DSEC VI

The Sixth Directionally Solidified Eutectics Conference

10 - 13 September 2019
University of Salerno
Fisciano (Italy)

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DSEC VI

Directionally Solidified Eutectics Conference

Book of Abstracts

TITLE

6th Directionally Solidified Eutectics Conference - Abstract Book

EDITORS

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The Sixth Directionally Solidified Eutectics Conference (DSEC VI) will take place at the University of Salerno (Italy) from 10 to 13 September 2019.

Since DSEC I, which was held in Paris in 2003, every three years the DSEC Conferences have brought together top scientists whose research activity focuses on the properties of eutectic systems, such as phase diagram analysis, solidification theory and modeling, novel processing strategies, microstructure and physical properties analysis etc.

While ceramic eutectics were originally studied for their high-temperature thermo-mechanical properties, current and emerging research is pushing into new functional applications such as photovoltaics, photoelectrochemistry, photonics, plasmonics and metamaterials.

In particular, this year, since the two organizing institutions of DSEC VI, i.e. the CNR SPIN Salerno and the department of Physics of University of Salerno, are mainly devoted to the synthesis, modeling and characterization of single crystals, the topics of the DSEC VI will include such topics. A special emphasis will be devoted to the synthesis and design of eutectics and to the observation and characterization methods, with a special focus on the study of interface properties and microstructure investigation.

The DSEC VI brings leading scientists from Asia, Europe, North America and South America, to discuss evolving and emerging research area in the field of eutectics. This conference provides an excellent forum for researchers and specialists from universities, research institutions and industry, as well as motivated students, to present their recent findings on eutectics science and technology, to exchange knowledge, to share new ideas, and also to extend cooperation in the field of the theory and applications of eutectic systems.

DSEC VI - Conference Chairs

Rosalba Tatiana Fittipaldi
Alfonso Romano

Conference Programme

Tuesday, September 10th, 2019

16:00	REGISTRATION	
18:00	**Welcome Cocktail**	

Wednesday, September 11th, 2019

9:15	Opening and Welcome: Prof. S. De Pasquale, Director of the Department of Physics and Dr. M. Cuoco, Deputy Director of CNR-SPIN Salerno	
9:30	Chair László Gránásy	**Invited** ***S. AKAMATSU*** Real-time observation of a rod-to-lamellar transition during eutectic solidification
10:00		**Invited** ***M. PLAPP*** Dynamics of spacing homogenization in lamellar eutectics with anisotropic interphase boundaries
10:30		***T. PUSZTAI*** Phase-field modelling of the ultrafine eutectic microstructure formed during laser additive manufacturing
10:50	Coffee Break	
11:20	Chair Ali Sayir	**Invited** ***L. MAZEROLLES*** Synthesis of ceramic eutectics from the melt: methods, microstructures and related mechanical properties
12:00		***S. MARLIN*** St Gobain eutectics for abrasive application
12:20		***K. ORLINSKI*** Research potential of MgO-$MgAl_2O_4$ eutectic - a second chance fully deserved
12:40		***M. THOURY*** Cu-Cu_2O eutectic through time: photoluminescence imaging and X-ray tomography approaches to investigate metallurgical processes
13:00	Lunch Break	
14:40		**Invited** ***U. HECHT*** Ultrafine Fe-Fe_2Ti eutectics by laser additive manufacturing

15:10	Chair Marie-Hélène Berger	***D. ROHRENS*** Directionally solidified eutectics by selective laser melting: Process optimization, materials design and melt-pool-dynamics simulation
15:30		***A. THEOFILATOS*** Fe-Fe_2Ti eutectics processed by Laser Metal Deposition: Modelling and validation of the coupled zone
15:50		***N. MARAŞLI*** Directional electro growth of Al-Cu eutectic alloy under different directions and magnitudes of electrical fields
16:10	**Coffee Break**	
16:40	Chair Paul V. Braun	**Invited** ***R. I. MERINO*** Selective Emitters for Thermophotovoltaics Based on Eutectic Composites
17:10		***K. ORLINSKI*** Effect of annealing conditions on photoelectrochemical response and stability of $SrTiO_3$-TiO_2 photoanodes
17:30		***Y. YOKOTA*** Improvement of thermoelectric properties on $SrTiO_3$ with eutectic morphology
17:50		**Invited** ***A. SHAHANI*** Emergence of two-phase spirals via eutectic crystallization
18:20	**Visit to the lab of CNR-SPIN and Department of Physics**	

Thursday, September 12th, 2019

9:30	Chair Leo Mazerolles	**Invited** ***L. LIU*** Microstructure evolution and optical properties of Al_2O_3/YAG: Ce^{3+} eutectic ceramic grown by laser floating zone melting
10:00		**Invited** ***T. DUFFAR*** Insights on the structure of the solid-liquid interface of Alumina-YAG-Zirconia eutectic
10:30		***H. SU*** Laser additive manufacturing of $Al_2O_3/GdAlO_3/ZrO_2$ ternary eutectic ceramics with fine microstructures
10:50		***M. H. BERGER*** Alumina-Zirconia eutectics processed using laser melting and ultra-high solidification rates
11:10	**Coffee Break**	

11:40	Chair Antonio Vecchione	**Invited** ***P. V. BRAUN*** Emergence of Archimedean lattices in template-directed eutectic solidification
12:20		**Invited** ***M. S. ANWAR*** Dynamic nature of Nb/Ru/Sr_2RuO_4 topological superconducting junctions
12:50		***V. GRANATA*** Growth of eutectics of strontium and calcium Ruddlesden-Popper series by the floating-zone technique
13:10	**Lunch Break**	
14:50	Chair Ali Sayir	**Invited** ***D. A. PAWLAK*** Advances in novel composite materials obtained by crystal growth
15:20		***M. TOMCZYK*** ZnO–$ZnWO_4$ eutectic composite: a new self-assembly route to highly tunable narrow-band optical filters
15:40		***V. FILIPOV*** Directional crystallization of eutectic alloys hexaboride - high-entropy diboride
16:00	**Coffee Break & Poster Session**	
18:00	**Walking in Salerno & Social Dinner**	

Friday, September 13th, 2019

9:30	Chair Antonio Vecchione	**Invited** ***H. KANEYASU*** Superconductivity in the eutectic Sr_2RuO_4-Ru
10:00		***M. CUOCO*** Superconducting and magneto-electric effects in eutectic ruthenates
10:20	**Coffee Break**	
10:50	Chair Rosa Merino	**Invited** ***A. LARREA*** Dopant Segregation and Oxygen Vacancy Enrichment in Gd-doped CeO_2/CoO and CeO_2/NiO Interfaces of Directionally Solidified Eutectics
11:30		***K. KOLODZIEJAK*** Thin layers of eutectic composites for photoelectrochemical water splitting
11:50		***K. KAMADA*** Development of X-ray Talbot-Lau imaging system using large area Tb doped GAP/α-$Al2O_3$ eutectic scintillator plates
12:10		**CLOSING REMARKS**

Contents

Wednesday, September 11th

Real-time observation of a rod-to-lamellar transition during eutectic solidification

Silvère Akamatsu[1], *Sabine Bottin-Rousseau*[1], *Victor Witusiewic*[2], *Ulrike Hecht*[2]

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Directionally solidified binary eutectics are of great practical interest as self-organized composite materials with various microstructural features. They are known to be a frozen-in trace left behind in the bulk solid by a diffusion controlled dynamics of coupled-growth front patterns. It has been extensively studied in metallic, as well as oxide and salt alloys of industrial interest, and by in situ experimentation in transparent systems and time-resolved numerical simulations for more fundamental investigations. Important results have thus been obtained on the morphological stability of eutectic growth shapes and pattern selection processes. In a first approach, binary-eutectic microstructures are usually classified into rod-like and lamellar ones. The latter correspond to regular, alternate stackings of platelet-like crystals of the two eutectic solid phases. The first ones –rod-like eutectics– designate a dispersion of fibers of one solid phase with a hexagonal order, at least locally, into a continuous matrix of the other one. However, there are clear experimental and numerical evidence for the existence of coupled-growth regimes during which rod-like, lamellar, and/or more complex shapes coexist in a given sample. The problem, in brief, that of the so-called lamellar-to-rod transition, still remains poorly explored. We have developed an in-situ experiment method that permits to visualize optically the evolution of coupled-growth front patterns in real time in bulk transparent eutectic alloy samples. In the succinonitrile-(D)camphor system, a well-characterized eutectic alloy that has been extensively used as a non-faceted model system for in situ studies of regular eutectic growth, we have identified and located the lower and upper limits (rod elimination, and rod splitting, respectively) of the stability interval of hexagonal eutectic-rod patterns [1]. In this system, we also discovered a hysteretic transition from rods to lamellae in the presence of a finite-size effect in semi-thin samples [2]. Those conclusions could be drawn from laboratory experiments during which thermosolutal convection in the liquid was negligible. On ground, this constraint actually narrows the range of explorable parameters (composition, size, thermal field) and prevents one to undertake a systematic study of the lamellar-to-rod transition in large samples. We undertook a science-in-microgravity project (ESA/NASA) called TRANSPARENT ALLOYS (TA). An apparatus for in situ directional solidification experiments in large samples has been installed in the MSG facility on board the International Space Station (ISS). We will present the results of the first TA campaign (January-March 2018 ; SEBA program).

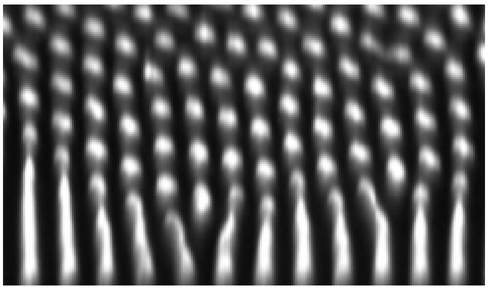

Figure: Eutectic growth pattern during directional solidification of a succinonitrile-d,camphor alloy, showing a coexistence between rods and lamellae (detail). In situ observation made on board the ISS with the TRANSPARENT ALLOY apparatus. Horizontal dimension: 490 µm.

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Role of solid-solid and solid-liquid interfacial energy anisotropies in structure formation of eutectics

Summeet Rajesh Khanna, Aramanda Shanmukha Kiran, Salapaka Sai Kiran, Kamanio Chattopadhyay, Abhik Choudhury

Department of Materials Engineering, Indian Institute of Science, Bangalore, India

Eutectic alloys are self-organising composite materials with a wide variety of microstructural features. Size, shape, distribution, and orientation of these features can be modified by process parameters (temperature gradient, velocity of interface) as well as material parameters (volume fractions, anisotropy of interfacial energies, diffusivities, impurity nature and its percentage etc.). The first aspect of our work is to study the morphological evolution in eutectic systems where the minority phase fraction is particularly low. We choose two alloys: 1) Sn-14at%Zn where the eutectic reaction gives rise to Zn(HCP) and Sn(BCT) as the solid phases with Zn(HCP) phase having a volume fraction of 9%; 2) Sn-85at%Te eutectic system with SnTe(Cubic) and Te(Trigonal) as the solid phases, with the minority phase SnTe having a volume fraction of 27%. Both the alloys were directionally solidified using a modified Bridgman setup, at different pulling velocities(V) in order to study the variation of the morphologies and for deriving the eutectic scaling parameter ($\lambda_2 V$), where (λ) represents the scale of the microstructure . While in the Sn-Zn eutectic alloy, the morphologies typically tend towards broken-lamellar structures with well defined lamellar orientations, in the SnTe-Te system; rod and labyrinthic microstructures are noticed. While the morphologies observed in the Sn-Te system are typical of eutectic alloys with such volume fractions, for the Sn-Zn alloy our results are contrary to what is usually observed in eutectic systems with similar minority phase fractions. We hypothesize that the underlying reason for this is the anisotropy in interfacial energy of the solid-solid interfaces. The second aspect of our work is devoted to the investigation of colony formation initiated through the addition of impurities. We have chosen the Sn-Te eutectic system as the base binary system which has SnTe and Te phases, with Ag/Sb as impurity additions for triggering the colony formation. The binary and ternary (Ag/Sb addition) alloys are directionally solidified at different interfacial velocities to study the morphological evolution. Upon addition of a third component, a diffusive instability (similar to a Mullins-Sekerka instability) leads to the formation of two-phase colonies that arise beyond a particular velocity. Critical velocities beyond which instabilities form are determined for each of the alloying additions. In our experiments we find colony structures having an internal sub-structure upon additions of both Ag/Sb. The internal structure due to Ag addition however, is different from Sb Addition (See figues). We explain the role of anisotropies in the free-energy of the interphase boundaries that lead to the formation of the different eutectic colony structures using results obtained from experimental characterization techniques.

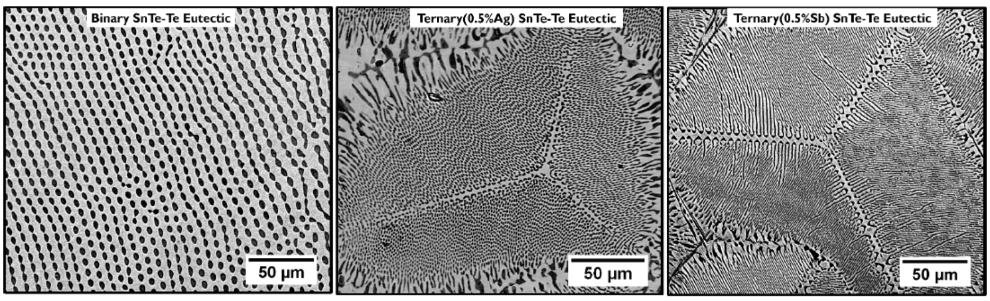


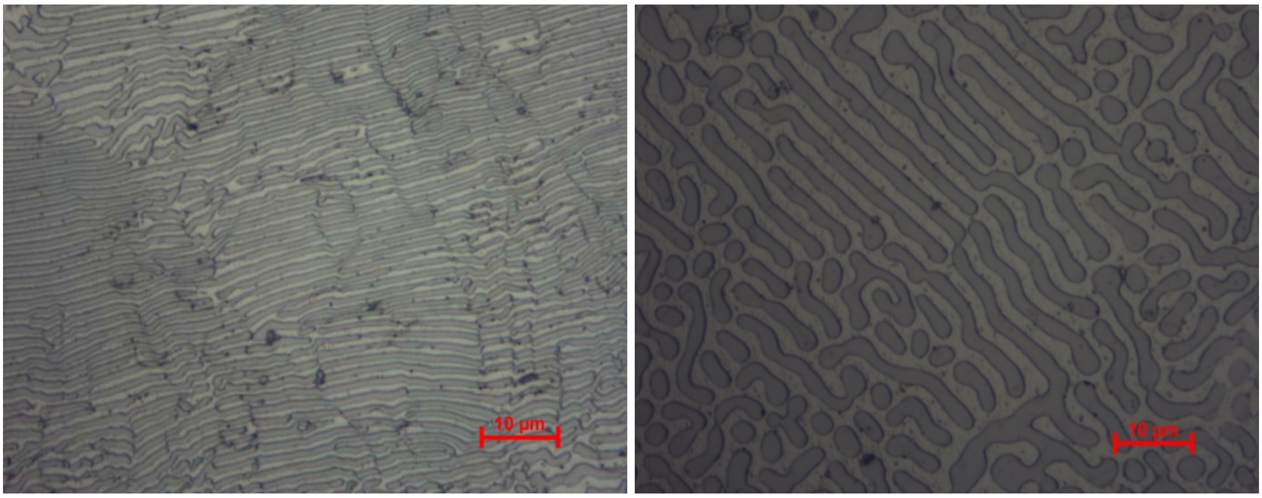
Figure: SEM micrographs showing transverse sections.

Directional electro growth of Al-Cu eutectic alloy under different directions and magnitudes of electrical fields

Sercan Basit, Semih Birinci and Necmettin Maraşli

Department of Metallurgical and Materials Engineering, Faculty of Chemistry and Metallurgical Engineering, Yıldız Technical University, 34210, İstanbul, Turkey

The effects of direction and magnitude of static electrical field on solidification of Al-33wt.%Cu eutectic alloy were investigated. For this purpose, a new directional solidification apparatus was specially designed to solidify the Al-Cu eutectic alloy under static high electrical field (E). For the first time, the Al-Cu molten eutectic alloy was solidified under different directions; parallel and antiparallel of the solid liquid interface growth direction (E_+ and E_-, respectively) and magnitudes (7-10 kV/cm) of static high electrical fields. Typical images of eutectic microstructures of Al-33 wt.%Cu eutectic alloy solidified under nonelectrical field and positive electrical field are shown in Figure 1 The lamellar spacing (λ), eutectic grain size (EGS) and hardness (HB) of the Al-Cu eutectic alloy solidified with different values of E_+ and E_- were measured with standards methods. It was observed that the static electrical field is an effective control parameter on solidification and the values of λ, EGS and HB are increased and decreased with increasing the values of E_+ and E_-, respectively in the Al-Cu eutectic alloy. Finally, the dependency of λ, EGS and HB values on E_+ and E_- values were obtained with linear regression analysis in the Al-Cu eutectic alloy.



(a) (b)

Figure 1: Eutectic lamellar spacing of Al-Cu eutectic alloy solidified under (a) none electrical field and (b) positive and parallel electrical field (7.5 kV/cm).

Acknowledgement: This research was supported financially by the Scientific and Technical Research Council of Turkey (TUBİTAK) under contract no. 118M695. The authors are grateful to the Scientific and Technical Research Council of Turkey (TUBİTAK) for their financial supports.

Synthesis of ceramic eutectics from the melt: methods, microstructures and related mechanical properties

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In the general context of energy savings and environmental issues, the improvement of the aircraft engine efficiency requires the development of new refractory materials allowing operating temperatures higher than 1300°C. Directionally Solidified Eutectics (DSE) oxides seem to be a promising option. Many works have been focused on these materials in the last 20 years. They may be defined as composite materials with a more or less complex and homogeneous microstructure which controls their properties. A crucial aspect is the understanding of the dynamics of eutectic growth that leads or not to homogeneous microstructures (coupled eutectic growth conditions). A special case of microstructure is found in oxide eutectics associating phases such as alumina and YAG or RE-aluminates (RE=Rare Earth), where the phases are continuously entangled in a three-dimensional interpenetrating network. The absence of grains and other larger scale irregularities together with excellent bonding between phases leads to structures with outstanding mechanical properties such as strength, creep resistance as well a high temperature stability and corrosion resistance

The key rule for regular homogeneous growth is to keep planar solid-liquid interfaces during growth requiring large thermal gradients. Using larger thermal gradients allows faster growth rates. These conditions are obtained with melt zone methods. From examples of different methods such as the floating zone (FZ) obtained in an arc image furnace, the edge-defined film growth (EFG) or the micro-pulling down (µ-PD) processes the influence of the solidification conditions on the microstructural, chemical and crystallographic features of the Al_2O_3-$REAl_5O_{12}$-ZrO_2 eutectics will be presented.

However, some drawbacks inherent to ceramic oxides (i.e. low fracture toughness, corrosion resistance for alumina) could impose serious limitations on their application as structural materials. The addition of zirconia which increases the resistance to crack propagation, allows significant improvements in toughness , but very often modifies the homogeneity of the microstructure. Others eutectic systems were investigated without added zirconia and displaying a similar toughness and a very homogeneous and isotropic microstructure. Corrosion resistance tests in moisture were performed on different DSE compositions coupling garnet, perovskite, zirconia and alumina phases and will be also presented.

Fused eutectic manufacturing and Industrial challenges

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The Specialty Grains and Powders Division (SGP) of Saint-Gobain owns several industrial equipment worldwide for mass production of fused ceramics and more specifically fused eutectics. Beyond the production of such eutectics for abrasive application that is currently our main market served, the SGP business is continuously looking for new fused materials to upgrade his current product portfolio to serve existing or new markets.

The SGP research and development teams have been working for years on new eutectic materials, not only to improve the performance level of our current fused abrasive grains based on the $Al2O_3$-ZrO_2 eutectic system but also to provide new solutions that could serve growing markets like Energy or Depollution for instance. To that purpose, collaborations with some academic partners took place for example on eutectics for SOFC anodes, high temperature turbines for aircraft engines or photo-electrochemical cells. However, all these efforts remain at the lab stage for now.

Indeed, the development of new eutectic materials faces multiple technical challenges that must be addressed to allow industrial and mass production at the right performance/cost level against competitive materials. Among those technical challenges, we can mention: acceptable purity levels to get targeted performances, the use of toxic components with significant HSE concerns, and the need of controlled solidification processes leading to crack/defect-free materials. All those issues are limiting factors for scale-up and eventually industrialization.

Taking all those aspects from the early development stage at the academic level and having close collaborations between Universities and Industrial partners to communicate on evolving industrial challenges are key to ensure commercial success of future development of new eutectics. We are proposing in this communication to share examples of current development we have on fused eutectics and highlight challenges we are facing and where we would need help from Academic partners to find solutions to move from lab scale to at least pilot scale production before ensuring full commercialization.

Effect of annealing conditions on photoelectrochemical response and stability of $SrTiO_3$-TiO_2 photoanodes

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$SrTiO_3$-TiO_2 directionally solidified eutectic was fabricated processed for active layers for photoelectrochemical (PEC) water splitting. The as-grown material showed good PEC activity as witnessed by the photocurrent density and stability (at static potential) with respect to time. It was shown the PEC response could be altered significantly by annealing the samples in H_2 or O_2 prior to the sample preparation. Interestingly, although annealing in O_2 yielded less defected structures, the overall performance of the photoanodes was reduced, suggesting a strong connection to the oxygen vacancies. Signs of corrosion, e.g. increased surface roughness, decreased resistivity, traces of Sr and Ti in the working solution were observed.

Cu-Cu_2O eutectic through time: photoluminescence imaging and X-ray tomography approaches to investigate metallurgical processes

Mathieu Thoury[1], Silvère Akamatsu[2], Mathilde Renouard[1], Manuel Castro-Roman[3], Yannick Thebault[4], Cécile Fossé[1,5], Maëva Lhéronde[1], Elin Figueiredo[6], Thibault Brulé[7], King Andrew[8], Pierre Guériau[1],, Jacques Lacaze[4], Luc Robbiola[9]

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Formation of Cu-Cu_2O eutectics have been observed within a wide diversity of archaeological copper-based artefacts, dating back to the origin of metallurgy and originating from sites of all around the world. In these ancient systems, fibrous Cu-Cu_2O eutectic have been observed in various states of conservation with hypo- or hypereutectic phase fractions of micrometric cuprous oxide rod-like crystals.

The microstructure of a fully corroded ancient as-cast copper amulet dating back from 6000 BCE has been studied using a novel photoluminescence multispectral imaging approach. This allowed some of us to reveal a "ghost" Cu-Cu_2O eutectic micro-structure [1]. Such a result triggered further development aiming at probing the stoichiometry variations Cu_2O as a marker of ancient metallurgy processes. More recently, the microstructure and thermal analysis of Cu-Cu_2O eutectic were performed on as-cast Cu and directionally solidified samples obtained in controlled laboratory conditions [2]. A microstructure quite similar to that of ancient remains and artefacts was evidenced in as-cast samples.

The present study aims at investigating the Cu-Cu_2O microstructure observed at different scales, both in archaeological artefacts and modern samples. We first performed a morphological characterization of the composite microstructure. Photoluminescence hyperspectral imaging (PL-HIS) was then used on cross-sectional samples to probe the stoichiometry variations of Cu and O within Cu-Cu_2O eutectic and dendritic phases, thus expecting gaining new information on the solidification process. Finally, 2D and 3D imaging using both PL-HSI and synchrotron X-ray tomography were used to determine the two-scale spatial organization of the eutectic in coexistence with dendritic structures.

These preliminary results based on a corpus of archaeological and modern samples aim at evaluating the use of a potential novel marker, based on a stoichiometric and 3D morphological parameters, to better understand the mechanisms of eutectic formation processes developing novel optimized imaging approaches at multiple spatial scales.

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Dynamics of spacing homogenization in lamellar eutectics with anisotropic interphase boundaries

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In directional solidification of thin samples, lamellar eutectic fronts generally exhibit a fairly homogeneous spacing. If the spacing varies along the front, either the variations are smoothed out with time, or the inhomogeneities amplify with time until lamella elimination occurs. This behavior has been studied theoretically in the long-wavelength limit, in which the variations of the spacing occur over distances that are much larger than the average lamellar spacing. It was shown that the spacing obeys a diffusion equation [1], which is an example for 'phase diffusion' that generally occurs in one-dimensional pattern-forming systems. If the diffusion coefficient is positive, spacing homogenization occurs; in the opposite case, the evolution leads to lamella elimination. These predictions were tested by numerical simulations and experiments in eutectic systems with isotropic interfaces [2]. However, it was recently shown that the presence of interfacial anisotropy drastically alters the steady-state growth of lamellar eutectics. In particular, an anisotropy of the solid-solid (interphase) boundaries can induce a tilt of the lamellae with respect to the direction of the temperature gradient. The tilt angle can be predicted to good approximation by the so-called symmetric pattern approximation [3,4]. Here, we investigate how this anisotropy alters the spacing homogenization mechanism. We find that the tilt of the base state modifies the evolution equation for the spacing. The modified equation allows for propagative solutions that can be amplified or damped with time. As a result, non-trivial coupled dynamics of spacing, tilt angle, and front shape are possible.

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Phase-field modelling of the utrafine eutectic microstructure formed during laser additive manufacturing

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Laser-based additive layer manufacturing is a powerful technique producing small but complex parts such as the Fe–Ti turbocharger compressor wheel for automobile engines, which is the demonstrator component of the M-era. Net project ELAM. An additional advantage of the method is that due to the very high cooling rate in the melt pool following the laser beam an ultrafine eutectic microstructure is formed in the Fe–Fe_2Ti eutectic system, which results in improved mechanical properties. We present a phase-field study of the microstructure evolution observed experimentally. Using a cyclic temperature programme, we successfully reproduced the layered structure consisting of a nucleation dominated thin, fine globular layer which then transfers to a lamellar arrangement building up the rest of the structure.

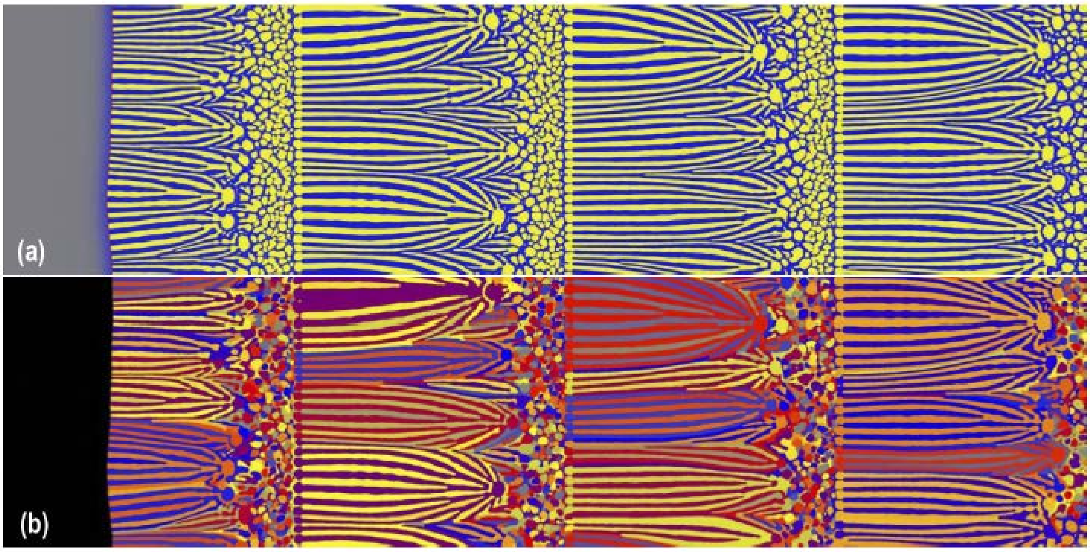

Figure 1: Phase-field prediction of the layered eutectic microstructure formed in an asymmetric model alloy. Panel a) shows the composition, panel b) shows the orientation map resulting from a cyclic temperature programme.

Insights on the structure of the solid-liquid interface of Alumina-YAG-Zirconia eutectic

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These last decades, directionally solidified eutectic oxides have drawn attention and are seen as an alternative to Ni based super-alloy for the development of high temperature turbine blades. Indeed, their 3D entangled and complex microstructure, called Chinese Script and the high quality of the interphases provide thermal stability and mechanical properties, creep and strength, constant up to 2000 K.
Our study focuses on the physico-chemical phenomena acting at the interface between the solid and the liquid, during directional solidification of the Al_2O_3-YAG-ZrO_2 eutectic alloy.
Samples have been grown by the EFG technique. The modeling of this process on a commercial software, COMSOL® gave a precise knowledge of the growth rate and the temperature gradient, needed for the study of the growth mechanisms. In parallel, sample composition has been confronted to the phase equilibrium diagram calculated by the CALPHAD method.
A characterization route of the microstructures obtained for different growth conditions has been set up in order to describe this irregular eutectic. Thus, the influence of speed and temperature gradient have been studied, showing identical growth behavior with eutectic metals (the famous $\lambda^2 V=Ct$ law). X-Ray topography performed at the European Synchrotron Research Facility have shown that this eutectic structure is composed of two single crystals: Al_2O_3 and YAG with their interface decorated by a fine, continuous, fishing net of ZrO_2:Y.
A microscopic structure of the eutectic front is proposed and the classical physico-chemical model acting in the establishment of the eutectic structure for metals is shown to be effective in the case of this eutectic oxide as well.
In the case of colonies, the shape of the destabilized interface (depth of the colonies) is derived from the experimental observations. Intrinsic and extrinsic electric field effects show that the destabilizing impurity in ours samples is zirconium ions, probably due to a tiny off-stoichiometry of the raw material.

Laser additive manufacturing of $Al_2O_3/GdAlO_3/ZrO_2$ ternary eutectic ceramics with fine microstructures

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Laser additive manufacturing is a new promising method to prepare high-performance structural parts with complex geometry. Based on melt growth, highly dense $Al_2O_3/GdAlO_3/ZrO_2$ ternary eutectic ceramics with different shapes and high surface finish of thin-wall and rod are directly fabricated from pure ceramic powders by laser additive manufacturing without any post processing. The formation quality, microstructures and mechanical properties under different laser processing parameters are systematically investigated and discussed. The as-built eutectic ceramics consists of only Al_2O_3, $GdAlO_3$ and ZrO_2 phases with uniform three-dimensional network structure in sub-micron size. Inside the colony, the microstructure in transverse section presents "Chinese script" structure and exhibits lamellar eutectic structure which is orientated to the building direction in longitudinal section. Periodic microstructure coarsening zones are produced in longitudinal section on account of the effect of heat transfer in the layer-wised building process. The width of the coarsened microstructure zone and the interphase spacing decrease with increasing the scanning speed. The hardness slightly increases from 14.3 to 15.3 GPa, and the fracture toughness increases from 6.1 to 7.8 $MPa \cdot m^{1/2}$ from the surface to bottom of the molten pool. The property differences in the molten pool can be primarily attributed to that cracks propagate in a straight line in the top zone, while the crack bridging and arrest are formed in the GAP phase in the bottom zone.

Microstructure evolution and optical properties of Al_2O_3/YAG: Ce^{3+} eutectic ceramic grown by laser floating zone melting

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A resin-free phosphor of $Al_2O_3/Y_3Al_5O_{12}$: Ce^{3+} (YAG: Ce^{3+}) eutectic ceramic has been fabricated by the laser floating zone melting (LFZM) method for the application in white light emitting diodes (WLEDs). The grown eutectic composite shows a typical eutectic structure of fine interpenetrating sapphire and garnet phases. The eutectic lamellar spacing λ exhibits an inverse-square-root dependence on the solidification rate V according to λ=22.0 $v^{-1/2}$, where λ has the dimension of μm and V is in μm/s. The TEM analysis indicates that the phase interface is clean and smooth without any other phase, which may produce homogeneous light with little scattering loss. The crystallographic relations are determined to be (100) Al_2O_3// (100) YAG and $[01\bar{1}0]$ Al_2O_3 // [001] YAG. The best luminous efficiency is measured to be 110.54 lm/W, which is superior to the traditional commercial WLEDs. The laser floating zone melting (LFZM) method is demonstrated to be applicable for manufacturing uniformly textured phosphors with improved luminous efficiency for high-power WLED applications.

Alumina-Zirconia eutectics processed using laser melting and ultra-high solidification rates

Liliana Moniz, Christophe Colin, Jean-Dominique Bartout, Marie-Hélène Berger

Centre des Matériaux MINES-ParisTech, PSL University FRANCE

Ceramic eutectics parts with complex shapes have been built by laser beam melting using Alumina-Zirconia powders of eutectic composition and Yb:YAG laser radiation. To melt the poorly IR absorbent powder, an absorbent has been mixed to the powder. With the ultra-high solidification rates encountered in this processing mode, bi-lamella with sub-micron widths have been obtained (e.g $\lambda = 30$ nm at 0.4 m/s). The paper will briefly present the strategy chosen to build 3D complex shapes by additive manufacturing using laser beam melting, and will focus on the microstructure and crystal orientation relationships generated by this specific fabrication route.

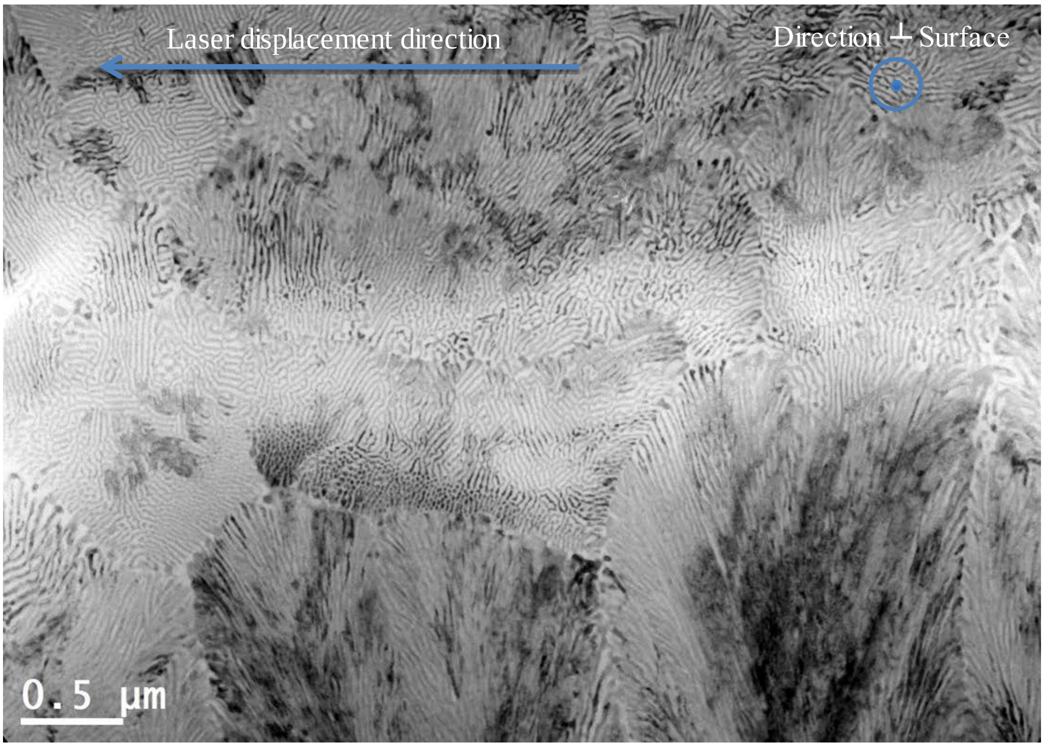

Figure 1: TEM image of a typical Alumina – Zirconia eutectic microstrutcture obtained by LBM.

Thursday, September 12th

Ultrafine $Fe\text{-}Fe_2Ti$ eutectics by laser additive manufacturing

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Eutectic alloys have been in the focus of materials science and engineering over many decades since, as *in-situ* composites, they promise unique mechanical and functional properties. Their properties depend among other on the eutectic spacing, which can attain values well below 200 nm if solidification occurs at high cooling rates. This has been demonstrated in suction casting experiments for various eutectic alloys. Remarkably, the ultrafine eutectics display improved plasticity compared to coarse eutectics, being attributed to size effects. We attempted to explore laser additive manufacturing (LAM) as a potential technology to produce ultrafine eutectics in bulk samples and components and to verify, if a favourable trade-off between strength and ductility can be achieved.
Here we will present results from a joint European research project dedicated to this subject using the binary $Fe\text{-}Fe_2Ti$ eutectic. We will give an overview on powder production, Laser Metal Deposition (LMD) as well as Powder Bed Fusion (SLM) while focusing on the details of microstructure formation. Preliminary results from micromechanical testing will be presented as well as an outlook to future research work.

Figure: Microstructure overview in a slightly hyper-eutetic $Fe\text{-}Fe_2Ti$ alloy processed by Laser Metal Deposition.

Directionally solidified eutectics by selective laser melting: Process optimization, materials design and melt-pool-dynamics simulation

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Recently, ultrafine eutectic alloys have gained increasing attention due to their mechanical properties and solidification behavior [1]. Certain eutectic systems are viewed as promising in the context of laser additive manufacturing (LAM), as they can provide high strength and improved ductility during fast solidification. Process conditions during selective laser melting (SLM) determine the microstructural properties of the obtained solids, i.e. interlamellar spacing, by directly influencing melt-pool dynamics, cooling rates and the velocity of solidification [2]. Within a certain range this allows for a control of structural features, which in turn greatly influences the elasto-plastic properties of the obtained materials.

In this study, binary Fe-Fe_2Ti eutectics consisting of the BCC and Laves C14 phases have been produced by SLM. The alloy composition Fe-16 at. %Ti has been selected to be slightly off-eutectic. Simulations of the melt-pool dynamics during laser processing have been conducted to estimate the local solidification conditions. Additionally, in situ monitoring of the temperature distribution in the melt pool has been applied to validate the simulation data. Taken together this allowed correlating the microstructure to the process conditions. We will report about the results of this correlation. We shall conclude our presentation with current research work dedicated to alloy development and to future work on the relationship between microstructure and mechanical properties.

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Fe-Fe_2Ti eutectics processed by Laser Metal Deposition: Modelling and validation of the coupled zone

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Eutectics demonstrate interesting mechanical properties especially when their characteristic lengths, such as the lamellar spacing is reduced into the ultrafine region [1]. In order to achieve lamellar sby conventional casting but proven feasible in centrifugal casting experiments when recurring to cylindrical capillary moulds of 2 to 5 mm diameter [2]. Laser based additive manufacturing (LAM) however, with intrinsically high cooling rates potentially offers the opportunity to produce bulk eutectics with ultrafine lamelpacings smaller than 200 nm, high cooling rates have to be employed, which is difficult or even impossible lar spacing. As a consequence of the high cooling rates, non-equilibrium phenomena arise during solidification which have to be understood and subsequently could be used to tailor the microstructure and enhance the ductility/strength balance.

Among the questions of fundamental interest are the extent of the coupled growth zone as function of alloy composition and the local solidification velocity in the melt pool. We implemented a model based on [3] and [4], which helps predicting the microstructure of a LAM-eutectic. In order to validate this model, Fe-16wt%Ti samples were additively manufactured by Laser metal deposition (LMD) also including graded samples with either increasing Ti or increasing Fe content. The graded samples are very well suited to verify the extent of the coupled growth zone.

In this presentation, we will present (i) our model and the way we used it to calculate the coupled growth zone, (ii) the printing method of the graded samples and finally, (iii) the validation of the model based on a comprehensive microstructure analysis of the Ti- and Fe-graded samples.

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Emergence of Archimedean lattices in template-directed eutectic solidification

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Template-directed self-assembly has been demonstrated to yield a broad diversity of highly ordered mesostructures, [1-3] which in a few cases even exhibit symmetries not present in the native material. [4, 5] Here we show using the directional solidification of a simple AgCl-KCl lamellar eutectic within a pillar template that interactions of the eutectic with the template lead to the emergence of an unprecedented set of microstructures, distinctly different from the eutectic's native lamellar structure and the template's hexagonal lattice structure (Figure 1). By modifying the solidification rate, in the same material-template system, disordered, trefoil, quatrefoil, cinquefoil, and hexafoil mesostructures with sub-micron size features are realized. Phase-field simulations suggest these mesostructures appear due to constraints imposed on diffusion by the hexagonally arrayed pillar template. Interestingly, the trefoil and hexafoil patterns bear a remarkable resemblance to Archimedean honeycomb and square-hexagonal-dodecagonal lattices, [6] respectively. We also find that by using monolayer colloidal crystals as templates, a variety of eutectic mesostructures, including disordered, trefoil, and hexafoil are observed, where the trefoil pattern resembles the Archimedean kagome lattice. We anticipate these results will stimulate new studies on template-directed organization of inorganic materials into unique and useful mesostructures, including mesostructures which may have important optical, magnetic, and mechanical properties.

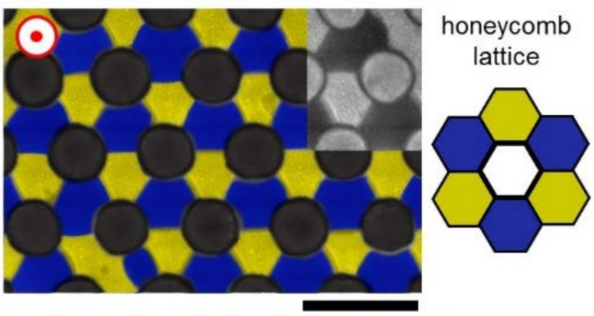

Figure 1: Example microstructure formed by template-directed eutectic solidification of a AgCl (bright) – KCl (dark) lamellar eutectic solidified in a pillar template sample Scale bar is 1 μm.

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Advances in novel composite materials obtained by crystal growth

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We will demonstrate how to utilize the crystal growth methods for manufacturing of novel composite materials for various applications and especially photonics (metamaterials, plasmonic materials [1-7]), and energy conversion [8-9]. We will focus on two novel bottom-up manufacturing methods: (i) method based on directionally-grown self-organized eutectic structures [1, 5-9]; and (ii) NanoParticles Direct Doping method (NPDD) [2-4] based on directional solidification of dielectric matrices doped with various nanoparticles. In both of these methods we can easily use all available resonant phenomena to develop materials with unusual electromagnetic properties. Eutectic composites are simultaneously monolithic and multiphase materials forming self-organized micro/nanostructures, which enable: (i) the use of various component materials including oxides, semiconductors, metals, (ii) the generation of a gallery of geometrical motifs and (iii) control of the size of the structuring, often from the micro- to nanoregimes. On the other hand, the novel method of NanoParticles Direct Doping enables doping of dielectric matrices with various nanoparticles (varying chemical composition, size and shape) and with the possibility of co-doping with other chemical agents as eg. optically active rare earth ions or quantum dots.

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$ZnO–ZnWO_4$ eutectic composite: a new self-assembly route to highly tunable narrow-band optical filters

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Lately, composites consisting of all-dielectric, transparent materials in which light does not interact with plasmons or phonons have been proposed as an alternative nanophotonic materials. [1] However, composite materials can be generally lossy due to scattering effects induced by the inhomogeneity at the interfaces between the different compounds. To overcome such problems, complicated and costly manufacturing procedures, like top-down approaches, are generally used. Moreover, few all-dielectric nanophotonic devices currently operate at wavelengths below 500 nm [2] because the high refractive index of these materials comes at a cost of increased absorption at short wavelengths.

Therefore, there is a need to develop novel approaches that utilize, for example, refractive index matching of inclusions and a dielectric matrix. This requires an appropriate choice of materials to be used and relatively simple and inexpensive fabrication methods suitable for the scalable production.

Here we demonstrate a new self-organization route to highly- tunable narrow-band all-dielectric optical filters and polarizers. This is achieved by combining refractive index matching of two component phases in a eutectic composite with its micro/nanostructure. As an example ZnO-$ZnWO_4$ eutectic composite, composted of thin layers of ZnO embedded in a $ZnWO_4$ matrix, exhibiting narrow-band transmission at ~400 nm, switchable by polarization and tunable by temperature is presented.

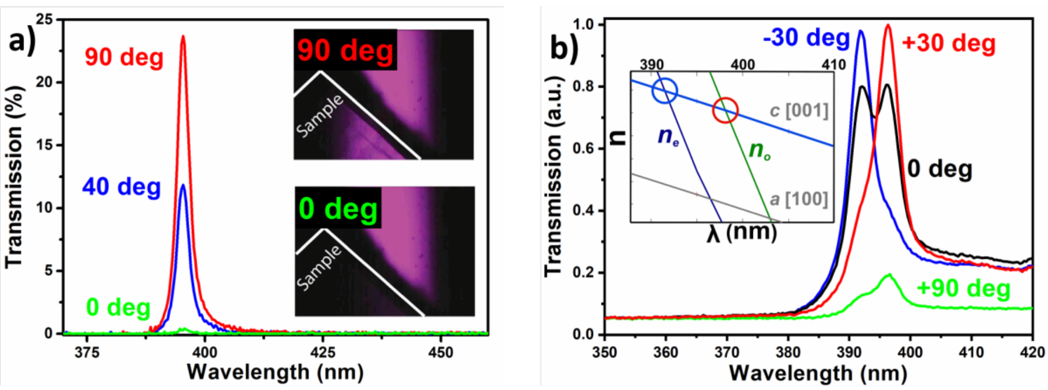

Figure 1: The on/off switching and tuning of the narrow-band transmission with polarization in the ZnO-$ZnWO_4$ eutectic composite with a) [100] and b) [001] oriented $ZnWO_4$.

This work was supported financially by the TEAM/2016-3/29 Grant within the TEAM programme of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund and HARMONIA Project (2013/10/M/ST5/00650) from the NCN.

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Directional crystallization of eutectic alloys hexaboride - high-entropy diboride

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The process of structure and properties formation of LaB_6-MeB_2 eutectics in the process of directional crystallization is determined by the magnitude of the crystal lattices mismatch of the phases and by the interaction on their interface.

Recently, the preparation and study of high-entropy alloys has attracted great interest. The presence of boron framework that largely determines the size of the crystal cell, makes it particularly promising to study high-entropy borides, and especially diborides, since they are formed by the vast majority of chemical elements.

The flux method or crucibleless melting are traditionally used for borides single crystals growth. In the first case, there is a risk of contamination of the crystal with elements of a solvent. In the second case, the characteristic decrease in surface tension forces for a multicomponent alloy cause difficulties with melt retention.

As we have already reported on the DSEC, the mutual solubility in the solid state is completely absent for a number of the MeB_6 – MeB_2 systems [1]. Studies of the LaB_6- (Ti, Zr)B_2 system showed a change in the mutual orientation of the crystal lattices of di- and hexaboride during directional crystallization depending on the Ti / Zr ratio.

We obtained self-reinforced alloys in the MeB_6 – MeB_2 system, where Me is a solid solution fromed by five (as in [2]) to nine metals (Ti, Zr. Hf, V, Nb, Ta, Cr, Mo, W). It must be emphasized that in this case even Mo and W crystallize in the AlB_2-type lattice.

In order to eliminate the influence of the crystallographic orientation of the matrix, all crystals were grown on one eutectic seed of LaB_6-ZrB_2.

All alloys had a fibrous structure and a fairly close volume content of diboride in the eutectic alloy. Even the first experiments showed a significant effect of the diboride composition on the distribution of fibers in the matrix.

Preparation of the alloys in hexaboride – high-entropy diboride systems opens up new possibilities for interaction on the phase interface studies and for the development of new materials.

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Selective Emitters for Thermophotovoltaics Based on Eutectic Composites

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Directionally solidified oxide eutectics showing good thermomechanical properties have been proposed as selective emitters for application in thermophotovoltaic (TPV) devices, and several works were published in the early 2000´s to investigate their emissive properties. [1] Their selective emissivity resides in the content of rare earth oxides or transition metal ions with absorption band in the desired spectral range, suitably matched to the absorption of photovoltaic cells.
Porous coatings [2] or ceramic fabrics [3] were investigated in lab-scale devices, as they need to withstand sudden temperature changes. The advantage of solidified eutectics over porous ceramics is that, being dense, light scattering is weaker. Therefore, thermal emission exiting the sample is generated in a larger depth below the surface, and broadening of the emissive band due to small absorbing tails or defects in the material can be smaller, and consequently the emitter is more selective.
Directionally solidified oxides can be produced in bulk by different procedures such as Bridgman, micropulling- down or laser floating zone (LFZ). They can also be prepared in the form of dense coatings on different substrates, thereby allowing manufacture adapted to the TPV device. In our laboratory we have used both kinds of procedures to prepare thermomechanical resistant eutectics that host rare earth or transition metal ions. More specifically, Al_2O_3-$Y_{3-x}Er_xAl_5O_{12}$ and Ni-doped MgO-MgSZ directionally solidified eutectics, and investigated their thermal-shock resistance [4] and the characteristics of their selective emission [5, 6]. Al_2O_3-$Er_3Al_5O_{12}$ (and other Al_2O_3-rare earth ion garnet) present very selective emission bands, with small broadening with temperature. On the contrary, Ni doped MgO-MgSZ presents severe broadening with small doping levels at high temperatures, as also observed in doped MgO, limiting the selectivity.
The purpose of this communication is to present the state of the art of the research of our team in the subject [7]. Nowadays we are particularly interested in the propagation of light in these microstructured materials, and how it can affect to the thermal emission.

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Research potential of MgO-$MgAl_2O_4$ eutectic - a second chance fully deserved

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An increasing interest in MgO-$MgAl_2O_4$ eutectic was observed in recent years, which forced some well established facts to be revisited. The growth-microstructure relationship was reformulated and it was shown the refinement can be precisely tailored using micro-pulling down method [1]. For larger samples, Bridgman [2] and Laser Floating Zone [3] methods could be successfully applied.

Both MgO and $MgAl_2O_4$ are described by regular crystal structures and very low absorption in the infrared. This makes them splendid for effective heat transport and thus for the crystallization process. Moreover, Mg^{2+} and Al^{3+} ions are easily substituted by di- and trivalent transition metal ions [4, 5] and rare earth trivalent ions [6, 7].

A challenging property, though, is a high lattice mismatch and a large difference of thermal expansion coefficients. This introduces strain in the composite microstructure and can potentially lead to crack nucleation. The effect can be considered mechanically constructive (toughening) or destructive (causing failure), depending on the scale (micro or macro, respectively). [3]

The research potential of MgO-$MgAl_2O_4$ eutectic remains very high, especially in the field of phosphors. It is expected that a new family of materials will emerge in the upcoming future.

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Improvement of thermoelectric properties on $SrTiO_3$ with eutectic morphology

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Thermoelectric materials which can convert waste thermal energy into electrical energy have been studied for thermoelectric devices in various fields such as industrial and power plants, automobiles and incinerators. There are many studies of thermoelectric materials which were fabricated using nanopowder and included impurity nanopowder to improve their *Figure of merit* (*ZT*) by decreasing the thermal conductivity originating from the phonon scattering at grain boundaries. On the other hand, eutectic material with a phase-separated structure (eutectic structure) can be fabricated by a unidirectional solidification from the melt with the chemical composition at a eutectic point [1]. If the eutectic structure composed of scattering phases in the matrix phase of a thermoelectric material can be achieved, the eutectic structure can improve the thermoelectric properties. Therefore, we tried to develop a novel thermoelectric material with the eutectic structure and the thermoelectric properties were investigated. In this study, the eutectic material of the $SrTiO_3$ [STO] and TiO_2 [TO] was selected as a first try of thermoelectric eutectic material.
Starting materials, $SrCO_3$ and TiO_2 powders (>4N), were mixed as the nominal composition at the eutectic point of STO and TO (SrO : TiO2 = 20 : 80) and the mixed powder was sintered at 1200°C in air several times. Then, a STO/TO eutectic material was grown from the melt the sintered powder by a micro-pulling-down (μ-PD) method using an iridium crucible. In addition, the Nd, La and Pr-doped STO/TO eutectic materials were grown under same growth conditions. The La-doped STO/TO eutectic materials were grown at various growth rates (0.02, 0.05, 0.25 and 1.00 mm/min). Grown eutectic materials were cut and polished for measurements of thermoelectric properties.
Grown STO/TO, and Nd, La and Pr-doped STO/TO eutectic materials were composed of the uniformly dispersed TO phase with a rod-shape in the STO matrix phase. As shown in Fig. 1, the diameter of the rod phase in the La-doped STO/TO eutectic materials systematically decreased with increasing the growth rate. The diameter of the rod phase systematically changed according to the equation of $v{\cdot}r^2$ = const. (v : growth rate, r : diameter of rod phase). The thermal conductivity of the Nd-doped STO/TO eutectic material was lower than half that of Nd-doped STO single crystal [2]. Details of the fabrication by the μ-PD method, the local structures, and thermoelectric properties will be reported.

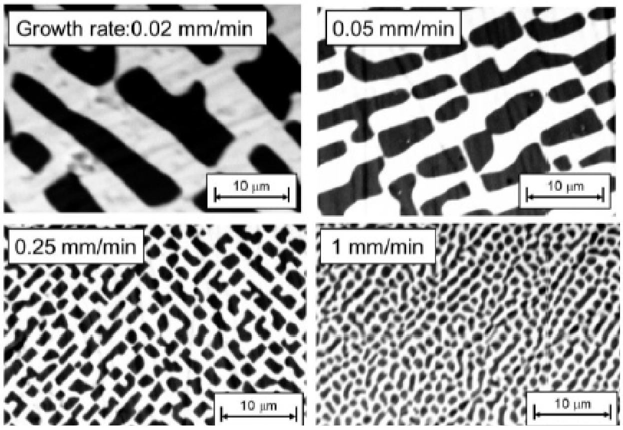

Figure 1: Microstructure on cross-sectional planes perpendicular to growth direction of La-doped STO/TO eutectic materials fabricated at various growth rates.

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Thin layers of eutectic composites for photoelectrochemical water splitting

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The increasing energy consumption requires new and efficient energy sources. Hydrogen is considered a promising energy source, especially when produced by direct conversion of solar energy in so-called photoelectrochemical cels (PEC). The possibility of considering versalite combinations of various component materials in eutectics provides a broad palette for many applications [1-3]. Eutectics obtained by the self-organization mechanism also seems to be very attractive as energy-generating materials. They have potential as photoactive materials, due to their multiphase character – various available photoactive phases, multiple band gap energies and high crystallinity.
The research on $SrTiO_3$-TiO_2 [4] and WO_3-TiO_2 [5] eutectic composites obtained by m-PD method confirmed that eutectic systems can be suitable for photoelectrochemical hydrogen production. In case of $SrTiO_3$-TiO_2, the generated photocurrents increased upon light irradiation up to 8.5 mA/cm^2 and for WO_3-TiO_2, the performed cyclic voltammetry experiments demonstrated electrodes photocurrent of 4.3 mA/cm^2 at 1.7 V versus normal hydrogen electrode under 6 suns illumination. Measured photocurrents strongly depend on the electrode thickness. The thickness of investigated till now eutectic-based electrodes in ITME, using m-PD method reached 10 μm. Therefore, to reduce the electrode thickness authors decided to use the thin layers of semiconducting eutectic composites for the application as photosensitive materials in photoelectrochemical cells by recently patented method of manufacturing thin layers of eutectic composites [6].
The aim of this work is to show the possibility of using eutectic composite thin layers as an active photoanode material for PEC. The characterization of the $SrTiO_3$-TiO_2 eutectic layers will be presented together with the preliminary photoelectrochemical measurements performed on fabricated photoanodes.

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Development of X-ray Talbot-Lau imaging system using large area Tb doped GAP/α-Al_2O_3 eutectic scintillator plates

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In X-ray Talbot-Lau interferometry, single or mulch absorption gratings between a sample and X-ray generate detector differential-phase, and visibility-contrast images. The absorption gratings generate Moire fringes and differential-phase, and visibility-contrast images are obtained from analysis of the spatial frequency of the Moire fringes. However absorption gratings absorbed the transmitted X-ray and sensitivity is degraded. So exposure dose can become a problem in medical and biological imaging.
Up to now, $GdAlO_3$(GAP)/ a-Al_2O_3 [1-3], have been reported as submicron-diameter phase-separated scintillator fibers (PSSFs). Tb:GAP/a-Al_2O_3 showed well aligned PSSFs eutectic with optical transparency structure. The high-resolution X-ray imaging was reported by combining with both the properties of an optical fiber and an X-ray-to-light conversion. The 65% of contrast transfer function (CTF) a gold grating phantom with a 4 mm aperture, corresponding to a bundle of 10 fibers, was achieved using a 2 x 2 mm square plate with 350 mm-thick Tb 8mol%:GAP/ a-Al_2O_3 scintillator[3].
In this study, large area growth technique of Tb doped GAP/α-Al_2O_3 eutectic scintillator using the micro pulling down (m-PD) method was developed for designing direct X-ray phase imaging. The 25 x 25 mm^2 wafers of Tb doped $GdAlO_3$ (GAP)/a-Al_2O_3 eutectic were fabricated by μ-PD method using the Ir crucible with a 25 x 25 mm^2 die. The prototype of x-ray phase imaging detector was developed using a CMOS sensor with a FOP and the eutectic wafer. X–ray spots with 8.24mm period was observed using the detector. X-ray phase imaging of the nylon ball with 4mm diameter was carried out in this study. It could be confirmed that a phase change of about 2 μm as the phase change occurs in the air and the nylon spherical interface. A technique of X-ray phase imaging could be realized in the absence of absorption grating.

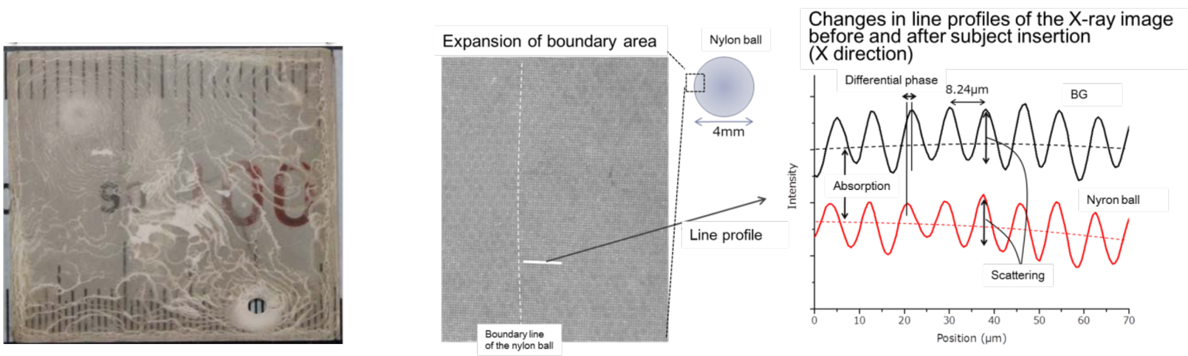

Figure 1: left) Grown 25 x 25 mm^2 wafers of Tb doped $GdAlO_3$ (GAP)/Al_2O_3 eutectic and right) results of X-ray phase imaging of the nylon ball with 4mm diameter.

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Dynamic nature of Nb/Ru/Sr_2RuO_4 topological superconducting junctions

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Single crystals of the Sr_2RuO_4-Ru eutectic system are known to exhibit enhanced superconductivity at 3 K in addition to the bulk superconductivity of Sr_2RuO_4 at 1.5 K [1]. It is believed that 1.5 K phase breaks time reversal symmetry that leads form domains with degenerate chirality of their superconducting order parameter. Sr_2RuO_4 exhibits spin-triplet, chiral p-wave state with a multicomponent order parameter, giving rise to chiral domain structure. In contrast, the 3 K phase is attributable to enhanced superconductivity of Sr_2RuO_4 in the strained interface region between Ru inclusion of a few to tens of micrometers in size and the surrounding Sr_2RuO_4. We fabricated Nb/Ru/Sr_2RuO_4 topological superconducting junctions, in which the difference in phase winding between the s-wave superconductivity in Ru microislands induced from Nb and the superconductivity of Sr_2RuO_4 mainly governs the junction behaviour. In these junctions, we observed unusual switching between higher and lower critical current states [2]. This switching is well explained by chiral-domain-wall dynamics. Furthermore, a striking difference between the 1.5 and 3 K phases is clearly revealed: the large noise in the 1.5 K phase sharply disappears in the 3 K phase. These results reveal the multicomponent order-parameter superconductivity of the 1.5 K, and the single component superconductivity of the 3 K phase [3].

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Growth of eutectics of strontium and calcium Ruddlesden-Popper series by the floating-zone technique

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Perovskite oxides display a wide variety of technologically important phenomena such as high temperature superconductivity, ferroelectricity, ferromagnetism and colossal magnetoresistance. Among them, an important role is held by Ruddlesden-Popper (R-P) series of $(Ca,Sr)_{n+1}Ru_nO_{3n+1}$ ruthenates. These nature's engineered layered systems with varying functionalities as the number of Ru-O layers per unit cell, *n*, increases show a variety of collective phenomena.
In the last few decades there has been growing interest in studying Mott insulators due to their ability to host novel quantum phenomena when the system is perturbed by various stimuli. Recently the antiferromagnetic Mott insulator Ca_2RuO_4 has received considerable attention due to metal-insulator transition induced by pressure and electric field respectively.
The details of the synthesis of a novel systems made by Ca_2RuO_4 and Ru metal inclusions will be presented. Samples with lamellae, rods and globules of Ru embedded in Ca_2RuO_4 single crystals were successfully synthesized by floating zone technique with an excess of Ru in the starting material.
The morphology and structural studies revealed a randomly orientated distribution of the shining Ru inclusions with an average size of few microns. Bulk and local transport measurements showed a decrease of the resistivity versus temperature of the composite system compared to Ca_2RuO_4 single crystals. This composite mainly shows additive properties, coming from the single constituent properties.
Regarding strontium compounds, they exhibit a very rich phenomenology like itinerant ferromagnetism and metamagnetism. In particular, the $n = 2$ member, $Sr_3Ru_2O_7$, is an enhanced Pauli paramagnet which at low temperatures undergoes a metamagnetic quantum phase transition induced by the application of moderate applied magnetic fields, ranging at the transition from 4.9 T (for H // *ab* plane) to 7.9 T (for H // *c*-axis). On the contrary, the third series member ($n = 3$), $Sr_4Ru_3O_{10}$, is an anisotropic ferromagnetism with $T_{Curie} = 105$ K, with an additional metamagnetic transition at $T^* \approx 50$ K induced by a magnetic field applied in the *ab*-plane. In this context, $Sr_3Ru_2O_7$-$Sr_4Ru_3O_{10}$ eutectic crystals, featuring a coexistence of metamagnetism and ferromagnetism, are likely to exhibit a magnetic behaviour qualitatively different with respect to the corresponding single phase crystals. In this scenario, the eutectic $Sr_3Ru_2O_7$-$Sr_4Ru_3O_{10}$ may play a fundamental role in studies of novel quantum critical phenomena specific to the itinerant magnetism.

Friday, September 13th

Superconductivity in the eutectic Sr_2RuO_4-Ru

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In the eutectic Sr_2RuO_4-Ru [1], the parent superconductor Sr_2RuO_4 (SRO, $T_{c,SRO}$ = 1.5 K) includes many μm-size Ru-inclusions which are in a metal state above $T_{c,Ru}$ = 0.5 K and a s-wave superconducting state below $T_{c,Ru}$. A filamentary superconducting state, arising in SRO at T_{onset}=3 K, is the interface state localized near the interface of Ru-inclusions. This interface state, called the 3-Kelvin (3K) phase, turns to the bulk state by lowering the temperature down to $T_{c,SRO}$=1.5 K. On an assumption that the bulk state is the chiral superconducting state such as $k_x \pm ik_y$ and k_z ($k_x \pm ik_y$), we found the following features on the 3K-phase model due to T_c enhanced near the Ru-interface.

1. A non-chiral interface state arises near Ru-interfaces at T_{onset} in the onset of the 3K-phase. This non-chiral interface state turns to a chiral interface state by lowering the temperature [2]. It is visible through a zero-bias anomaly in quasiparticle tunneling spectroscopy appearing below T*=2.3 K [1].
2. The interface state can have the phase winding around the Ru-inclusion by a circular geometry of the Ru-interface [3]. The winding states are frustrated between many Ru-inclusions, and then it generates a frustrated Josephson network current. The winding state transits to the no-winding chiral state below T*. In the no-winding chiral state, the chiral current flows around the Ru-inclusions, and then it generates the magnetic field induced which causes critical currents different in opposite directions in the RuO_2-plane. This theoretical result qualitatively reproduces the temperature dependence of the critical current which differs by the directions of magnetic field, observed in experiments [1].
3. In a Pb/Ru-SRO junction, a s-wave superconducting state is into the Ru-inclusion above $T_{c,Ru}$=0.5 K by attaching the Pb superconductor ($T_{c,Pb}$=7.2 K) to the Ru-inclusion. The s-wave state is coupled with the superconducting state of SRO at the interface between SRO and the Ru-inclusion. By phase-coupling with the s-wave state above $T_{c,SRO}$, the winding state in SRO is stabilized due to the phase agreement, while the no-winding state is suppressed due to the phase difference [4]. Hence the phase winding changes near $T_{c,SRO}$, and it causes a change of the Josephson current limiting [5]. It consists with an anomalous temperature dependence of the Josephson critical current, observed in experiments [1].
4. By the phase-coupling with the s-wave state in the Ru-inclusion, the chiral state of SRO generates the spontaneous magnetic flux at the interface of the Ru-inclusion. Upon increasing the coupling strength, the magnetic flux transforms into a flux structure with a vortex locating in the center of the Ru-inclusion [6].
5. The non-chiral interface state, arising near the onset of the 3K-phase, transits to the chiral interface state by applying the magnetic field perpendicular to the RuO_2-layer [7]. This theoretical result is in agreement with the magnetic field dependence of the chiral stability, observed in experiments [1].

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Superconducting and magneto-electric effects in eutectic ruthenates

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The Ruddlesden-Popper (RP) ruthenates $A_{n+1}Ru_nO_{3n+1}$ are layered perovskite oxides exhibiting a large variety of quantum phenomena as the cationic element A and the number *n* of Ru-O layers forming the unit cell are varied. High-quality eutectic systems based on ruthenates have been synthesized in the shape of naturally occurring mesoscopic and nanoscopic interfaces. Such materials represent a natural way to interpolate between the different integer members of the RP series opening novel routes for quantum tuning of collective properties due to unit cell substitution or to intrinsic interfaces embedded within the same single crystalline phase. Indeed, the modification of the pairing wave function in the proximity of normal or magnetic systems as well as that of the magnetic long range due to the interface between the embedded phases may lead to novel states of matter. The main drive behind eutectic growth is thus given by the possibility of developing composite materials with distinct properties from those of the pure constituents. For example, in a sample with a majority of the n =2 RP phase with respect to the n =3 [1], the system is ferromagnetic with magnetization along the c-axis and a single metamagnetic transition is observed at a critical magnetic field that is smaller to that obtained in the pure $Sr_3Ru_2O_7$ but greater than that in the $Sr_4Ru_3O_{10}$. On the other hand, the superconductivity in the newly grown eutectic system has been shown to occur at 3 K instead of 1.5 K as in the pure Sr_2RuO_4 system. The increase in T_c is mainly believed to be due to interface states [2]. At the interface of Ru and Sr_2RuO_4 various types of superconducting reconstruction can occur and we discuss their manifestation especially due to the possibility of singlet-triplet pairing mixing and emergent magneto-electric phenomena [3,4,5]. Furthermore, eutectic materials with n=1 and n=2 members of the SRO RP [6] family presents defects at the nanometer scale where one or two unit cells of one phase are replaced by those of the other crystalline state. The presence of nanometric stacking faults has been experimentally verified and can play a key role in as a source of resonant centers for pair scattering in a way that long-range pair correlations can be developed on a distance that is typically larger than usually expected in a conventional proximity scenario where the Cooper pairs can travel in the normal host up to a distance of the order of the coherence length. We discuss the relevant features for such a long-range proximity mechanisms in n=1-n=2 eutectic ruthenates [7]. Finally, due to the observed differences in the collective behavior of the eutectic systems and to the light of the crystallographic composition, it is worth to address the following issues: (i)how does it change the electronic structure close to the Fermi level due to the presence of c-axis stacking faults for both the defect and the host and (ii) how the low-energy corrections influence the collective behavior. To handle these questions, we present the electronic structure for inhomogeneous systems [8] and we address the change of the ordered configurations by means of basic criteria for broken symmetry states based on the weak coupling theory of itinerant electron systems [9].

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Dopant Segregation and Oxygen Vacancy Enrichment in Gd-doped CeO_2/CoO and CeO_2/NiO Interfaces of Directionally Solidified Eutectics

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Directionally solidified eutectic ceramics (DSECs) formed by ionic conductors, such as Gd-doped CeO_2 o Y-doped ZrO_2, and 3*d* transition metal oxides, NiO or CoO, have been proposed as precursor materials to obtain cermets with applications as energy materials, mainly in the fields of heterogeneous catalysis and solid oxide fuel cells (SOFCs). In addition to their technological interest, DSEC are ideal model systems to investigate low-energy interfacial configurations, since minimization of the interfacial configuration is one of the main laws governing DSEC growth. Moreover, the conductivity of ceramic ionic materials is highly influenced by dopant segregation at the grain boundaries or interfaces, which usually induces a depletion of charge carriers. Hence, the study and pursuit of interfacial configurations that promote the formation of oxygen vacancies is highly desired. DSEC are unique systems for unravelling the fundamental mechanism underlying the interfacial dopant segregation in thermodynamically stable oxide interfaces.

In this work we have combined high resolution electron microscopy (HREM) and density functional theory (DFT) to elucidate the equilibrium state of cerium-gadolinium oxide /cobalt oxide and nickel oxide eutectics, CGO-CoO and CGO-NiO, respectively. Electron microscopy demonstrates the presence of a single interface oxygen plane in both eutectics and evidences that in CGO-CoO the concentration of gadolinium ions and oxygen vacancies at the interface are enhanced by a factor of about three as compared to the bulk, while they distribute homogeneously in the CGO-NiO system. DFT explains the experimental findings and shows that Gd segregation in the CGO-CoO reduces the interface energy, contributing to its stability. The Gd-oxygen vacancy defects compensate the interfacial ionic charge density discontinuity and the induced local distortions around the defect release the strain associated with the lattice mismatch. The strong bond and disorder of both interfaces, CGO- CoO and CGO-NiO, are also established and oxygen at the common interface plane present different coordination to those of the two constituent oxides. We demonstrate that in CGO-based eutectics the structure and ionicity of the constituent oxides are essential to promote the interface dopant segregation. These results show a new way to produce nanocomposites with enhanced oxygen vacancy concentration at the interface.

Emergence of two-phase spirals *via* eutectic crystallization

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Crystallization is a prototypical self-assembly strategy for synthesizing patterned structures across length scales. By tuning the growth conditions, it is possible to steer the system down different kinetic pathways to produce transient or metastable states (*e.g.*, polytetrahedral or disordered phases) on intermediate time-scales. An understanding of crystallization phenomena is the key to lock into place materials with functionalities and/or morphologies not present in equilibrium states. Particularly appealing are spiral eutectics [1-2], mixtures of two or more solid phases that grow simultaneously from a liquid and arrange into intricate spiraling patterns, in some cases akin to a DNA helix. The intrinsic chirality of spiral eutectics offers a new strategy for rapid, bottom-up manufacturing of large-area photonic materials in the visible/IR spectrum [3], owing to the fact that conventional top-down techniques – whose speed and complexity scale up with the number of helices – sets a bottleneck for large-scale production. Unfortunately, spiral growth is the least understood among all eutectic morphologies (including lamellar and rod), yet it produces quite dramatic effects. Unraveling the spiral growth dynamics requires multiscale, three-dimensional, and time-resolved measurements. Herein, we pursue a systematic investigation to uncover the origin of spiral growth in binary metal alloys produced *via* directional solidification. The as-solidified microstructures are chiral, faceted, and periodic with interphase spacing comparable to the wavelength of infrared light. To trace the emergence of such structures from the parent liquid phase, we employ multiscale microscopy encompassing 3D microstructural measurements together with *in situ* and atomic-resolution imaging. Machine learning (random forest classification [4]) was used to analyze the 3D datasets for robust tracking of the interfaces of the complex eutectic colonies.
Taken altogether, our correlative imaging spans over six orders-of-magnitude in length-scale.
We find that crystallization proceeds *via* a non-classical, two-step pathway consisting of the initial formation of a metastable polytetrahedral embryo, followed by ordering of two solid phases that nucleate heterogeneously on the embryo and grow in a strongly coupled fashion. Our multimodal characterization reveals that crystallographic defects within the seed provide a template for spiral self-organization. These observations demonstrate the ubiquity of defect-mediated growth [5-6] in multi-phase materials and establish a pathway towards bottom-up assembly of chiral patterns.

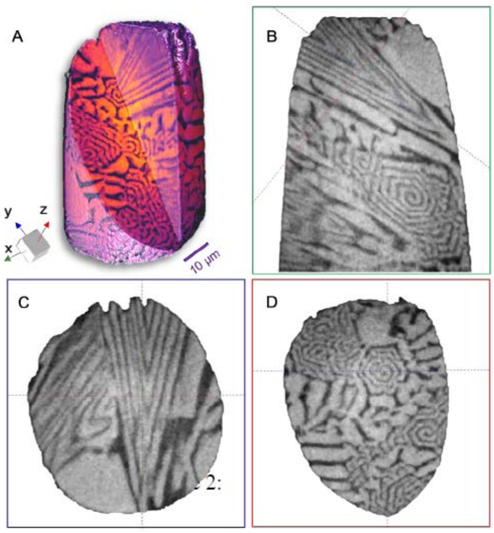

Figure 1: (a) 3D rendering of spiral microstructure, together with (b-d) orthogonal views along x, y and z.

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Poster session

P01 Nanoscale investigation of metal-insulator transition in Ca_2RuO_4 layered perovskite

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A_2RuO_4 layered perovskites can result in many different electronic phases depending on the metallic element A. For instance, a ruthenate with $A=Ca_{2-x}Sr_x$ behaves as a time reversal symmetry breaking superconductor (with T_c=1.5K) when x=2, and shows a Mott-insulating behavior when x=0. Such a substantial modification of the electronic structure comes from the lattice distortion of Ru-O octahedra chemically pressurized by the substitution of Sr with Ca.

Herein, we report on the use of scanning probe microscopy techniques to investigate the metal-insulator (MI) transition of Ca_2RuO_4 single crystal, grown by using floating-zone furnace technique. Driven by temperature and/or electric field, the MI transition is always accompanied by a structural transition: the c-axis parameter elongates from 11.9Å – in the insulating orthorhombic state - to 12.3Å – in the metallic tetragonal state. We show that the MI transition can be induced by applying a voltage between the crystal and the AFM probe, given that the intensity of the electric field overcomes a certain threshold value (30-40 V/cm). In this case, localized nano- or micro-metric structural deformations take place, as proved and studied by atomic force microscopy (AFM) and Conducting-AFM (C-AFM). This study paved the way to the investigation of the metal-insulator (MI) transition in the Ca_2RuO_4-Ru metal eutectic system.

P02 Nano-layered mirrors for gravitational wave detectors

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The first direct observation of gravitational waves – ripples in space-time predicted by A. Einstein 100 years earlier – was performed by Laser Interferometer Gravitational-wave Observatory (LIGO) on September 14th, 2015. LIGO founders (Rainer Weiss, Barry C. Barish e Kip S. Thorne) were thus awarded the Nobel Prize in Physics in 2017 [1]. Being the expected gravitational wave signals extremely weak, the reduction of the noise in the most sensitive frequency band ($50 \div 300\,Hz$) where the first signals have been detected, represents the highest modern challenge of the presently operating detectors (Virgo, LIGOs, Kagra). To date, the predominant noise in the frequency range of interest is due to the thermal noise of the highly reflective optical coatings of cavity mirrors. The design of such mirrors in currently operating interferometers is based on the alternance of two materials with high and low refractive index and thickness equal to a quarter of wavelength $\lambda/4$. Such design can be optimized with respect to the thermal noise, for example, by reducing the thickness of the material with higher optical losses [2,3]. Here, we report a study of innovative reflective optical coatings, based on dielectric oxides (TiO_2, SiO_2, ZrO_2, NbO_2,…), replacing homogeneous layers with stratified nano-composites. As already reported in the literature [4], the main advantage of this strategy is the inhibition of crystallization upon annealing. Indeed, while on the one side the annealing process is necessary to relax intrinsic material stress/strain, to guarantee smooth surfaces and interfaces, and to set-up the correct material stoichiometry, on the other hand it induces the formation of crystallites, which will work as scattering centres for the light, with a consequent blow up of optical losses and thermal noise. Starting from TiO_2 (refractive index of 2.32 @ 1064nm and crystallization temperature around 300°C), we have combined it with ZrO_2 and SiO_2 (refractive index of 2.12 and 1.44 @ 1064nm, respectively), in nano-layered structures, to study crystallization temperature and morphology at different annealing temperatures, through X-Ray diffractometry (XRD), small-angle X-ray scattering (SAXS) and scanning probe microscopy (SPM) techniques. By using a plasma-assisted (Ar) Electron Beam evaporator, we have deposited TiO_2 single material by varying its thickness in the range between 3.4 and 200nm. Then, we have combined TiO_2 with ZrO_2 and SiO_2, by making TiO_2/ZrO_2 and TiO_2/SiO_2 multilayers, keeping fixed the total thickness and increasing the degree of segmentation (from a minimum of 2 alternating layers to a maximum of 85), thus decreasing the thickness of each layer inside the heterostructure. XRD and Atomic Force Microscopy (AFM) analyses performed on the as-grown samples have shown amorphous material growth with surface roughness of few nm, SAXS and advanced-SPM measurements have provided a characterization of the thickness of the layers and the quality of the interfaces inside the structure. Annealing treatments have been performed in high-vacuum and air conditions. XRD and SPM analyses after annealing have been compared to the as-grown ones to identify crystallization temperature of nano-composites and variation in surface roughness.

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P03 Magnetic behavior of $Sr_3Ru_2O_7$ crystals grown via eutectic solidification

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Strontium ruthenates properties are dramatically tuned by impurities and disorder. In particular, $Sr_3Ru_2O_7$ shows a strong variation in transport and magnetic properties depending on synthesis process. Using a flux-feeding floating-zone technique (FFFZ) under high pressure (10 bar) we succeeded in growing Sr_2RuO_4-$Sr_3Ru_2O_7$ eutectics. In this study we report a comparative study between $Sr_3Ru_2O_7$ crystals grown as single phase and in $Sr_3Ru_2O_7$ -Sr_2RuO_4 eutectics. Our analysis by magnetic measurements, X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) reveals that $Sr_3Ru_2O_7$ domains of the eutectic have a significantly lower level of impurities compared to $Sr_3Ru_2O_7$ single-phase crystals, where intergrowths of $Sr_4Ru_3O_{10}$ and $SrRuO_3$ phase are seen. These results identify the eutectic solidification as a fruitful way to grow highly pure crystals of $Sr_3Ru_2O_7$ and open a pathway for understanding of its intrinsic physical properties.

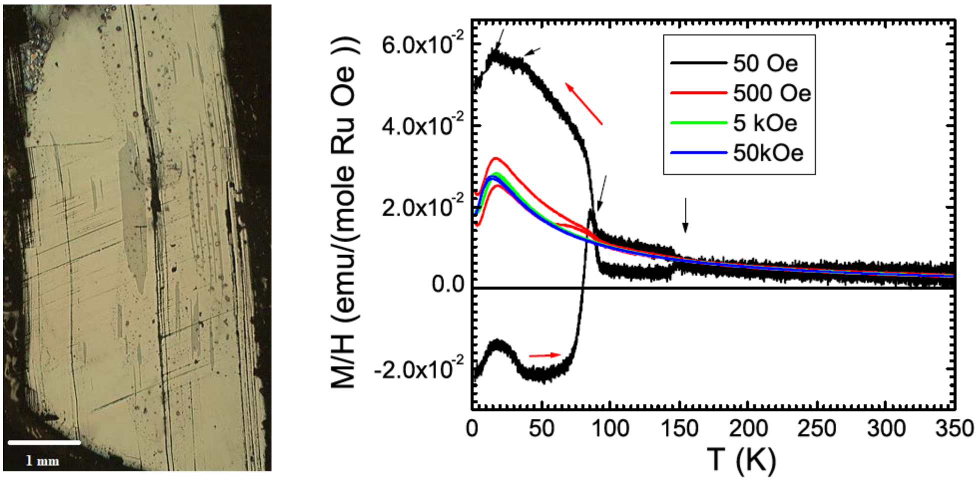

Figure 1: (left) Polarized-light optical microscopy image of a polished $Sr_3Ru_2O_7$ -Sr_2RuO_4 eutectic. Sr_2RuO_4 islands (darker regions) are embedded in the $Sr_3Ru_2O_7$ crystal. (right) Susceptibility versus temperature of a $Sr_3Ru_2O_7$ -Sr_2RuO_4 eutectic sample measured applying a magnetic field ranging from 50 Oe up to 50 kOe parallel to the c axis of the sample.

P04 Synthesis of a Lamellar $Sr_3Ru_2O_7$ - $Sr_4Ru_3O_{10}$ Eutectic System

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$Sr_3Ru_2O_7$ -$Sr_4Ru_3O_{10}$ eutectics with lamellar morphology have been grown in a double-mirror optical floating zone furnace. A flux feeding floating zone configuration with Ru self-flux has been adopted. Moreover, the synthesis procedure of the polycrystalline rod is found to be a critical factor for the crystal growth. The morphology, structure, phase purity, and composition of the samples were analyzed by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). Results from backscattered electron (BSE) imaging as well as from energy dispersive spectrometry (EDS) were combined with the electron backscatter diffraction (EBSD) data to obtain complementary chemical and crystallographic information. In particular, XRD analysis indicated that the $Sr_3Ru_2O_7$ and $Sr_4Ru_3O_{10}$ phases match the same crystal with parallel in-plane and out-of-plane lattice parameters. The resistance measurements showed a Fermi liquid behavior at low temperatures analogous to the one found in the single phases.

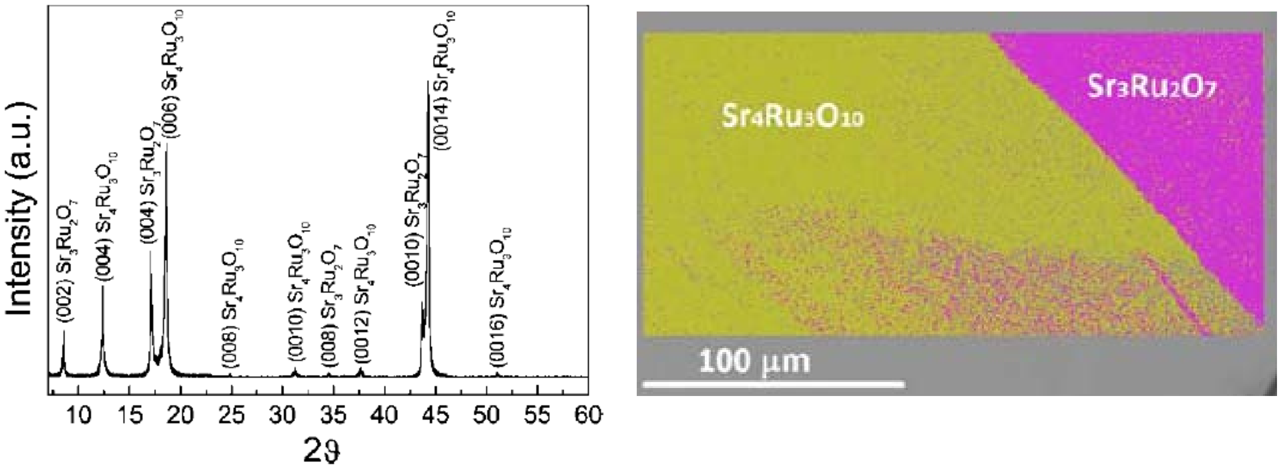

Figure 1: (left) X-ray diffraction pattern of a cleaved surface of the $Sr_3Ru_2O_7$ – $Sr_4Ru_3O_{10}$ eutectic system. All the peaks correspond to reflections due to Sr_3Ru_2O and $Sr_4Ru_3O_{10}$ phases. (right) EBSD compositional map overlayed to the secondary electron image of a cleaved surface of the $Sr_3Ru_2O_7$ – $Sr_4Ru_3O_{10}$ eutectic system. The yellow area corresponds to $Sr_4Ru_3O_{10}$ phase while the violet on is the $Sr_3Ru_2O_7$ phase.

P05 Growth and characterization of Ce:$LaBr_3$ based eutectic systems

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Submicron-diameter phase-separated scintillator fibers (PSSFs) were reported and they possessed both the properties of an optical fiber and a radiation-to-light conversion. The PSSFs were fabricated using a directionally solidified eutectic (DSE) system. The DSE systems have been discovered in various materials for many applications. Up to now, $GdAlO_3/Al_2O_3$ have been already reported as PSSFs for high resolution X-ray imaging and particle tracking applications. Ce:$LaBr_3$ has attracted attention due to its high light yield of 61000 photons/MeV and fast decay time of 25 ns with enough density of 5.1 g/cm^3 for x-ray and g-ray detection [2]. In this research, exploration of PSSFs by directional crystal growth method will be reported. In this study, Ce doped $LaBr_3$/ $AEBr_2$ (AE=Mg, Ca, Sr, Ba) eutectics were explored. Crystal growth was performed by Bridgeman (BZ) method at the eutectic point. Investigations of their crystal structure and eutectic phase were performed. Luminescence and scintillation properties were also evaluated.

Ce doped $LaBr_3/AEBr_2$ (AE=Mg, Ca, Sr, Ba) eutectics were grown by the Bridgman–Stockbarger (BS) method in quartz ampoules. The eutectics（AE = Mg, Ca） showed optical transparency like bundle optical fibers (Fig.1). Grown Ce doped $LaBr_3/MgBr_2$ eutectic shows 350-360 nm emission ascribed to Ce^{3+} 4f-5d transition under X-ray excitation. The light yield of Ce: $LaBr_3/MgBr_2$ was the best among the grown samples and 34,300 photon/MeV Scintillation decay time under 662keV gamma-ray was 19 ns. These results indicate to realize faster particle tracking system using Ce: $LaBr_3$ based PSSF even $LaBr_3$ is hygroscopic.

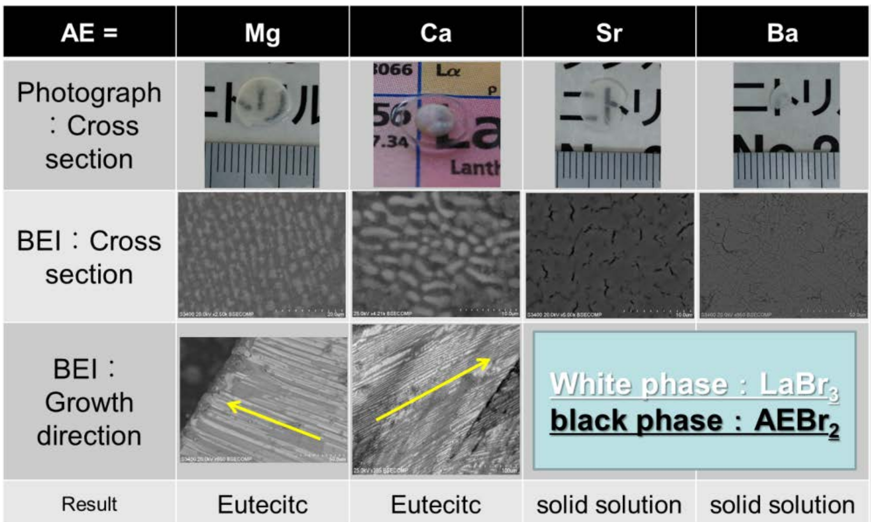

Figure 1: Growth results and BEI of $LaBr_3/AEBr_2$ (AE=Mg, Ca, Sr, Ba) eutectics.

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P06 Phase diagrams of BaI_2-REI_3 and growths of eutectic scintillator in the systems

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X-ray flat panel detectors (FPD) using inorganic scintillator materials have been widely used for digital X-ray imaging such as a medical imaging system, nondestructive security and industrial inspection systems. For excellent X-ray imaging, high light yield and light guiding efficiency are desired for the scintillators. Recently, phase-separating scintillators grow by unidirectional solidification at an eutectic point were developed and they indicated high light guiding efficiency because of a light transportation in scintillator fibers [1,2] We developed various oxide and fluoride scintillators with eutectic structure (eutectic scintillator) to improve their light guiding efficiency or neutron detection efficiency [2,3,4]. However, there are few reports of heavy halide (such as chloride, bromide and iodide) eutectic scintillators due to their strong hygroscopicity and absence of their diagrams. Therefore, we investigated phase diagrams of halide materials to develop a heavy halide eutectic scintillator and revealed that the phase diagram of BaI_2-LuI_3 had an eutectic point.. In this study, we tried to create phase diagrams of BaI_2 and Rare-earth (*RE*) iodide system in addition to LuI_3 and and grow heavy halide eutectic scintillators at the eutectic point.

BaI_2 and *RE*I_3 (*RE* : Lu, Gd, Ce, La, and Y) [> 3 N] were mixed as various molar ratios in a dry room or glove box. The mixed powder was set in a carbon crucible and it was melted in Ar using a halide-micro-pulling-down furnace [5] after vacuuming to 10^{-4} Pa. Phases of the specimens were identified by an X-ray diffraction (XRD) measurement. In addition, the mixed powder was set in a sealed quartz ampule after evacuating the inside of the ampule and thermal analyses were performed by a differential scanning calorimetry (DSC). Then, halide eutectic scintillators were grown by a Vertical Bridgman (VB) method using a sealed quartz ampule including mixed powder with the eutectic composition. The microstructures of the grown eutectic scintillators were observed by a Scanning Electron Microscope (SEM).

In the DSC curves of BaI_2-GdI_3 system, there were two or three endothermic peaks in elevated temperature process except for the 70 mol%BaI2/30 mol%GdI_3 with only one peak. The peak of the 70 mol%BaI2/30 mol%GdI_3 appeared at 584 °C and it was also observed for all specimens. Figure 1 is the phase diagram of the BaI_2-GdI_3 using the results of DSC measurements. In the phase diagram, there is an eutectic point around 70 mol% BaI_2/30 mol% GdI_3 and an eutectic scintillator can be grown from the melt. Eutectic points were also observed in the phase diagrams of BaI_2 and other REI_3 while the compositions of eutectic points were different. Details of phase diagrams, crystal growths of the euctectic scintillators and their properties will be reported.

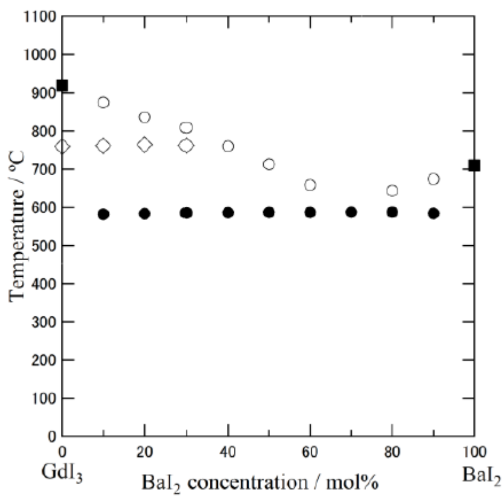

Figure 1: Phase diagram of BaI_2-GdI_3.

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