Point defects in ceramics – 06.05.2025

1. *Write equations of reactions of incorporation of defects and corresponding mass constants assuming defect equilibrium. If you think that more than one mechanism is possible, state it briefly and write all possibilities.*
    a. Schottky defects in WO_3
    b. Frenkel-type cationic defects in Ta_2O_5
    c. Anionic Frenkel defects in MoO_3
    d. oxygen from atmosphere enters interstitial sites in Sr_2TiO_4
    e. Loss of Me in $Me^{+2}X^{-2}$ (Me evaporates)
    f. dissolution of CaO in HfO_2
    g. dissolution of Ta_2O_5 in $LaGaO_3$ - Ta goes to Ga sites
    h. dissolution of La2O3 in BaTiO3 ***Consider 3 possibilities:*** (La goes to Ba sites, to Ti – sites or to both)

2. Donor doping of $BaTiO_3$ can result in compensation with electrons or cation vacancies. Different possibilities will be explored in this exercises. In interior of the grains, where there is no atmospheric oxygen available, the compensation tends to be electronic, while at grain boundaries , where O is more readily available from the atmosphere, the compensation tends to be by cation vacancies.

Propose 3 possible reactions of $BaTiO_3$ doping with La, where La occupies sites of Ba. Use as reactants La_2O_3 + TiO_2 .

3. The effect of mechanical conditions on the piezoelectric response is investigated. To do it, two $BaTiO_3$ samples are made. Both samples are thinned down in the x_3 direction. Sample **I** is kept in mechanically free conditions (**Fig.2.I**). Both (001) surfaces are electroded. The voltage V is applied to the electrodes, and the change in the distance between (001) surfaces is measured in order to find the longitudinal piezoelectric response $d_{33}^{\text{free}} = \Delta L/V$.

Sample **II** is glued onto a thick electroded substrate, which fully inhibits any change of its dimensions in the x_1x_2 plane, whereas the expansion or contraction of the sample along the x_3 direction is not limited (**Fig.2.II**). Thus, the thinned sample is clamped in the plane of the substrate ($\varepsilon_1 = \varepsilon_2 = \varepsilon_6 = 0$) and otherwise mechanically free ($\sigma_3 = \sigma_4 = \sigma_5 = 0$). The upper (001) face of the sample is electroded again. The voltage V is applied to the electrodes, and the change in the distance between (001) surfaces ΔL is measured in order to find the longitudinal piezoelectric response $d_{33}^{\text{sub}} = \Delta L/V$.

Evaluate the impact of the clamping effect on the piezoelectric coefficient by calculating the relative difference between the two measured longitudinal piezoelectric responses $\frac{d_{33}^{\text{free}} - d_{33}^{\text{sub}}}{d_{33}^{\text{free}}}$. All measurements are done at constant temperature.

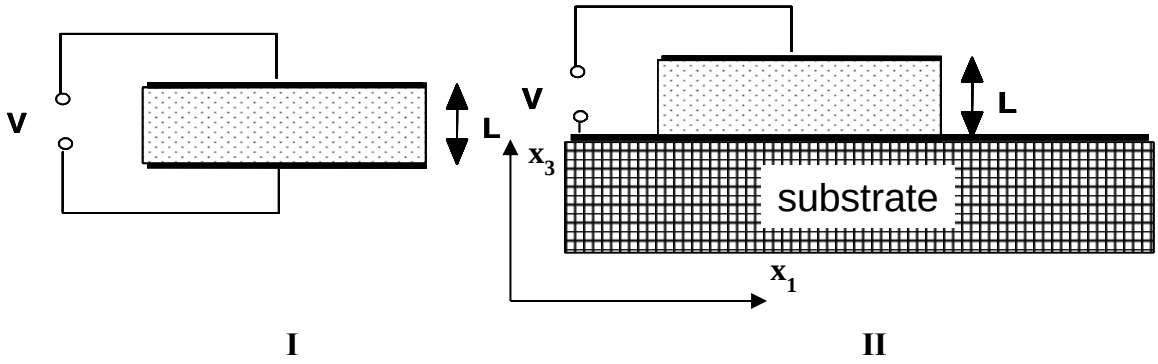

Figure 2

Two $BaTiO_3$ samples used for piezoelectric measurements