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Perspective on rare earth crystals

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Rare earth crystals represent our society utilization of rare earth resources via crystallization engineering strategies. Rare earth crystals include more than 30 types of functional and structural crystals, with more than 30 kinds of inorganic or metal compounds. Multiscale nature of rare earth crystals was proposed, and future challenges of rare earth crystals were clarified.

In the periodic table, there are 17 elements called as rare earth (RE) elements, when they wholly occupy one lattice site within a specific crystallographic frame a RE crystal is formed [1]. RE crystals include both intrinsic and extrinsic RE crystals. Intrinsic RE crystals also called pure RE crystals: RE crystals that are not doped with anything. Extrinsic RE crystals: RE crystals with other impurities. A well-defined energy level by the chemical environment and accompanied by large spin-orbit coupling, RE cations bring many excellent optical, electric and magnetic functions. RE crystals may be classified into around 30 types as shown in Figure 1. For instance, hydrogen storage crystals utilize its structure for hydrogen energy storage [2]. A new family of superconducting hydrides was developed, which possessed a clathrate-like structure in which the host atom was at the centre of a cage formed by hydrogen atoms [3]. Piezoelectric crystals introduced local structural heterogeneity to manipulate interfacial energies. RE-doped $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ was synthesized, as rare-earth dopants tend to change the local structure of Pb-based perovskite ferroelectrics [4].

As shown in Scheme 1, the nature of multiscale originates from the variation of chemical bonding modes [5], which bridge the gap between chemistry and materials science. During nucleation process, the chemical bonding modes vary rapidly as the number of nucleating atoms increases and finally get relatively stable when the length scale reaches the critical size. The chemical bonding modes match the energy-decrease requirement upon crystallographic lattice. In the

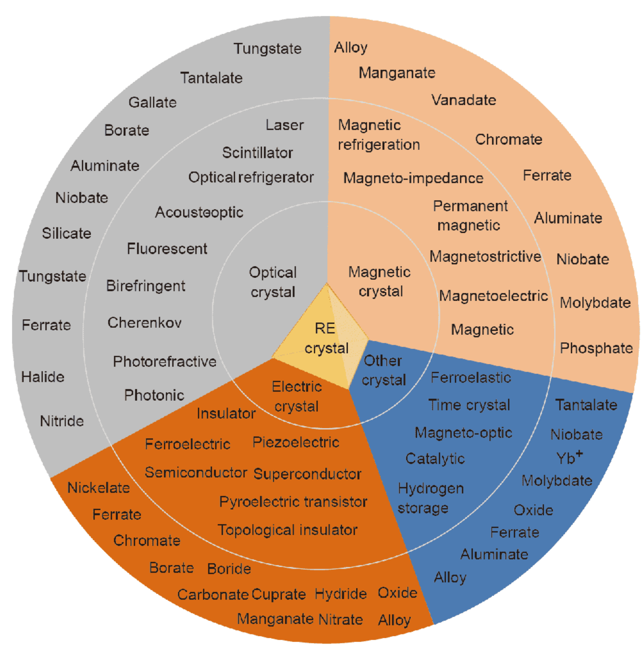

Figure 1 (Color online) Landscape of research and development of RE crystals. Main functions and their possible compositions were summarized.

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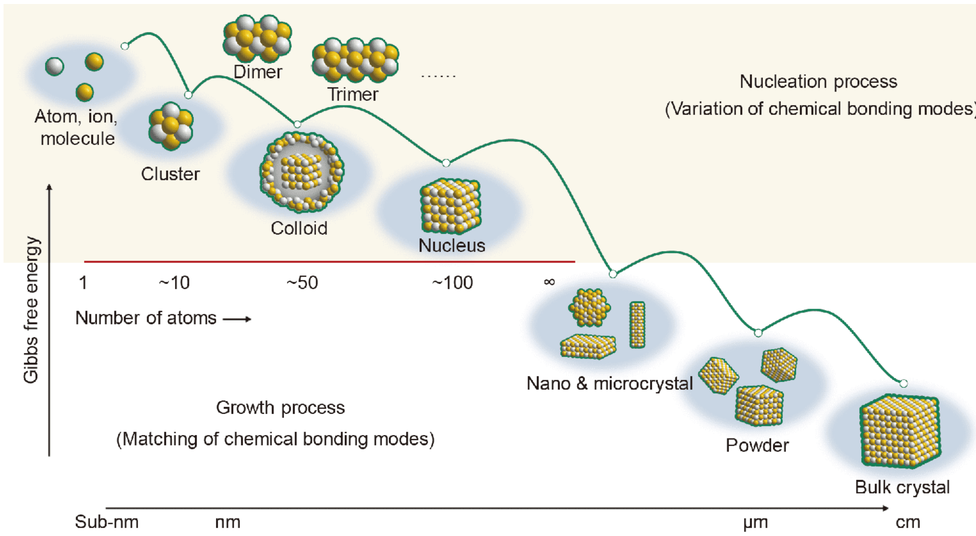

Scheme 1 (Color online) Crystallization engineering of RE crystals. Both nucleation and growth of crystals have clear multiscale features. The cross-scale may include atoms, ions, and molecules, clusters, colloids, nanocrystals, microcrystals, powders and bulk crystal. The scale increases determines the stage of both nucleation and crystal growth, in which the system Gibbs free energy always decreases.

view at chemistry level, rare earth elements have a strong bonding ability in variable hybridization modes, leading to a wide coordination number range of 2–16 [6]. Furthermore, the occupancy of lattices in the crystallographic frame can be quantified by their ionic electronegativity scales [7]. In the view at materials level, crystallization engineering of rare earth crystals bridges their multiscale design and fabrication upon elementary chemistry [8].

Research and development of RE crystals is the design and understanding of crystalline materials, which involves the investigation of both structural and functional features of RE cations within crystal [9]. Many promising findings have been shown, for example, the polarization of RE garnet crystals during elastic wave propagation [10], RE dopants offsetting phase change along growth direction [11], trace RE dopants improving magnetostrictive effect of alloys [12], the strong magnetoelectric coupling in high zonal materials $Ba_3NdRu_2O_9$ [13].

Challenges of RE crystals are as follows.

(1) Cross-scale models are a key to the crystallization engineering of RE crystals.

(2) Composition design of novel RE crystals. The objects of this world have already entered the mineralogical and physicochemical agenda, multidisciplinary thoughts may function well. Phase diagram studies are encouraged.

(3) Deep physicochemical insights into optical, magnetic, electric and catalytic performances dependent crystal structure lead to novel RE crystals with updated demands

(4) 4f chemistry brings physicochemical principles of rare earth crystals, enhancing the accurate prediction of the composition, structure and property of RE crystalline compounds.

(5) Processing control of rare earth crystals. Mass and heat transfers are a key to well control crystallization engineering, which may be optimized by reaction/solubility control or heating unit of facilities.

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