Editorial

Compounds with Polar Metallic Bonding—Reloaded

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In June 2019 the first volume of a Special Edition of Crystals with the subject Compounds with Polar Metallic Bonding was presented. It contained eight original research publications [1–8] and covered a wide spectrum of aspects: preparative studies, structural and physicochemical characterisations, materials for theoretical applications, theoretical considerations and chemical modifications were illustrated by authors from all around the world. Here, we present the second volume on this topic. Polar intermetallic phases are an emerging and evolving playground for chemists, physicists and material scientist and have attracted high interest over the years [9–11]. This broad interest shows anew in four publications which adress new aspects and reveal new insights and the rapid progress of this scientific community over a relatively short period of time. This fast and diverse evolution is very significant for the world of polar intermetallic materials: the numerous and very diverse scientific groups over the world are in a constant and highly cooperative exchange of ideas, each participating with different sets of techniques, concepts and task assignments. This highly intermodal cooperation without negative influences of competitive pressure leads to fast and targeted progress on the main aspects. International congresses but also explicite to be mentioned the platforms provided by dedicated scientific journals with high reputation and visibility are the driving forces for the necessary exchange of ideas and the direct interaction of all players in this scientific field. The diversification of scientific journals makes it sometimes difficult to focus a special area of expertise and to keep track of all evolutions in one field. The instrument of the Special Editions provided by Crystals helps to present specific modern scientific fields, their main actors, its main questions and answers with respect to relevant topics and to show how vivid and buoyant a special field of interest presents itself.

In the last three years, we have collected four original publications from outstanding groups working on the field of polar intermetallic phases. This collection can be regarded as a representative cutout of modern research concerning preparation of new phases, structure elucidation and striving for a deeper understanding of the complex structure-property relations of this fascinating class of materials.

Our group is concerned with the first systematic studies on ternary amalgams. Amalgams of the less noble metals serve as ideal model systems to investigate structure-property relations of polar intermetallic phases. The crystal structure of CsNa$_2$Hg$_{18}$, presented in the article ’Structure and Bonding in CsNa$_2$Hg$_{18}$, a New Ternary Amalgam with Strong Coulombic Bonding Contributions’ [12], is a well-suited example of such a new ternary amalgam with the typical bad metal behaviour so often observed in polar intermetals.

The group of Caroline Röhr shows the crystallographic relationship of a series of Ga-rich gallides of the alkali metals in the article’ A Coloring Study of the Ga Richest Alkali Gallides: New In- and Hg-Containing Gallides with the RbGa$_7$- and the K$_3$Ga$_{13}$-Type Structure’ [13]. The cluster phases are close to the Zintl regime and can incorporate a certain amount of In or Hg, which is accompanied by specific changes in the respective band structures. The close comparison of the binary gallides and their Hg-substituted relatives reveals how the properties can be influenced by tuning the electronic states.
The Bobev group presents in the article ‘On the New Oxyarsenides Eu$_5$Zn$_2$As$_5$O and Eu$_5$Cd$_2$As$_5$O’ [14], how complicated multinary Zintl phases can form ‘double salts’ together with isolated oxide anions. Ionic Eu–O interactions are present together with covalent As–As and M–As interactions. This interplay which is so typical for highly polar intermetallic phases leads to interesting mixed valency for Eu and to the overall behaviour of a narrow band gap semiconductor.

The article ‘Revisiting the Zintl-Klemm Concept for ALn$_2$Ag$_3$Te$_5$-Type Alkaline-Metal (A) Lanthanide (Ln) Silver Tellurides by Dronskowski, Steinberg and coworkers [15] again deals with multinary intermetallic compounds with Zintl-like structures. The close study of the electronic structures and the role of tellurium reveals an intriguing mixture of ionic and metallic interactions within a framework structure with high impact on the understanding of thermoelectric materials.

This compendium of studies of new intermetallic structures with high ionic polarity, represents in an excellent way the modern ‘state of the art’ in the field. Materials with high thermoelectric efficiencies [16,17], interesting combination of electronic [18], multiferroic [19], chemical and catalytical properties [20] for potential applications in energy storage [21], electronics [22,23], chemical synthesis [24] and all other fields of modern material science, can only be optimised for application when the understanding of those parameters which decide on the macroscopic behaviour of the materials can be identified and independently be adressed by chemical methods. For the identification of those crucial parameters and their comparative role on the properties, a large number of studies on different systems is necessary. This Special Issue gives new impulses and new insights with this respect.

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