Research activities

Effect of an External Electric Field on Grain Boundary Evolution in the Course of Nano-Ceramic Sintering

PI: Dr. Shmuel Hayun, Department of Materials Engineering.

Consolidation of oxide nanoparticles in the presence of an electric field has provided promising results for retaining the nanostructure in the bulk. Although the sintering of nanoparticles shares the same basic principles as those for the sintering of coarser particles, a number of issues and challenges are specific to nanosintering. From a thermodynamic point of view, solid state sintering can be described as a thermally activated process during which the total interfacial free energy of an assembly of particles of equilibrium chemical composition decreases. Moreover, the consolidation and the grain growth pattern are determined by the ratio of the solid-vapor interfacial energy to the solid-solid interfacial (i.e., grain boundary) energy of the material. We propose to take a first step towards elucidating these processes in the presence of an external electric field by testing the synergistic effects of an external electric field and dopants on the grain boundary energy and sintering mechanism of oxide nanoceramics. Our first objective is to study the individual contribution of the dopant on the surface and interfacial energies. To accomplish this objective we have developed experimental setup for measuring these energies during the consultation process. We hypothesize that the dopant will significantly affect these energies and thereby change the sintering course. Our second objective is to study the effect of a DC electric field on the dopants, the interfacial and surface energies, the space charge layer, and the grain size of the materials. We will map the contribution of each parameter to the consolidation process. The most promising parameter will be further investigated by studying the properties of the resulting material. The experiments proposed here will increase our understanding on the consolidation mechanism of nanoceramics in the presence of external electric field.

Experimental methodologies for assessing the surface and energy of highly hygroscopic materials: *The case of nanocrystalline magnesia.*

S. Hayun et. al. , *J. Phys. Chem. C*, 115 (48),(2011) 23929-23935

Determination of the surface energy of materials at nanometric scale has remained a thorny problem mainly because this energy is shaded by the species absorbed on the surface of material, particularly water. Navrotsky and collaborators have reported a systematic approach to estimate the contributing effect of adsorbed water to the surface energetics of oxides. However, the application of this methodology to highly hygroscopic materials (MgO, La_2O_3, CaO) is hindered by the difficulty of creating an anhydrous surface state in samples at the nanometric scale (Fig. 1)

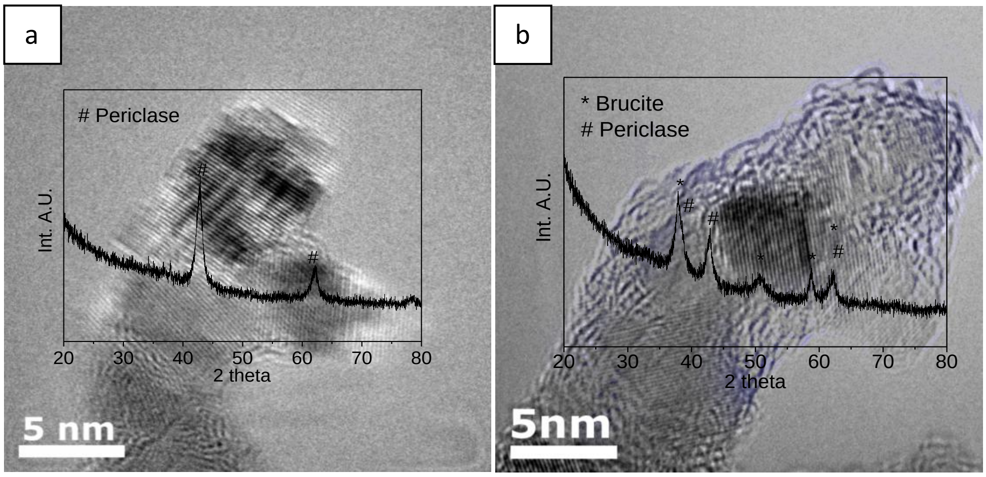

Fig. 1- a) Anhydrous nano MgO particles formed by laser ablation, b) After exposition to wtaer vapor outside the TEM, brucite/amorphous hydroxide forms on the surface.

In this work, we developed new methods to assess the anhydrous surface energy of highly hygroscopic nanomaterials. We synthesized anhydrous MgO nanoparticles by laser ablation in a water-free environment and, for the first time ever, were able to directly assess the energy of its anhydrous surface using high temperature oxide melt drop solution calorimetry and differential scanning calorimetry (Fig 2); the surface energies were 1.2(0.1) and 1.3(0.1) J/m^2, respectively. Although the method was applied to study nanocrystalline MgO, there is no reason to believe that its success is restricted to this material.

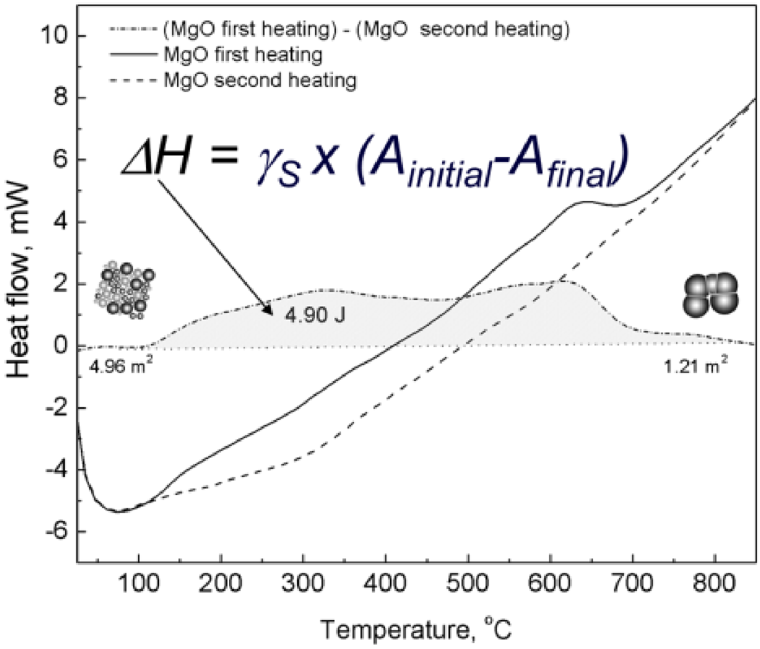

Fig. 2. Heat flow traces of the first (solid line) and second (dashed line) DSC runs on a single MgO sample. The heat flow trace obtained by subtracting the second DSC run from the first run is presented as a short dashed dot line. A linear baseline was chosen for the integration. BET surface areas measured before and after heating and the integration results are labeled under the curve. The areas indicated in the beginning and at the end of the exothermic effect represent the total area of the sample (specific surface area multiplied by the mass). In this particular experiment, 18.13 mg was used, and 4.90 J represents the integrated area, i.e., the total energy released during the process.

How to retain nanostructure during ceramic sintering: New approach to advanced understanding. (BSF project 2011-2013)

PIs. Dr. Shmuel Hayun and Prof. Alexandra Navrotsky

Due to unique and indispensable properties of nanoceramics there is an urgent need for those materials in modern technology and industry. However, maintaining the nanostructure through the processing stages is still a challenge. Spark Plasma Sintering (SPS) is an advanced sintering technology that combines axial pressure, superfast heating rate and DC electric field. These set of features allows fabricating materials with nanostructure. Although the effect of axial pressure and heating rate on nanoceramics has been extensively studied, only little information is available on the impact of electric field on the interfaces during sintering.

In this project we will explore the impact of the electric field on the interfacial energy and microstructure and on the ability of the ceramic to retain nanostructure based on the methodology that present in Fig. 3. The study is conducted on $MgAl_2O_4$ spinel due to its cubic structure and consistent morphology. Moreover, the intrinsic space charge layer allows identifying directly the influence of electrical field on interface formation and energetics. The interfacial energy of doped and undoped $MgAl_2O_4$ nanoceramics produced using SPS will be studied by differential scanning and oxide melt solution calorimetry.

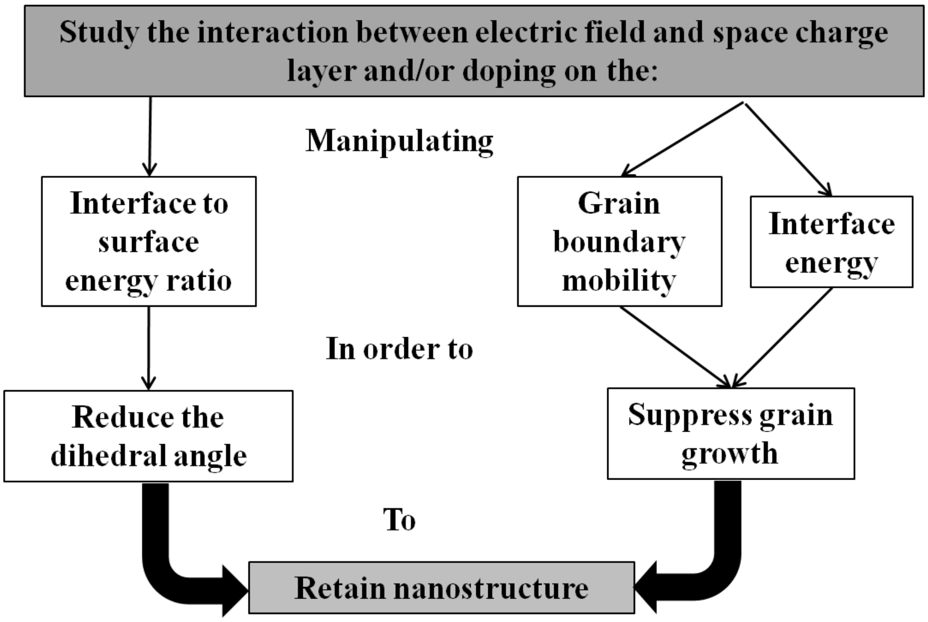

Fig. 3 Summary of the methodology in the proposed work