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EDITORIAL

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Mercouri G. Kanatzidis: Pioneer of Discovering New Materials

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It is our great honor to organize the themed issue to celebrate the 65th birthday of Professor Mercouri G. Kanatzidis. Mercouri is recognized as one of leading scientists in solid-state chemistry. His research interest covers exploratory synthesis in chalcogenides and multianionic materials, thermoelectric applications, hard radiation detectors, hybrid perovskite materials discovery and solar cells, which can be summarized as the quote on his group website "Where will the new materials come from?" And Mercouri always believes that each material discovered has some properties for purpose, which inspires us and many young researchers to discover the potential use of all new materials.

Mercouri Kanatzidis was born in Thessaloniki, Greece in 1957. After obtaining a B. Sc. from Aristotle University in Greece, he received his Ph. D in chemistry from the University of Iowa in 1984. He was a post-doctoral research associate at the University of Michigan and Northwestern University from 1985 to 1987 and is currently the Charles E. and Emma H. Morrison Professor of Chemistry at Northwestern University. Mercouri moved to Northwestern in the fall of 2006 from Michigan State University where he was a University Distinguished Professor of Chemistry since 1987. Mercouri also holds an appointment at Argonne National Laboratory and is the editor-in-chief of the Journal of Solid-State Chemistry. He has published over 1350 publications and over 40 patents, to date (citations >146,000; H index 176).

Mercouri has been recognized through a number of prestigious awards for the scientific accomplishments attained during his career. Recently, Mercouri received the Global Energy Prize for "the major advances made in solar energy conversion with the use of novel perovskite halides". He also received DOE Ten at Ten Scientific Ideas Award for the first demonstration of all-solid-state solar cells using halide perovskite materials - 2019, American Institute of Chemistry Chemical Pioneer Award - 2018, Hershel and Hilda Rich Visiting Professorship, Technion – Israel Institute of Technology - 2017, University of Crete - Honorary Doctorate Degree - 2017, Samson Prime Minister's Prize for Innovation in Alternative Fuels for Transportation - 2016, American Physical Society (APS) Fellow - 2016, APS James C. McGroddy Prize for New Materials - 2016, American Chemical Society (ACS) Award in Inorganic Chemistry - 2016, ENI Award for the "Renewable Energy Prize" category - 2015, Awarded Wilhelm Manchot Professorship, Technical University of Munich - 2015, Elected Fellow of the Royal Chemical Society - 2015, Royal Chemical Society De Gennes Prize - 2015, Materials Research Society (MRS) Medal - 2014, International Thermoelectric Society Outstanding Achievement Award - 2014, Einstein Professor, Chinese Academy of Sciences - 2014, Cheetham Lecturer Award, University of California Santa Barbara - 2013, American Association for the Advancement of Science (AAAS) Fellow - 2012, MRS Fellow - 2010, Charles E. and Emma H. Morrison Professor, Northwestern University - 2006, Morley Medal, American Chemical Society, Cleveland Section - 2003, Alexander von Humboldt Prize - 2003, John Simon Guggenheim Foundation Fellow - 2002, University Distinguished Professor MSU - 2001, Sigma Xi Senior Meritorious Faculty Award - 2000, Michigan State University Distinguished Faculty Award - 1998, Camille and Henry Dreyfus Teacher Scholar - 1993-1998, Alfred P. Sloan Fellow (see Sloan Fellows) - 1991-1993, Beckman Young Investigator - 1992-1994, ACS Inorganic Chem-

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istry Division Award, EXXON Faculty Fellowship in Solid State Chemistry - 1990, Presidential Young Investigator Award, National Science Foundation - 1989-1994.

Thermoelectrics are semiconductors that convert waste heat into electricity. By harvesting waste heat, thermoelectric materials can save energy in many thermal processes — including in automobiles — significantly increasing vehicle mileage and reducing carbon dioxide emissions. Mercouri has made great contributions to the thermoelectric community for innovative and revolutionary contributions to the design, synthesis, and characterization of advanced thermoelectric materials, including bulk nanostructured chalcogenides, endotaxially nanostructured materials, and hierarchical material architectures.

Perovskites are materials that has the same crystal structure as the mineral calcium titanium oxide, the first-discovered perovskite crystal, which are recognized as one of the most promising candidates for high-efficiency solar cell. Mercouri is the pioneer in perovskite research. He published the first solid state solar cell device using a film of $CsSnI_3$ perovskite in a solid state dye-sensitized Gratzel cell with ~10% efficiency. He was the first to demonstrate functioning $CH_3NH_3SnI_3$-based solar cells. He also demonstrated first $CH_3NH_3SnI_3$-based solar cells and discovered the anomalous bandgap dependence between lead and tin based solid solutions $APb_{1-x}Sn_xI_3$ (A=Cs, CH_3NH_3, formamidinium).

In this special issue, the former Ph.D. students and postdoctoral researchers from Kanatzidis group contributed several articles, mainly thermoelectrics and perovskites, to show their respect and best wishes to Mercouri. They wish Mercouri and his family good health and happiness. And they also hope that young researchers could get inspirations from Mercouri's innovative and fruitful achievements through this themed issue.

1. "Grain boundary scattering was long recognized and widely utilized to regulate the transports of charge carriers and phonons in thermoelectric materials; nevertheless, the understanding of grain boundaries in lots of literatures seems somewhat lopsided and way too simplified, without distinguishing the exact microstructural characters for each individual case. In this perspective, we first review the well-known functions of grain boundaries on the electrical and thermal transport properties based on some representative thermoelectric series. Next, we try to deepen the understanding of the roles of grain boundaries in the following two aspects: (1) whether the grain boundaries are large-angle or small-angle ones, and what the difference between them in affecting electrical/thermal performance is; (2) whether the grain boundaries are clean and sharp as lattice discontinuity defects, if not, how can the grain boundaries as an individual phase affect the thermoelectric transports. At last, we suggest that further investigations engaging more detailed microstructural information of grain boundaries are urgently necessary in order to better realize a positive trade-off between lattice thermal conductivity and electrical power factor for an overall enhanced thermoelectric performance."[1]

By **Di Wu**, **Jiaqing He** (postdoctoral researcher, 2008-2010)
https://faculty.snnu.edu.cn/wudi12/zh_CN/xsxx/148462/content/27740.htm,
http://jqhphy.sustech.edu.cn/

2. "Miniaturization, lightweight and highly integration have gradually become the main trends in the development of modern science and technology. Two-dimensional (2D) SnSe/SnS-based materials have recently received widespread attention in the field of thermoelectricity because of the remarkable physical transport properties. However, the peculiar crystal structure also ensures that SnSe and SnS materials can meet the requirements of the miniaturized and highly integrated functional devices, which make them the most notable interdisciplinary hotpots. In this review, we initially analyzed the basic physical properties and outlined the important achievements in thermoelectric field of SnSe/SnS. With the development of preparation technology for thin-film materials and nanomaterials, SnSe/SnS has been successfully utilized in multiple fields, including photothermal, photoelectric and ferroelectric fields. We then elaborated the multifunctions in SnSe/SnS, such as solar cells, photodetectors, photocatalysis, etc. Eventually, some personal summaries and prospects are demonstrated, which might highlight the importance of multifunction and promote the potential applications of 2D materials including SnSe/SnS."[2]

By **Bingchao Qin**, **Li-Dong Zhao** (postdoctoral researchers, 2011-2014)
http://shi.buaa.edu.cn/zhaolidong/zh_CN/index.htm

3. "Tin halide perovskite solar cells (TPSCs) have been recognized as one of the most promising candidates for efficient and stable eco-friendly photovoltaic technology. The certified power conversion efficiency of TPSCs has delivered to over 14% recently. Emerging low-dimensional tin halide perovskites such as Ruddlesden-Popper (RP), Dion–Jacobson (DJ), or 2D-3D perovskite structures have recently offered new approaches to stabilizing tin perovskite devices. Given the important role of low-dimensional tin perovskites, in this review, we focused on the dimensionality regulation in TPSCs to clarify the rule of performance and stability. We first discussed the structural flexibility and optoelectronic properties of tin halide perovskites. Moreover, the updated development along with the use of large organic spacer cations was assessed. Last, we reviewed the status of RP, DJ, 2D-3D mixed perovskites, and surface passivation strategy to boost the efficiency and operational stability of TPSCs, further highlighting the current challenges to enhancing these key performance metrics."[3]

By **Feng Hao**, postdoctoral researchers (2012-2016)
https://materials.uestc.edu.cn/info/1122/3233.htm

4. "It is commonly believed that wide band gap ferroelectrics are electrically insulating and can hardly be promising thermoelectric materials. However, things could be different if their gaps are reduced while the ferroelectricity is well reserved. Here we propose that the exploration of narrow band gap semiconductors with ferroelectric characteristic might lead to simultaneous optimization of electrical and thermal transport properties for advanced thermoelectric materials. Narrow gap endows the materials with good dopability, which is a prerequisite for high electrical conductivity. In the meanwhile, ferroelectricity-induced Rashba band splitting and lattice softening would yield large Seebeck coefficient and low thermal conductivity, respectively. Altogether, excellent thermoelectric performance can be expected in the narrow gap ferroelectric semiconductors (NGFS). We also pro-

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pose the design principles of potential NGFSs."[4]

By **Gangjian Tan**, postdoctoral researcher (2013-2017)
http://sklwut.whut.edu.cn/rcdw/yjry/202009/t20200906_878604.shtml

5. "The all-inorganic semiconducting perovskite Cesium Lead Bromide, $CsPbBr_3$, exhibits promising properties for ionizing radiation detection applications. In this work, polycrystalline $CsPbBr_3$ was synthesized from the melt of binary compounds CsBr and $PbBr_2$. Moisture and oxides in the synthesized $CsPbBr_3$ compounds were removed by a reduction process under hydrogen. The $CsPbBr_3$ materials were purified and grown into high-quality single crystals via a modified zone refining process. The single-crystal samples obtained from the combined zone-refining/crystal growth process exhibited total trace impurity levels below 1 ppm (w.t.). Obtained single crystals exhibited an electrical resistivity within a range of 108~109 Ω·cm. Stoichiometry imbalance was observed in the $CsPbBr_3$ crystal growth. Around 1% Cs deficiency was observed in all the samples, despite different ratios between the starting materials of $PbBr_2$ and CsBr. The positive impact of excess $PbBr_2$ in starting materials was also revealed. With a slight excess Pb (2%), $CsPbBr_3$ single crystals displayed significantly higher photosensitivity compared to the stoichiometric or excess Cs samples."[5]

By **Peng Li Wang**, postdoctoral researcher (2013-2015)
https://uniweb.time.queensu.ca/members/733

6. "A new class of aerogels based exclusively on metal chalcogenide frameworks has been developed, opening up a series of novel properties and applications. Further expanding the application of such chalcogels in electrocatalytic CO_2 reduction is of significance for mitigating the rise of atmospheric CO_2 concentration. Herein, the tin sulfide chalcogel was employed as a pre-catalyst for the construction of efficient electrocatalysts for CO_2 reduction. $SnS_{0.09}$ and $SnS_{0.55}$ supported on carbon cloth ($SnS_{0.09}$/CC and $SnS_{0.55}$/CC) were obtained with different amounts of sulfur by cyclic voltammetry activation of the tin sulfide chalcogel at different potential intervals. Compared to $SnS_{0.09}$/CC, $SnS_{0.55}$/CC with higher S content exhibited higher formate Faraday efficiency of 93.1% at -1.1 V vs. RHE, and the partial current density of formate was 28.4 mA/cm^2. The difference in performance between $SnS_{0.09}$/CC and $SnS_{0.55}$/CC could be attributed to the varying sulfur which could favor the formation of formate."[6]

By **Jian Liu**, postdoctoral researcher (2014-2017)
https://jl.qust.edu.cn/

7. "Understanding the nature of phonon transport in solids and exploring the way to minimize the thermal conductivity are important in many fields, including the development of efficient thermoelectric materials. For a long time, the contribution of optical phonons to the lattice thermal conductivity is considered to be very small and negligible. Until recent decade, a series of studies have shown that, for some materials with special electronic configuration, optical phonons can dramatically affect the lattice thermal conductivity. Specifically, in these materials, part of their cations would be off-centering from their equilibrium positions and lead to the local distortion of the coordination structure. This off-centering behavior would introduce some low-frequency optical phonons, which can couple with the acoustic phonons and cause additional phonon scattering, thus, it is very effective to suppress the lattice thermal conductivity. This perspective clarifies the lattice dynamics of off-centering behavior and illustrates how this off-centering behavior could lead to the acoustic-optical phonon coupling. This paper also demonstrates the off-centering behavior can be introduced into a material by using the lone pair element doping and the weak sd^3 orbital hybridization, and proposes a strategy to design materials with low thermal conductivity based on this."[7]

By **Hongyao Xie**, postdoctoral researcher (2018-2022)
https://chemgroups.northwestern.edu/kanatzidis/group/Hongyao.html

8. "Thermoelectric technology has immense potential in enabling energy conversion between heat and electricity, and its conversion efficiency is mainly determined by the wide-temperature thermoelectric performance in a given material. Therefore, it is more meaningful to pursue high ZT values in a wide temperature range (namely high average ZT) rather than the peak ZT value at a temperature point. Herein, taking lead chalcogenides as paradigm, some rational routes to high average ZT value in thermoelectric materials are introduced, such as bandgap tuning and dynamic doping. This perspective will emphasize the importance of dynamically optimizing carrier and phonon transport properties to high-ranged thermoelectric performance, which could judiciously be extended to other thermoelectric systems."[8]

By **Yu Xiao**, Visiting researcher (2018)
http://mse.xjtu.edu.cn/info/1063/6222.htm

9. "High-entropy materials have attracted enormous attention since the discovery of high-entropy alloys, which exhibit exceptional properties compared to conventional alloys, such as better strength-to-weight, higher fracture resistance, higher tensile strength, and higher corrosion resistance. High-entropy materials are generally defined as materials that are formed by mixing equal or relatively large proportions of five or more elements, or materials with entropy larger than 1.61R (R is the molar gas constant). These two definitions have a close relationship: assuming five elements are equimolarly mixed at a single crystallographic site, the entropy of new material $S = -R\Sigma x_i \ln(x_i) = -R\ln(0.2) = 1.61R$. The high entropy could provide a dominant driving force to form new high-entropy stabilized compounds, according to the Gibbs law $\Delta G = \Delta H - T\Delta S$, whose composition could exceed the maximum solubility of conventional alloys. With the fast development within 20 years, high entropy investigation has extended the research field beyond alloys to other fields, such as thermoelectrics."[9]

By **Cheng Chang**, Visiting researcher (2018)
https://scholar.google.com/citations?user=_rwEMCsAAAAJ&hl=en

10. **Kanishka Biswas**, postdoctoral researcher (2009-2012)
https://www.jncasr.ac.in/faculty/kanishka

11. **In Chung**, Ph.D. student (2001–2008) and postdoctoral researcher (2008–2012)
https://inchung.snu.ac.kr/

12. **Maria Ibáñez**, visiting researcher (2013)
https://ibanezgroup.pages.ist.ac.at/
(Their submissions are on the way.)

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