Minicolloque n° CPR25 **x Invited Oral** **Poster**

Defect structure in advanced nanostructured materials

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Nanostructured materials are in the forefront of materials science due to their unique properties (e.g., improved mechanical and magnetic performances). The properties of nanomaterials can be tuned by changing the lattice defect structure, such as the amount, type and arrangement of dislocations, planar faults and grain boundaries [1]. The defect structure can be tailored by an appropriate selection of the processing conditions and post-processing treatment (e.g., anneling). In this presentation, the influence of the manufacturing circumstances and the subsequent thermal treatment on the lattice defects in advanced nanomaterials is overviewed. This effect is investigated on bulk nanocrystalline metals and alloys (such as high entropy alloys) processed by top-down methods (i.e., by severe plastic deformation) as well as thin films, nanoparticles and metallic nanofoams manufactured by bottom-up techniques. Special emphasis is placed on the study of the defect structure by X-ray line profile analysis [2]. The latter method is very effective and non-destructive way of the study of the lattice defects with good statistics. The correlation between the defect structure and the properties of the novel nanostructured materials is revealed and discussed in detail.

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Minicolloque CPR25 ⊗ **Oral** ☐ **Poster**

Structural defects in fine-grained $MgAl_2O_4$ sintered ceramics through the elaboration process: from the powder to the post-densification treatment

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Compounds with the spinel structure AB_2X_4 have been predicted to exhibit high tolerance to ionizing irradiation, due to low energy formation of structural defects such as F-centers (anionic vacancies), V-centers (cationic vacancies), antisite defects and their combinations [1]. Between them, $MgAl_2O_4$ is considered for extensive optic applications as a radiation tolerant material stable in extreme environments [2]. High-density of grain boundaries in the bulk ceramic is required for the effective capture and recombination of defects induced by ionizing radiation, providing an improved material functionality [3]. The relevant $MgAl_2O_4$ ceramics have to possess high mass density and small grain size at the nanoscale. In this context, the understanding of their electronic band structure and defects induced by the elaboration of spinel ceramics is mandatory.

In this work, we investigated the structural defects contained in fine-grained magnesium aluminate spinel ceramics obtained by spark plasma sintering, as well as their influence on optical and magnetic properties. We studied the evolution of these defects at each steps of the elaboration process (raw powder, SPSed ceramics and after heat treatments) for a better understanding of their nature, their stability and their eventual conversion. We also investigated the effect of Ta-doping. The microstructural and crystallographic properties were characterized by SEM and XRD, the structural defects by photoluminescence (PL) and Electron Paramagnetic Resonance (EPR), and the static magnetic properties by SQUID. The Figure 1 shows the impact of the sintering process on the EPR signals, revealing the emergence of new paramagnetic defects depending on the sintering treatment and structural properties.

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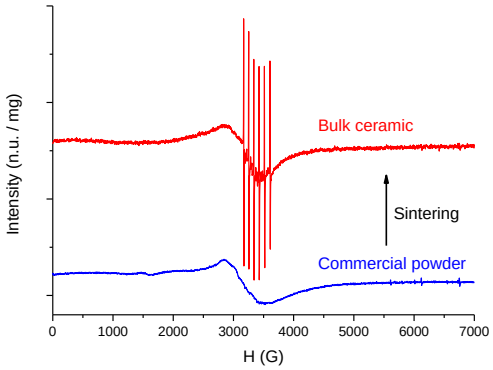

Figure 1 : Electron Paramagnetic Resonance (EPR) first derivative signals for the used commercial powder (blue curve) and for the bulk ceramic after Spark Plasma Sintering (red curve)

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Microstructure effects on thermal and electric conductivity in silver-based ceramics for die-attachment

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We develop here the elaboration by a "bottom-up" strategy of a new intermetallic phase based on Ag_3Sn compound. This system is a good candidate to replace lead-based solders ensuring the interconnection in electronic power devices. We firstly synthesized particles of submicron sizes by a soft chemistry method: the polyols process [1-2]. After a de-binding step, the synthesized powders were consolidated by Spark Plasma Sintering. The combinations of the various shaping parameters (temperature, pressure, temperature rise ramp, etc.) have led to the development of materials with different microstructures (relative densities, grain size, nature of grain boundaries. ..). In order to study the microstructure effect on the thermal and electric conductivity of the Ag_3Sn-based ceramics, we discuss here our experimental results on relevant SPS-sintered samples. The grain and crystalline properties are characterized for sintering temperatures between 200°C and 390°C and for applied pressures between 5 and 100 MPa. All samples present the same mono-phased characteristics of the sintered-powder and the evolution of their microstructure is studied in straight connection with the physical properties. The thermal diffusivity increases with the relative density of samples and present a peculiar evolution in temperature depending on this latter (see Figure 1 left-hand side) showing the key role of the microstructure on the optimization of the thermal conductivity of Ag_3Sn-based samples. The electric resistivity was measured by a 4-contact configuration in a standard PPMS system. At high temperature the resistivity increases with temperature putting in evidence the good metallic behaviour of our samples. On the other hand, at a ground state energy level (2K) the resistivity values decrease when the grain size increases confirming again the important role of the microstructure (grain size and grain boundary..) on the electric conductivity (see Figure 1 right-hand side).

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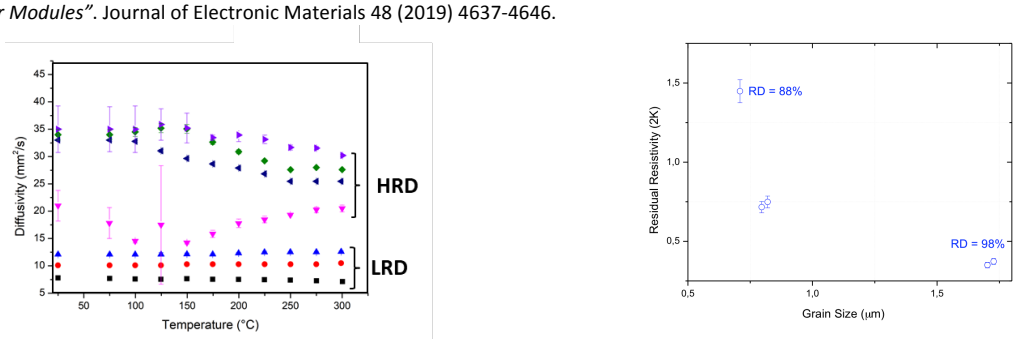

Figure 1: (left) Thermal diffusivity measurements versus temperature for High Relative Dense (HRD) samples and Low Relative Dense (LRD) ones; (right) residual resistivity @ 2K as fonction of the grain size.

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Effect of microstructure on the diffusion property of polycrystals

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Hydrogen is seen as a clean, mobile energy carrier and source of fuel as it has the great advantage of being present on the planet in abundant amount. A genuine 'hydrogen economy' is henceforth envisioned. However, there are still many obstacles to overcome before realizing a real hydrogen economy. Indeed, a major concern the performance and lifetime of materials, which are reduced with the presence of hydrogen (Hydrogen Embrittlement). This phenomenon results from a combination of different parameters related to the material's characteristics, the source of hydrogen (internal or external), the mobility of the solute and to the mechanical solicitations. Hydrogen transport in metallic polycrystal is affected by numerous phenomenon, as trapping on defects, mechanical fields, material heterogeneities like grains boundaries, etc… Hydrogen diffusion parameter, however, is usually identified using experimental setups and sample features that only give access to an average estimation of its value. The transition scale between elementary processes at atomistic scales and a physical property (hydrogen mobility) at macroscopic scale remains a challenge [1-3]. Hydrogen permeation across metallic polycrystals is here focused on, from a numerical point of view, to point out the effect of several polycrystalline mechanical and metallurgical features. First, the effect of stress fields and evolving plasticity on the global permeation curves is considered [4]. Second, the influence of grains boundaries, acting as short-circuit of diffusion, and their morphology, on the overall diffusion property is analyzed [5].

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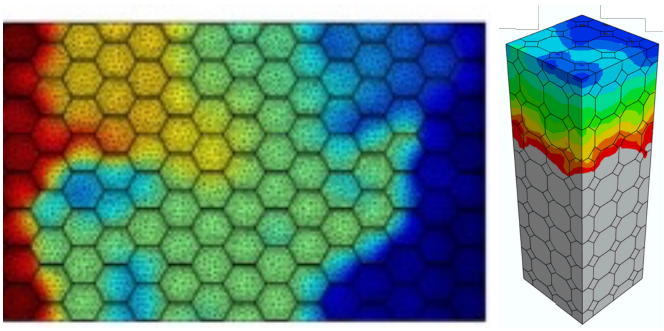

(a) (b)

Figure 1: Hydrogen concentration in a metallic polycrystal (a) affected by an heterogeneous grain boundary diffusive properties and (b) by mechanical fields heterogeneities. 2D and 3D hydrogen distributions [4,5].

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Magnetic properties of nanostructures

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Over the past three decades, much attention has been paid to the development of nanoarchitectures, particularly their elaboration, using either direct chemical synthesis routes or/and post-treatments using different processes. Although the chemical nature of surfaces of nanoparticles must be well correlated to physical properties, the role of interfaces in nanoarchitectures needs to be better understood. Indeed, many new synthesis routes have been developed to prepare well-defined magnetic nanoparticles while the role of the different chemical parameters has been studied in depth resulting in their high reproducibility: their size, morphology, chemical composition, structural and physical properties can now be well controlled and tuned. The following strategy consists in manipulating these nanoparticles using temperature, pressure, mechanical stimuli to design new architectures dealing with new physical properties.

The main strategy to characterize these magnetic nanoarchitectures is based on the combination of diffraction techniques, microscopies, magnetic measurements and local probe techniques to get a detailed insight at different scales. The goal is to correlate magnetic characteristics (saturation magnetization, coercive field, exchange bias, dipolar interactions) to local atomic structures including that of interfaces and/or grain boundaries. We therefore report some recent examples of studies, illustrating in particular how such effects can be identified and modelled to understand experimental data.

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Aimants submilimétriques à base de nanobatonnets de Cobalt assemblés par magnétophorèse en vue d'une intégration dans un récupérateur d'énergie

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Les microsystèmes magnétiques font désormais partie de notre vie quotidienne, que ce soit dans le domaine automobile, télécommunications ou médical. Cependant l'intégration d'aimants permanents est un verrou technologique majeur.
Une technique alternative aux procédés classiques de fabrication est la réalisation d'aimants submillimétriques de forme contrôlée à partir de nanobâtonnets de cobalt synthétisés chimiquement [1]. Initialement en suspension dans une solution, les nanobâtonnets peuvent être assemblés par magnétophorèse (e.g. l'application d'un champ magnétique extérieur) lors du séchage de cette solution [2]. Des plots de nickel électrodéposés sont utilisés afin de créer des gradients de champs locaux et ainsi contrôler la forme et la localisation de l'aimant.
Cette méthode permet d'obtenir des aimants de quelques centaines de micromètres de côtés ayant une aimantation dans le plan ou hors plan (Fig 1.) et compatibles avec les méthodes de microfabrication usuelles, donc intégrables dans des microsystèmes tels qu'un récupérateur d'énergie électromagnétique [3,4]. Nous présenterons l'élaboration de ces aimants puis la comparaison des performances de récupérateurs intégrant ces aimants à base de nanobâtonnets de Co à ceux réalisés avec un réseau épais d'aimants de NdFeB déposé par voie physique.

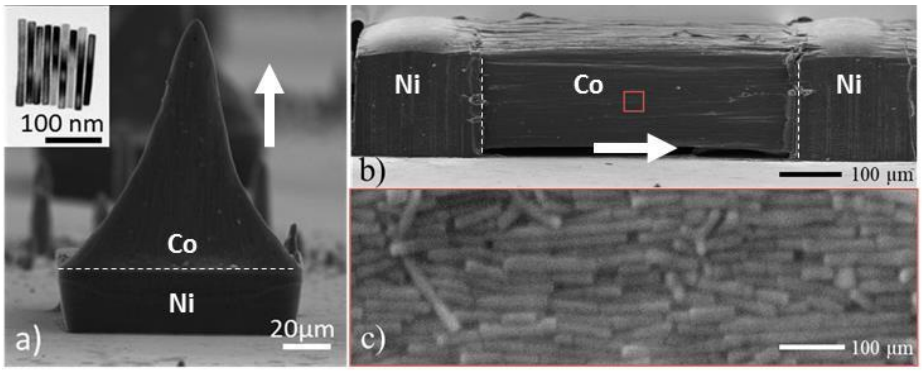

Figure 1. *Image en microscopie électronique à balayage (MEB) d'aimants nanostructurés avec une aimantation a) hors plan et b) dans le plan. c) Image en microscopie électronique à transmission (MET) de nanobâtonnets de Co préparés par synthèse polyol, vue agrandie de l'aimant, mettant en évidence l'alignement des nanobatonnets.*

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Minicolloque n° CPR25 ☐ **Oral** ☐ **Poster**

Determination of the microstructure-property relationship of a magnetic nanomaterial thanks to a coupled laboratory-synchrotron approach

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In the search of new magnetic nanomaterials, organizing magnetic nanoparticles within a solid matrix is of great interest. For that purpose, our group developed an original bottom-up approach, based on coordination and sol-gel chemistry. It consists in the confined growth of Prussian Blue Analogs $A_4[B(CN)_6]_{2.7}$ (A,B=Co,Fe) nanoparticles (Np) within the organized mesoporosity of a silica monolith, which is then calcinated in a controlled atmosphere to transform the PBA in an oxide or an alloy [1,2]. On the one hand, the use of PBA Np as a precursor of the oxide/alloy Np enables a full control of the stoichiometry of the final phase. On the other hand, the use of a mesoporous silica monolith allows for a combined control of the Np size, shape and organization within the matrix and for an organization at the macroscale of the matrix, since surfactant-templated sol-gel chemistry enables to play with the internal organization [3] and external shape of the silica template.

In order to get a complete picture of the relationship between our elaboration process and the final nanocomposite (i.e. the oxide/alloy Np within the silica matrix) properties, we characterized its magnetic properties by SQUID magnetometry, and we systematically compared our synthesis pathway with another one widely used in literature, namely the use of metallic salts as precursors of the oxide/alloy. Despite the combination of powder and Small Angle X-ray Diffraction, IR and UV-Vis spectroscopies, and transmission electron microscopy, the macroscopic information obtained does not always enable to fully understand the properties of the nanocomposites. So we coupled this laboratory investigation with X-ray Absorption Spectroscopy to get fine information at the local scale.

We will present through the example of the Co oxide and metal nanocomposites how this coupled laboratory-synchrotron approach enabled to finely determine the microstructure of the nanocomposite (Figure 1), and hence better understand its microstructure-property relationship [1].

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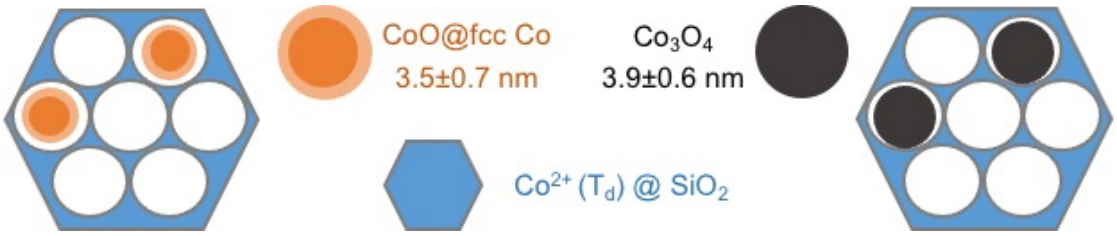

Figure 1 : Microstructure of the *(left)* Co metal and *(right)* Co_3O_4 nanocomposites determined by our coupled laboratory-XAS approach.

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Tunable magnetic anisotropy in nanostructured rare earth free magnet obtained by field assisted bottom-up strategy

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Nowadays Nd-Fe-B [1] and Sm-Co [2] systems are the most used materials in the field of permanent magnetism and magnetic recording. However, because of the toxicity of the rare earth extraction and their high price, a major effort is being made in terms of research to develop new materials as an alternative. In this context, several works in the recent years have shown that the anisotropic nanoparticles have proven their interest. Indeed these particles show high remanence and high coercivity. Such characteristics are mainly governed by three parameters (i) the ratio aspect defined by the ratio L/D, (ii) the mono-domain character of the nanoparticle and (iii) the good crystallinity and thus the absence of defects [3]. We have also recently demonstrated by micromagnetic simulation [4-5] and static magnetic measurements [6] that a judicious well-organized dispersed assembly of these anisotropic nanoparticles can bring to tunable magnetic energies suitable for applications. In this purpose, we succeed in developing a novel bottom-up strategy [7] in order to obtain an anisotropic organized nanostructured bulk system enhancing the magnetic behavior of the nano-magnets ensemble. This novel method combines forced hydrolysis in polyol-medium synthesis of rare earth free nanowires [8], and magnetic field assisted Spark Plasma Sintering (SPS) to ensure their consolidation [7]. The first step allows the production of nano-magnet with optimized magnetic properties and it takes benefit from the properties of polyol which act as solvent, complexing and reducing agents to produce a great variety of inorganic materials (oxides, metals, layered hydroxyl salts). The external applied field likely controls the nucleation and growth processes. The second step allows the sintering of massive material with an organized nanostructure resulting from the alignment of the nanowires along the applied magnetic field. This non-conventional compaction technique minimizes the grain growth inside the solid sintered material showing a high relative density (close to 100%). Thus the nanostructured bulk material likely preserves the optimized magnetic performances of the rare earth free nano-magnets as well as presenting the good mechanical properties of the bulk system. We will present our recent studies showing that a macroscopic magnetic anisotropy of the remanent magnetization as well as a good magnetic energy is supported by high mechanical robustness in our nanostructured bulk materials. We will analyze the different experimental parameters used for the field assisted-bottom up strategy (pressure, temperature and magnetic field) as well as the magnetic static properties experimented by two different measurements (DC-SQUID and Vectorial-VSM (see Figure 1)). Our results show that the field-assisted bottom up strategy is a valuable way to create an alternative to standard rare earth magnet. Last but not least, this strategy can be applied to a variety of ferromagnetic compounds, which makes the technique highly versatile in terms of applications.

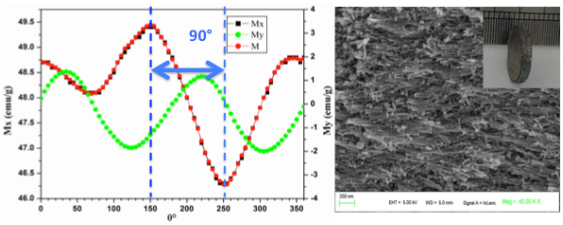

Figure 1: (left hand) Remanent magnetization as function of the in-plane angle of the magnetic field applied. M_x is the component parallel to the field, M_y is the one perpendicular to the field and M is the global magnetization intensity; (right hand) SEM image of the nanostructured magnet.

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Minicolloque n° CPR25 **X Oral** **Poster**

Etude des propriétés des aimants NdFeB recyclés

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Nous présentons ici les travaux de recherches menés dans le cadre d'un projet ANR ASTRID (N° ARN-17-ASTR-0014-02) portant sur le frittage par Spark Plasma Sintering (SPS) de poudres $TR_2Fe_{14}B$ (TR = Nd, Pr…) obtenues par décrépitation à l'hydrogène d'aimants en fin de vie. Une série d'essais de faisabilité a d'abord été réalisée à l'aide d'une poudre commerciale afin de comprendre les mécanismes intervenant pendant la densification du matériau. Les propriétés magnétiques des échantillons ont été caractérisées afin de déterminer le cycle SPS permettant d'optimiser l'aimantation à saturation Ms, l'aimantation rémanente Mr, le champ coercitif Hc et le produit énergétique maximal BHmax. Ce cycle a ensuite été appliqué à une poudre recyclée dont les propriétés sont comparées à celles des échantillons obtenus avec la poudre commerciale. La relation entre les analyses structurales, microstructurales et les propriétés magnétiques sera discutée.