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Numerical model for electro-poling

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ABSTRACT

A theoretical model for describing the time evolution of concentration profiles in thermal electro-poling experiments is being presented. The model is based on a Monte Carlo formalism. It takes into account the field dependent mobility of cations as well as electrons. Model calculations are presented for a 46S4 bio-glass. Upon application of a DC field Na^+ ions start to move toward the cathode giving rise to a depletion zone. The electric field increases in this zone. Once a specific threshold value is reached the electrons become mobile and move toward the anode leaving behind a basically neutral zone. Thus, the full double layer capacity has developed after a few seconds. The concentration depletion profiles continue to develop on a much longer time scale of tens of minutes. In the 46S4 glass Na^+ ions as well as Ca^{++} ions develop a depletion profile. The numerical calculations account for all essential experimental observations available in the literature. The model is also capable of predicting under which conditions two different cations move on the same or on different time scales.

1. Introduction

Poling of materials is based on the application of an electric field to a sample [1]. In general, the field can be generated via different techniques, e.g. by laser pulses which produce strong time dependent fields or by the simple application of an electrical potential drop for an extended period of time via two electrodes that are fixed to either side of the sample. The latter method is often referred to as electro-poling [2]. Mobile charge carriers inside the sample, e.g. mobile cations will move according to this field. As it turns out, often a depletion zone is formed in the vicinity of the corresponding electrodes. Thermal electro-poling is a variation where the poling is performed at elevated temperatures to increase the ion mobility [3]. After the poling the temperature is often lowered again and the conditions of the sample are frozen. Scientific interest in thermal electro-poling has been stimulated e.g. by the observation that the poling process may generate second order nonlinear optical response which turns the sample into an interesting optical material [1,2,4–8]. Additionally, the influence of the poling on piezoelectric properties [9,10], as well as its influence on the crystal growth [11] have been investigated. In the field of medicine the influence of the poling process on the bone binding capability of bioactive phosphosilicate glasses is of major interest [12,13]. Conceptually, poling is a rather simple experiment. Yet a detailed understanding of the underlying transport processes on a microscopic scale is still missing.

It is known, that the thickness of the depletion zone depends on the poling parameters, e.g. the potential applied across the sample. Typical zones may reach several micrometers into the sample for poling voltages on the order of some kV [14,15]. The time dependence as well as the composition of the depletion zone has been investigated [14,16,17]. In general the depletion zone exhibits a structure different from that of the bulk of the sample due to rearrangement in the material [18–21]. As a consequence, the properties of this layer may be modified with respect to the bulk of the sample, as well.

Recently, the thermal electro-poling of a bioactive sodium-calcium phosphate glass has been investigated [22]. The authors observed that the poling current dropped on two distinctly different time scales. An analysis of concentration profiles performed ex-situ after the poling revealed that both, sodium and calcium, had been mobile. The amount of carriers moved during the experiment suggests that charge compensation by electron conduction must have taken place [23,24]. The authors suggested a mechanism according to which the fast process was caused by the sodium motion while calcium moves on a longer time scale. There is a number of reports in the literature on the theoretical description of the poling process in general [25,26]. However, to our knowledge there is no full theoretical or numerical investigation yet which may explain all the experimental results found by the authors of Ref. [22].

The aim of the current work is to present a model based on a Monte-Carlo simulation that describes a poling process in an ion conducting glass with more than one mobile ion species. The Monte Carlo approach has been demonstrated to be a powerful tool for describing diffusion in glassy systems [27–29]. The pivotal aspect of the model presented here is that the electrons are essentially immobile at small electric fields and become mobile once a certain breakdown field strength is exceeded. The mechanism proposed for the coupled electron–ion transport is believed to be relevant for a wide range of electro-poling processes.

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2. Theory

In order to describe the poling process, we employ a model based on the Monte-Carlo formalism. Since the influence of the poling process on the carrier distribution occurs mainly in the first few hundred nanometers below the anode and the bulk of the glass remains nearly unaffected by the experiment, we concentrate the calculations on the zone below the anode exclusively. The bulk of the sample will be described via appropriate boundary conditions.

We assume that the poling electrodes are perfectly parallel to each other and their radial extension is much larger than the thickness of the glass. As a consequence, we may concentrate on the movement of the ions in the direction perpendicular to the electrodes (x-axis) and neglect radial motion. For the numerical calculations, we divide the zone below the anode into space elements Δx (Fig. 1). We assign an average carrier density $n_{\alpha,i}$ for every carrier species α to every space element i. The same procedure is applied for the potential ϕ.

The ions move according to the gradients of potential and concentration that are present between two adjacent space elements while the electrons become mobile only when the electric field is comparable to the breakdown field [23, 24]. As a consequence, we treat electrons and ions differently. The ion flux from space element i into the adjacent space element j within one calculation step is given by

$$\frac{dn_{\alpha,i}}{d\xi} = -n_{\alpha,i}\cdot\nu_\alpha\cdot p_\alpha^{i\to j} = -\frac{dn_{\alpha,j}}{d\xi} \text{ with } j = i-1 \text{ or } j = i+1, \qquad (1)$$

Where the hopping frequency ν_α determines how often the ions try to pass the potential barrier to the neighboring space element during the time $d\xi$ that is represented by a single calculation step. ν_α is related to an average vibrational frequency of the ions inside the potential well and is a parameter to this model that describes the mobility of the respective ion species. The probability of a successful jump is given by [28]

$$p_\alpha^{i\to j} = \min\left[1, \exp\left(\frac{q_\alpha\left(\phi_i - \phi_j\right)}{k_B T}\right)\right], \qquad (2)$$

with the carrier charge, q_α, the potential difference, $(\phi_i - \phi_j)$ and $k_B T$ the Boltzmann's constant times the temperature. If the potential gradient is sufficiently large, the jump probability is 1 such that the motion is limited by the hopping frequency, ν_α.

We neglect the possible blocking of a target site (e.g. by preceding jumps) assuming there is always a sufficient number of empty sites in the vicinity of every ion. Additionally, (1) and (2) imply that the hopping distance is always the same. We expect that there is no fundamental difference in the predicted poling mechanism (sequence of processes) due to these two simplifications. However, there is an influence on the relation between real time and the number of calculation steps. Hence, we renounce the discussion of absolute times and restrict ourselves to the fundamental sequence of processes as well as the ratios of time constants for the occurring processes. Once the real duration of a certain process is known, the real durations of the other processes may be estimated using these ratios.

At sufficiently low electric fields the electrons are almost immobile. Only if the electric field is on the order of the electric breakdown field (10^9 V/m for the glasses we investigate here), the electrons start to move. In this case the mobility of the electron is much larger than the mobility of the ions such that the electrons will instantaneously reduce the electric field strength just below the breakdown threshold. As a consequence, we may formulate the following calculation procedure

a. Create a first random number that defines the initial position on the spatial grid.
b. Create a second random number that defines the jumping direction.
c. Calculate the carrier flux from the actual space element into the neighboring space element (in the direction given by step b).
d. Calculate the electric potential according to the new carrier distribution.
e. Check whether the electric field exceeds the breakdown field at any position.
f. If the electric field exceeds the breakthrough field, move electrons toward the anode until the field drops below the breakdown field strength.
g. Restart the algorithm with step a.

The electric potential may be written as

$$\phi(x) = \phi(L) - (x-L)E(L) - \frac{1}{\varepsilon_0\varepsilon_r}\int_L^x (x-x')\left(\textstyle\sum_\alpha q_\alpha n_{\alpha,i}\right)dx', \qquad (3)$$

with the dielectric permittivity ε_0 and the dielectric constant ε_r, the electric field and the electric potential at the end of the explicitly calculated zone, $E(L)$ and $\phi(L)$. Partial integration of the term containing the integral shows the validity of Eq. (3). According to Eq. (3), the potential is determined by the carrier distribution via the integral term and influenced by the potential and the electric field at the boundary of the calculated zone. Initially before carriers have moved, the electric field is spatially independent inside the sample and given by the poling potential and the thickness of the sample. Choosing the sample thickness to be 1 mm, the poling voltage to be 50 V and $L = 200$ nm, the contribution of boundary condition $E(L)$ to the potential is smaller than 10^{-2} V everywhere in the zone of interest below the anode. Correspondingly, we find $\phi(L) = 49.99$ V under these conditions. The contribution of

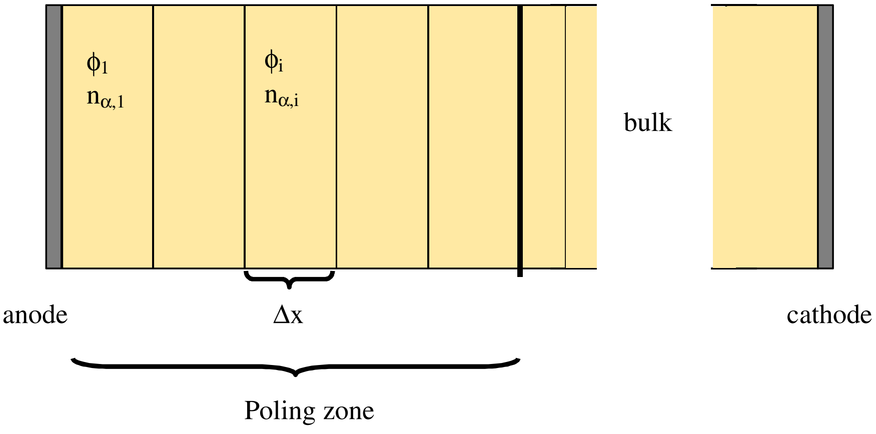

Fig. 1. Sketch of a poling setup including the discretization of the calculated zone.