Introduction to rare earth materials

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The rare-earth elements include Sc, Y and the 15 lanthanoids from La to Lu. Owing, in part, to their diverse coordination numbers and geometries and relatively localized orbitals, the rare-earth materials find application in lighting, displays, catalysis, hydrogen storage, photovoltaics, magnetism, magnetocalorics, thermoelectrics, biomedical science and sensing, amongst others.[1] In addition to their various applications, there are diverse classes of materials that can be synthesized using rare-earth elements including coordination complexes, polymers, metal–organic frameworks (MOFs),[2] solid-state inorganic materials, and nanoparticles, etc.[1] Therefore, in addition to the structural diversity of rare-earth materials, the unique electronic properties of the rare-earth elements, particularly the lanthanoids, engenders the resulting materials with tunable luminescence, and magnetic behaviour, etc.[1,2] This themed collection showcases both the structural diversity and versatile physical properties of rare-earth materials. Here we have chosen several papers from this themed collection to feature, while there are other papers in the collection that advance the materials chemistry of rare-earth elements, and we believe that all papers will be of high interest to the community.

Rare-earth coordination polymers and MOFs are of interest due to the interplay between organic linker molecules and rare-earth metal nodes, which can lead to unique polymeric structures, sometimes having porosity.[2] In one example, de Andrade et. al¡. (10.1039/D4TC03823A) demonstrated the importance of short bridging linkers, and thus reduced metal-metal distances (8.3-8.5 Å compared to > 9.2 Å), to generate upconversion luminescence in 1D rare-earth coordination polymers. Firmino.et.al¡ (10.1039/D4TC02589J) highlighted the utility of phosphonate linkers for the construction of robust rare-earth MOFs, leading to an extremely thermally stable MOF that maintains structural features up to 800 °C. In another example that underscores the diversity that rare-earth elements bring to MOF chemistry, Loukopoulos et. al¡. (10.1039/D4TC03317E) reported the first hexagonal 6-connected RE_6-cluster building block to be observed in a MOF, which also gives rise to a novel MOF topology. This themed collection also features research from Chen et. al¡. (10.1039/D4TC03221G) on the encapsulation of dyes in the pores of rare-earth MOFs as a strategy for tuning the photoluminescent properties of the resulting composite materials. Psalti et.al¡ (10.1039/D4TC02806F) reported a series of near-infrared (NIR) emitting MOFs where the organic linker used to sensitize the NIR emission allows for excitation in the visible region of the electromagnetic spectrum (450 nm) – a rare feature compared to most NIR emitting rare-earth MOFs reported to date. While Djanffar et. al¡ (10.1039/D4TC00781F) showed that mixed-metal rare-earth cluster-based MOFs have potential as luminescent thermometers, with high thermal sensitivity near room temperature.

Magnetism of rare-earth materials is mainly derived from the f-electrons, which as a signature mostly possess relatively large magnetic moments that manifest in diverse and interesting behavior.[3,4] In a study on lanthanide calcium oxyborates $LnCa_4O(BO_3)_3$, with a series of f-electron rare-earth elements, Azrour and coworkers discovered strong magnetic anisotropy originating from the polar crystal structure of this system (10.1039/d4tc03249g). This results in excellent rotating magnetocaloric effect (RMCE) values in the He cryogenic region, particularly for the Er compound, rivalling those of well-known $Gd_3Ga_5O_{12}$[5] Direct solid-state cooling via materials is attracting increasing interest for potential expanded applications for magnetocaloric cooling and Peltier cooling.[6-8] Moving away from oxides, Li et.al., focused on rare-earth–chalcogen coordination and synthesized a novel series of rare-earth chalcogenidotetrachloride clusters (10.1039/d4tc02778g). While a super-exchange antiferromagnetic interaction is observed for the Gd phase, with the magnitude being relatively small because of the weak bridging effect of the chloro ligand, interestingly in contrast, a ferromagnetic interaction is indicated for only the Dy sulfide phase. The smallest Dy-Dy separation of the sulfide phase resulted in the strongest dipole-dipole ferromagnetic coupling and therefore, enabled it not to be engulfed by the antiferromagnetic super-exchange interactions. Calculations are carried out to confirm this, and optical properties of the novel compounds are also characterized.

In addition to magnetism, luminescence properties of the rare-earth materials have also been an intensively investigated topic.[9] There are some reports on traditional rare-earth ion doped phosphor materials in this themed collection, such as $BaY_2Sc_2Al_2SiO_{12}:Ce^{3+}$ (10.1039/D4TC02906B) and $Ca_3Sc_2Si_3O_{12}$: Ce^{3+}, Cr^{3+}, Li^{+} (10.1039/D4TC03017F), however, their applications have been expanded from white LEDs, to emerging near-infrared laser-driven lighting. Moreover, some interesting luminescence properties and mechanisms have been investigated, like the concentration quenching behavior of Stokes and upconversion luminescence for Pr^{3+}-doped $Y_3Al_5O_{12}$ (10.1039/D4TC03386H). Balhara et.al¡ also took an interesting approach when they utilized negative thermal expansion (NTE) in the host $Sc_2Mo_3O_{12}$ and synthesized the Sm^{3+} doped material (10.1039/d4tc01817f). Thermal quenching of the photoluminescence of rare-earth phosphors has been an issue for applications, and utilizing NTE host matrixes to counter that is an effective emerging strategy. Their Sm^{3+} phosphors are reddish orange emitters and display robust anti-thermal quenching behavior. Another hot topic in the field of luminescent materials is rare-earth halide perovskites or their derivates, which can be easily prepared in the form of nanocrystals, and their applications have been expanded. Li et¡.al¡ reported rare-earth-based $Cs_2NaRECl_6$ (RE = Tb, Eu) halide double perovskite nanocrystals with multicolor emissions for anticounterfeiting and LED applications (10.1039/D4TC01697A). Ding et¡.al¡ contributed a very nice review on the lead-free lanthanide-based Cs_3LnCl_6 metal halides (10.1039/D4TC03748K). In this leading review, the authors summarized several synthesis approaches towards both Cs_3LnCl_6 polycrystals and nanocrystals. The association of the crystal/electronic structure, optical properties and applications is discussed.

As a traditional research topic with new emerging directions, rare-earth materials will continually serve for traditional applications like lighting, catalysis, magnetism, etc., while bringing about some newer research in photonic quantum technologies, perovskites based optoelectronic devices, etc. As guest editors of this themed collection, we extend our gratitude to the colleagues who have contributed to and reviewed the articles included in this collection. We also hope this collection serves as both an inspiration and a valuable resource for researchers across disciplines in rare-earth materials.

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