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# Diffusional penetration of silver from electrodes into PZT ceramics

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Diffusion of silver was studied in a ceramic based on lead zirconate–titanate, $Pb_{0.95}Sr_{0.05}(Zr_{0.53}Ti_{0.47})O_3$ + 1 wt%. $Nb_2O_5$ (PZT), by means of a radio-tracer method. Parameters of silver diffusion and silver content in PZT after continuous diffusion saturation of the ceramic by this impurity were determined in the temperature range 500–850 °C. Concentration–depth profiles and silver content in the ceramic were obtained as a result of metal diffusion from the electrode during ceramic silvering. Our results show that silver has a high diffusivity. No evaporation of silver during metallization ($T_{max}$ = 750 °C) was found, but part of it ($\sim$ 0.1 mg cm$^{-2}$) penetrates into the ceramic from the electrode to a depth of more than 1000 µm, and the silver concentration varies from $\sim 2 \times 10^{19}$ to $\sim 2 \times 10^{18}$ at cm$^{-3}$. The silver concentration does not exceed 0.2 at% at diffusion saturation of the ceramic during 100–120 h over the temperature range 650–850 °C.

## 1. Introduction

Silver electrodes are important constituents of piezoceramic elements. One of the most common methods of their fabrication is heating of a ceramic covered with silver paste at 750–850 °C [1]. However, these conditions of ceramic metallization and regimes of piezoelement exploitation (strong electric fields, relatively high temperatures) can cause the diffusional penetration of silver into the ceramic and changing of the piezoceramic resonator parameters. Therefore, in the present paper the diffusional behaviour of silver in a ceramic based on lead zirconate–titanate (PZT) was studied under both isothermal and non-isothermal conditions of silvering of this ceramic using a radiotracer sectioning technique. A brief report of these results was given earlier [2]. In addition we estimated the silver solubility by means of diffusional doping and silver diffusion under the influence of a constant electric field.

## 2. Experimental procedure

A modified PZT, $Pb_{0.95}Sr_{0.05}(Zr_{0.53}Ti_{0.47})O_3$ + 1 wt% $Nb_2O_5$, was synthesized using metal oxides by means of conventional ceramic techniques. Samples were prepared either by hot (HP) or by cold (CP) pressing. The sintered ceramic density was up to 99% (HP) and 95% (CP) of theoretical and the grain size was about 5–10 µm. The polished sample surface was covered by silver paste with $^{110m}Ag$ tracer in all the experiments except diffusion in the electric field, where $^{110m}Ag$ tracer was dried on the sample surface using $^{110m}AgNO_3$ solution.

Isothermal diffusion treatments were performed at temperatures of 500–820 °C for 1h. After heat treatment the silver covering was removed by $HNO_3$ (1 : 1) and the backs and sides of samples were ground. Silver activity profiles were obtained by the serial sectioning technique and by measuring the residual γ-activity of the sample. The activity in each removed section was counted and converted to the concentration ($C$) with the help of the known relation between silver activity in the electrode and the silver concentration in it. Diffusion coefficients ($D$) were calculated from the standard solution of Fick's equation for a constant source, $C(x, t) = (C_0/2)\,\mathrm{erfc}[x/2(Dt)^{1/2}]$, with relative error 20%.

Ceramic silvering was carried out in a furnace with linear heating from 200 to 750 °C at a rate of 100 °C h$^{-1}$. When the necessary temperature was reached (starting from 500 °C, every 50 °C) four samples were taken out of the furnace after 10 min of exposure (40 min at 750 °C). After etching the electrodes we determined the silver content in the ceramic as a result of its diffusion from the electrode and analysed the silver concentration distribution.

The diffusional saturation of the ceramic by silver was conducted in the range 500–800 °C for 100–120 h. In this case samples with thickness 2 mm were coated on all sides with a thick layer of silver paste. After the treatment and removal of the silver covering, the homogeneity and fullness of saturation were estimated by serial sectioning of two opposite sides of the sample followed by measurement of residual γ-activity.

Silver diffusion under the influence of a constant electric field of intensity $E$ was investigated on massive

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samples (HP) of 2 mm thickness at 400 °C ($t = 11$ h, $E = 0$–$4\ \mathrm{kV\,cm^{-1}}$) and on ceramic discs with silver electrodes on both sides (HP, CP, thickness 0.3 mm) at 85 °C ($t = 1000$ h, $E = 8.3\ \mathrm{kV\,cm^{-1}}$) and at 150 °C ($t = 500$ h, $E = 11.7\ \mathrm{kV\,cm^{-1}}$). The conditions of thermal treatment of the discs corresponded to those of the exploitation regimes of piezoelements. A drop of $^{110\mathrm{m}}\mathrm{AgNO_3}$ solution was placed on one side of the disc or sample and this side served as a cathode or anode depending on the direction of electric field. Control samples in which silver diffusion took place in the absence of electric field were used in all cases. Possible penetration of silver from the electrode into ceramic discs was estimated by measuring the absorption of low-energy β-radiation of $^{110\mathrm{m}}\mathrm{Ag}$ and the residual activity of discs after etching of electrodes, and the same for massive samples by means of the sectioning technique.

## 3. Results and discussion

Typical concentration–depth profiles of silver after isothermal diffusion are shown in Fig. 1a. It can be seen that the distributions of the silver concentration in cold- and hot-pressed samples are close. However, the profiles for HP samples are less sharp and the diffusivity is always somewhat greater than for CP samples. One can propose that ceramic porosity has an insignificant effect on the diffusion of silver and even slightly decreases its diffusivity. The diffusion coefficients of silver in cold-pressed samples follow the Arrhenius law $D = 0.83 \exp[-(124 \pm 4)\ \mathrm{kJ\,mol^{-1}}/RT]\ \mathrm{cm^2\,s^{-1}}$ (Fig. 2). Silver has a high diffusivity in PZT ceramics. For example, $D = 5 \times 10^{-7}\ \mathrm{cm^2\,s^{-1}}$ is obtained at the temperature 750 °C, corresponding to the optimal regime of electrode fabrication. It seems that the diffusion transport of silver along grain boundaries has the main significance.

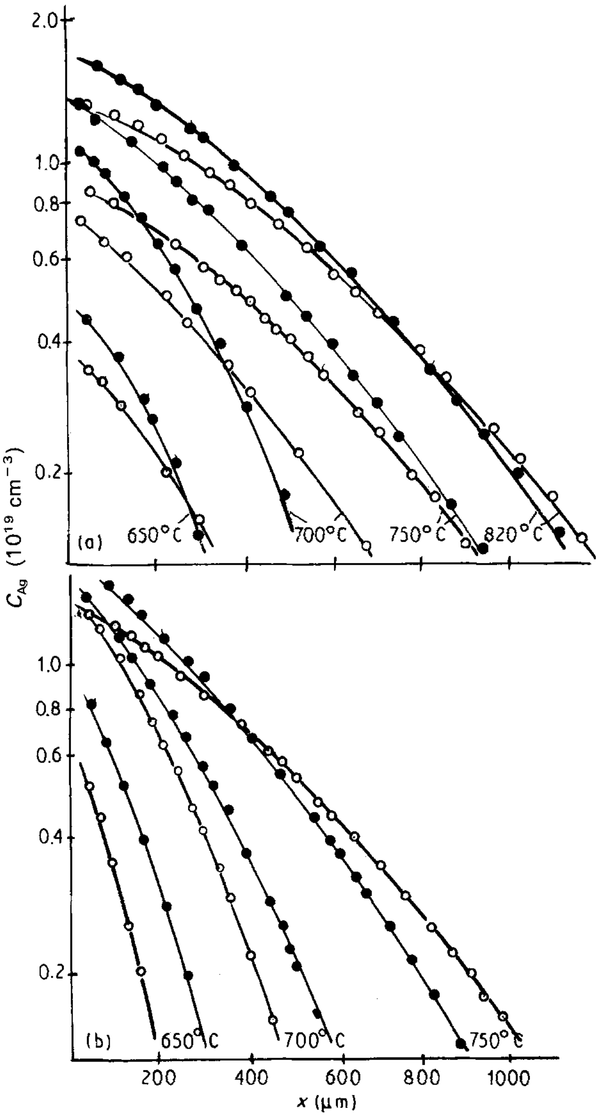

*Figure 1* Distribution of silver concentration in PZT after (a) diffusional annealing for 1 h and (b) the metallization process: (○) hot pressing, (●) cold pressing.

Distribution of silver in ceramics during the metallization process under non-isothermal conditions is of interest in itself. No evaporation of silver during the metallization process was found ($T_{\max} = 750$ °C) but a part of the silver penetrated into the ceramic from the electrode. The distributions of silver concentration obtained were similar to the diffusion profiles (Fig. 1b). The silver content in the ceramic at 500–600 °C is small, 0.002–0.004 mg cm$^{-2}$; at 750 °C it reaches the value $0.12 \pm 0.03$ mg cm$^{-2}$. In the latter case the diffusion depth of silver is more than 1000 μm; however, the layer concentration has a relatively small value and changes from $2 \times 10^{19}$ to $1 \times 10^{18}\ \mathrm{cm^{-3}}$ ($x = 1000$ μm) along the diffusion profile. Adding palladium to the silver paste decreases the penetration depth and the concentration of silver in the ceramic about 2–3 times (Fig. 3).

It should be noted that even after continuous diffusion saturation of the ceramic by silver its upper

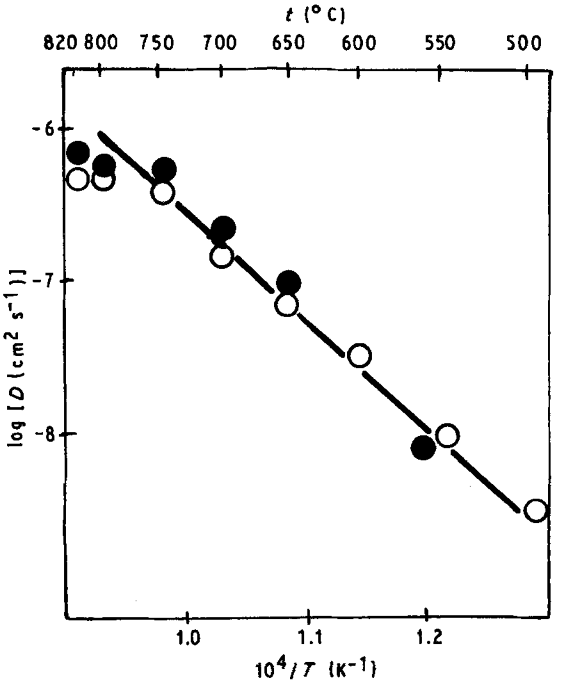

*Figure 2* Arrhenius plot of temperature dependence of silver diffusion coefficient in PZT ceramic: (●) hot pressing, (○) cold pressing.

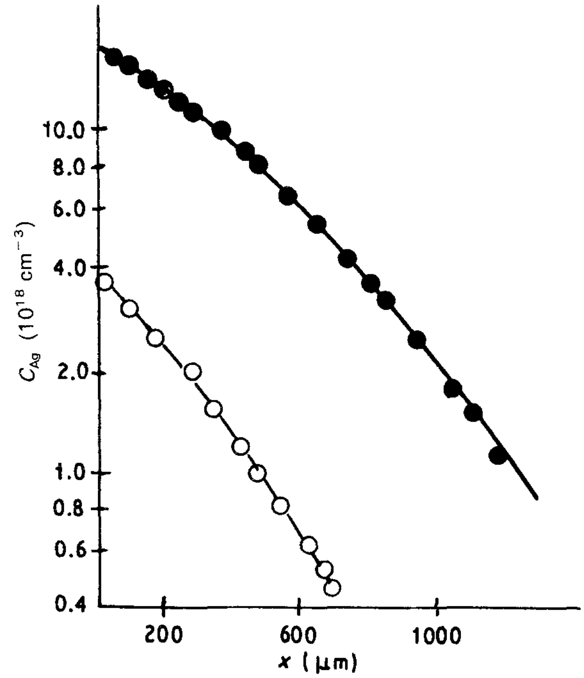

*Figure 3* Distribution of silver concentration in cold-pressed PZT ceramic after its metallization at 820 °C: silver paste (○) with Pd, (●) without Pd.

TABLE I Silver concentration in ceramics obtained after diffusional saturation

| $t$ °(C) | 650 | 700 | 750 | 800 |
|---|---|---|---|---|
| $C_{Ag}$($10^{19}$ at cm$^{-3}$) | 1.0 ± 0.2 | 1.3 ± 0.2 | 1.8 ± 0.3 | 2.6 ± 0.4 |

limit of concentration in the ceramic is also small and depends weakly on temperature (Table I).

The apparent enthalpy of silver solubility is 57 ± 7 kJ mol$^{-1}$. At all temperatures a uniform distribution of silver impurity in the ceramic was already observed after 48 h of treatment, and the level of layer concentration reached did not change with an increase of the duration of diffusion annealing up to 100–120 h. It was supposed that only saturation of grain boundaries was reached in these experiments, so we therefore made an attempt to conduct chemical extraction of silver from intergranular boundaries. For this purpose a pre-weighed probe of powder obtained from a $^{110m}$Ag-doped sample was washed several times with dilute nitric acid. After drying the powder was weighed, its integral activity was measured and the silver concentration calculated. This process was repeated up to a constant silver concentration. The results showed that approximately the same quantity of silver was washed from the powder, 42–55%, regardless of the temperature. It is obvious that not all of the intergranular boundaries were subjected to chemical washing, so it was unreasonable to expect complete removal of silver which was not in the grain volume. However, these data show that a significant quantity of silver is concentrated at intergranular boundaries. In this case the local concentration of silver must be large, and it may exceed the layer concentration values obtained by 1–2 orders of magnitude depending on the diffusion width of grain boundaries; however, X-ray spectral microanalysis (detection limit > 0.1 wt % Ag) did not observe silver in the ceramic, where according to our data the total silver concentration in the temperature range 650–800 °C is 2–5 × $10^{-2}$ wt %) or 0.07–0.2 at %. Literature data concerning silver solubility in PZT are not available. It is known that the silver solubility is more than 0.4 at % in $BaTiO_3$ [3] and about 4 at % in PLZT [4], so it is unreasonable to expect a high silver solubility in PZT.

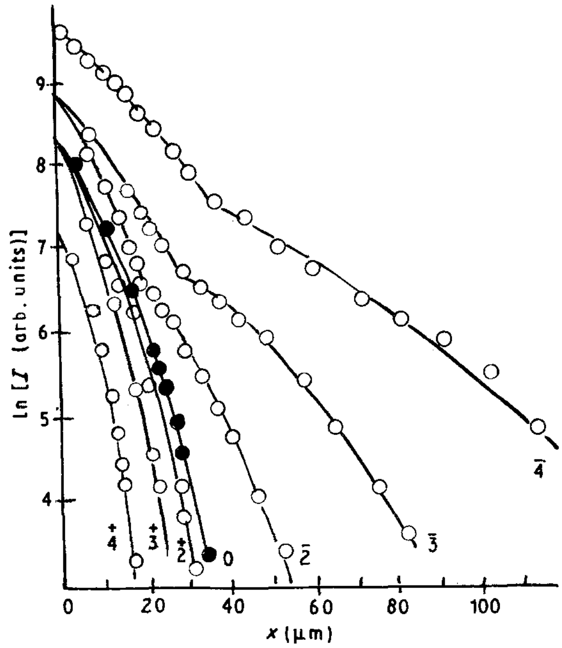

*Figure 4* (○) Penetration plots for $^{110m}$Ag diffusion at 400 °C in a constant electric field with intensity 2, 3 and 4 kV cm$^{-1}$ and (●) in its absence (0). $\overset{+}{2}$, $\overset{+}{3}$, $\overset{+}{4}$ to anode; $\bar{2}$, $\bar{3}$, $\bar{4}$ to cathode.

Fig. 4 presents the distribution of residual activity ($I$) of $^{110m}$Ag versus penetration depth in (HP) ceramic at 400 °C under a constant electric field of $E = 0$–$4$ kV cm$^{-1}$. One can see the influence of electric field on diffusion: the penetration depth of impurity in a direction towards the cathode (curves $\bar{2}$, $\bar{3}$ and $\bar{4}$) is higher than towards the anode (curves $\overset{+}{2}$, $\overset{+}{3}$, and $\overset{+}{4}$). This difference arises with the increase of electric intensity from 2 to 4 kV cm$^{-1}$. The effective diffusion coefficient of silver is $3.7 \times 10^{-11}$ cm$^2$ s$^{-1}$ in the absence of an electric field. By means of Fick's second law for forced diffusion the drift velocity and mobility of silver in an electric field were calculated. The silver mobility is $2.7 \times 10^{-11}$ cm$^2$/Vs. Calculation of the effective charge of silver by the Nerst–Einstein equation gave a value close to zero (~ 0.04). Perhaps the greater part of diffused silver is electroneutral and does not take part in drift under the electric field.

Under the conditions of piezoelement exploitation regimes (85 and 150 °C) diffusional penetration of silver from the electrode into PZT ceramics was not observed. The absorption method showed no reduction of $^{110m}$Ag β-radiation and the residual activity of all discs including the control ones after removing electrodes was close to the background.

## 4. Conclusion

The results obtained should be taken into consideration in the fabrication and exploitation of ceramic products with a silver covering. Without taking into account the ability of silver to penetrate deep into PZT ceramics in the metallization process one can obtain apparent losses of silver which will reach 2 g m$^{-2}$ at high-volume silvering. After the continuous diffusion saturation of PZT ceramic by silver its upper limit of concentration does not exceed 0.2 at % at 800 °C. Diffusional penetration of silver from the electrode into the ceramic under conditions of piezo-element exploitation was not found by the radiotracer method.

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