Today's technology requires new 'tailored-on-demand' materials, which should be optimized to best perform in given applications. It has been long recognized that the properties of these materials depend not only on their bulk chemical and phase composition, but also on their microstructure, especially at nanosized scale. One of many strategies to produce new application-oriented materials is to stabilize their high-temperature advantageous (e.g. highly conducting) crystalline phases down to room temperature, using different synthetic strategies. These are cases of α-AgI (an excellent Ag^+ ionic conductor, stable at >147°C) and δ-Bi_2O_3 (an excellent O^{2-} ionic conductor, stable in a 730-825°C temperature range). In both cases it is possible to stabilize these phases down to room temperature in form of nanosized crystallites embedded inside respective glassy matrices. Unfortunately, the mechanisms of such stabilization have not yet been reliably and ultimately established. One can only find partial studies on special cases of those phenomena.

In this project we plan to fill that fundamental gap by exploring in detail the mechanisms of stabilization of δ-Bi_2O_3 down to room temperature. We feel obliged to do that, because we had experimentally discovered that stabilization effect in our studies on thermal nanocrystallization of bismuthate glasses [1]. Therefore, this will be a natural continuation of our previous work. We plan to establish the mechanism of stabilization of δ-Bi_2O_3 by carrying out an integral vast program of complementary experimental and computer-modelling studies. The experimental side will include syntheses and many methods which should give a complete information on the structure, phase composition, local order, thermal properties, microstructure at scales of tens nm and below, electrical transport, interfacial structure and dynamics. The numerical calculation side will be focused on finding stability conditions for δ-Bi_2O_3 nanoclusters and nanocrystallites embedded inside a glassy phase. The studies will be carried out in cooperation with leading academic and research centers in Poland, Europe (Germany, France) and USA. The experimental methods will include temperature dependent X-ray diffraction, differential thermal analysis (DTA), differential scanning calorimetry (DSC), synchrotron radiation-based XANES/EXAFS absorption spectroscopies, solid state nuclear magnetic resonance spectroscopy (MAS NMR), scanning- and high-resolution transmission microscopies (SEM and HR-TEM), and impedance spectroscopy (IS). Numerical modelling will use molecular dynamics (MD) and/or density functional theory (DFT) approaches.

We strongly believe that the ambitious program of these studies will enable us to present a complete, reliable and well-evidenced mechanism of the stabilization of nanocrystallites of a high temperature phase (here δ-Bi_2O_3) down to room temperature. We are also convinced that the conclusions of this project will be valuable for other systems in which a high-temperature phase can be stabilized down to room temperature.

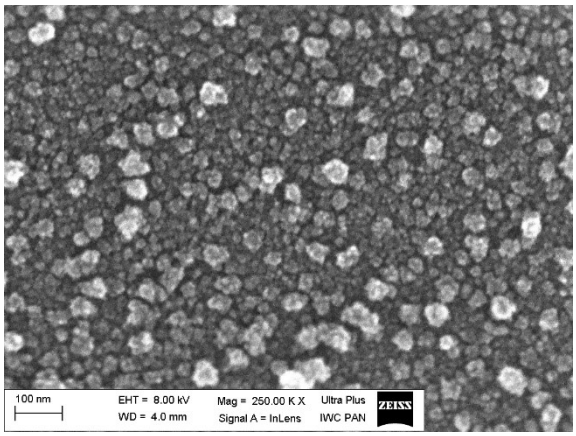

Fig. 1. Nanocrystallites of δ-Bi_2O_3 phase stabilized down to room temperature by confinement effect in a glassy matrix [1].

Literature

[1] T. K. Pietrzak, J. E. Garbarczyk, and M. Wasiucionek, "Stabilization of superionic δ–Bi_2O_3 phase at room temperature by thermal nanocrystallization of bismuth oxide glasses," *Solid State Ionics*, vol. 323, pp. 78–84, 2018, https://doi.org/10.1016/j.ssi.2018.05.021.