form kinds of Pd–Pb compounds, which further leads to the decomposition of the PNN ceramic and the increase of the pyrochlore phase. It is evident that the reaction kinetics of Pd–PNN ceramic lies in the activity of palladium and the chemical stability of PNN ceramic. In this respect, silver can lower the activity of Pd so that a 70:30 mol% mixture of silver and palladium has less serious reactions with PNN ceramic. Moreover, $BaTiO_3$ and $SrTiO_3$ ceramic can to a certain extent suppress the Pd–PNN reaction because of raising the structural stability of PNN ceramic. So the addition of $BaTiO_3$ and $SrTiO_3$ into electrode paste will play dual roles in preventing detrimental Pd–Pb interfacial reaction and in tailoring the densification mismatch of inner electrodes with relaxor ceramics.

Acknowledgements

This work was supported by the National Natural Science Foundation of PR China. (Serial Number: 59995523)

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