Rare-earth-incorporated low-dimensional chalcogenides: Dry-method syntheses and applications

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Abstract
Chalcogenide thin films incorporating rare-earth (RE) elements with applications in optics, electronics, and magnetics have received considerable attention. Aiming at growing pure chalcogenides, dry-method syntheses have been developed. In this review, we summarize the progress thus far on low-dimensional RE-based chalcogenides (RECs), covering fabrication methods, structures, and applications. This review also provides the summary and perspectives of the challenges of fabrication and opportunities on the application of RECs in the future.

KEYWORDS
chalcogenide, dry-method synthesis, rare earth elements

1 INTRODUCTION

The thin films of transition metal dichalcogenides (TMDs) have been of great interest in the past decade for their special physical and chemical performances, including the quantum spin Hall effect,¹ valley polarization,² and two-dimensional superconductivity,³ with potential applications for novel catalysts and functional devices.⁴,⁵ Hence, a mass of effort has been devoted to the development of TMD thin films, and a series of progress on TMD thin films have been achieved on fabrication, characterization, and application. Among the TMD thin films, the films of chalcogenides containing rare-earth (RE) elements are expected to show unique structures and properties because of the 4f electrons, regardless of the RE functioning as dopants or hosts.

However, although the numerous TMD compounds have been obtained, only a few thin films incorporating REs have been fabricated, generally more via dry methods than via wet chemistry methods. This is because the RE³⁺ ions (as typical hard acids) in solution tend to show high affinity to hard bases (such as oxide and chloride anions) to form stable compounds, rather than to chalcogenide anions.⁶ To facilitate the formation of chalcogenide-containing RE compounds, alkali metals can be introduced as mediators to obtain NaRES,⁷ and
alkali-metal-doped RE$_2$O$_2$S. In brief, the RE-based chalcogenides (RECs) thin film can rarely be synthesized by wet chemistry methods.

Compared with wet chemistry methods, dry-method syntheses (including physical deposition methods and chemical deposition methods) do not suffer from the above-mentioned problems. For the physical methods, the films can directly form on the substrates with the help of electron beam, ion sputtering or pulse laser; for the chemical methods, RE precursors and chalcogenide precursors can react in the gas phase and deposit films on substrates. Therefore, for these materials, dry methods are the most promising and practical approaches. The compositions, structures, and properties of the prepared materials can be optimized by varying the parameters in the preparation process such as temperature, flow velocity, precursors, and so on. Herein we review the reported works on RECs thin films prepared by dry methods, and summarize the fabrication techniques, structures, properties, and applications of the materials, as shown in Scheme 1.

2 | MATERIAL CLASSIFICATION AND SYNTHESIS

2.1 | Structure and classification of the materials

Thus far, the RE-containing chalcogenides of low dimension have been prepared by dry methods. In general, among those obtained materials, the forms of the RE incorporated chalcogenides can be generally classified into three types: host type, doping type, and misfit-layer-compound type. We summarized the synthesis methods of these different types of RE-incorporated chalcogenides in Table 1.

2.2 | Dry-method synthesis

2.2.1 | Host type

Up to now, only a few classes of low-dimensional RECs materials have been achieved by dry methods, almost focused on the compounds of REX and RE$_2$X$_3$ (X = S, Se, Te). The RECs in the form of the host part of the thin films or wires have exhibited fascinating performances in optical and electrical applications by virtue of their unique crystal and electronic structures. As the main part of the materials, the RECs are generally polycrystalline, typically fall in the categories of α-phase of orthorhombic LaF$_3$-type structure (Pnma) and γ-phase of Th$_3$P$_4$-type with plenty of defects, whose band gaps are 1.74 to 1.88 eV and 2.55 to 2.74 eV, respectively. Therefore, to obtain the RECs of low-dimensional scale with refined structure and property, various dry synthesis approaches have been reported, including metal-organic chemical vapor deposition (MOCVD), sputtering, pulse laser deposition (PLD) and molecular beam epitaxy (MBE) methods.

MOCVD has been applied as a new type of epitaxy technique developed on the basis of the vapor phase epitaxy (VPE). Metal organic compounds are used as growth sources to carry out vapor phase epitaxy on a substrate by thermal decomposition reaction. Through MOCVD, heterogeneous materials with multiple compositions, large area, and ultrathin layer can be obtained. La$_2$S$_3$ thin films have been synthesized by using the precursor of [La(bipy)(S$_2$CNET$_2$)$_3$] on different substrates. It was found that the growth of La$_2$S$_3$ films was easiest on Si, but difficult on SiO$_2$. Along with the variation of preparation temperature, the films with thickness up to 2 to 9.5 μm were also polycrystalline, composed of small grains, which shows isotropic properties. LaS thin films have also been fabricated on Si substrates by PLD. According to the results of the scanning electron microscopy (SEM) images, the films showed the cubic NaCl-like structure with a lattice mismatch of 8% between the LaS and Si.

Precursors are reported to be very crucial to the structures and properties of the RECs prepared by MOCVD. Therefore, various new metal-organic complexes have been exploited as the precursors of RECs. Devi et al reported that they prepared the Nd$_2$S$_3$ films using two...
| Thin Films   | Synthesis Method | Lateral Dimensions | Thickness | Application/property Performances | Ref. |
|-------------|------------------|--------------------|-----------|-----------------------------------|------|
| MoS₂:Er     | CVD              |                    |           | Up-conversion Down-conversion     | 9    |
| MoS₂:Er     |                  | 1000 nm            | 25 nm     | Photodetector (735 nm)            | 10   |
| MoS₂:Eu     |                  | 250 nm             | 20 nm     | Photodetector (735 nm)            | 11   |
| MoS₂:Er     |                  | >5 μm              | 0.7 nm    |                                    | 12   |
| MoS₂:Eu     |                  | >25 μm             | <1 nm     | Photoluminescence 640-723 nm (532 nm excitation) | 13   |
| SrS:Ce      | MOCVD            | >1.0 μm            | >30 nm    | Electroluminescent Device         | 14   |
| La₂S₃       |                  |                    | 2.0-9.5 μm|                                    | 15   |
| Nd₂S₃       |                  | >10 μm             | 60 nm     | Photoluminescence 450-500 nm (325 nm excitation) | 16   |
| SmSe        | Sputtering       |                    | 8-50 nm   | Piezoresistive On/off ratio 1.1 × 10³ | 17   |
| SmS         |                  |                    | 10-20 nm  |                                    | 18   |
| Ga-Ge-Sb-Se:Pr |                |                    | 5 μm      | Waveguide 4.7 μm (1.55 μm excitation) | 20   |
| Ga-Ge-Sb-S:Er |                |                    | 4 μm      | Waveguide 2.8 μm (1.54 μm excitation) | 21   |
| LaS         | PLD              | >100 μm            | 1 μm      | Sheet resistance 0.1 Ω cm⁻²        | 23   |
| GaLaS:Er    |                  |                    | 45 nm     | Waveguide 1.54 μm (980 nm excitation) | 25   |
| GaLaS:Pr    |                  |                    | 500 nm    |                                    | 26   |
| WSe₂:Yb/Er  |                  | >100 μm            | 0.8 nm    | Waveguide 1.54 μm (980 nm excitation) | 27   |
| ZnTe:Yb     | MBE              |                    | 1.5 μm    |                                    | 28   |
| EuTe/Pb₁₋ₓEuₓTe |              |                    | 1-2 μm    | Magnetic Phase Diagram Hₑ,FM = 230 mT | 29   |
| EuS:Gd      |                  | >10 μm             | 60 nm     | Ferromagnetic Tᶜ = 86.3 K β = 0.43; γ = 1.20 | 30   |
| EuS         |                  | >10 μm             | 60 nm     | Ferromagnetic Tᶜ = 14.6 K β = 0.39; γ = 1.20 | 31   |
| EuTe        |                  |                    | 1.5 μm    | Antiferromagnetic Tₛ = 9.9 K β = 0.36 | 56   |
| EuTe:Gd     |                  |                    | 500 nm    | Semiconductor 3.85 eV | 57   |
| [Yb₁₋ₓS₂]ₓNbS₂ | CVT             |                    |           | Thermoelectric S²/lρ =250 μW K⁻² m⁻¹ ZT = 0.1 (@300 K) | 59   |
| [Yb₁₋ₓS₂]ₓ₁NbS₂ |                |                    |           | Thermoelectric S²/lρ =200 μW K⁻² m⁻¹ ZT = 0.11 (@300 K) | 46   |
| (LaS)₁₋ₓCrS₂ |                  |                    |           | Thermoelectric S²/lρ =170 μW K⁻² m⁻¹ ZT = 0.14 (@950 K) | 39   |
| (LaS)₁₋ₓNbS₂ |                  |                    |           | Thermoelectric S²/lρ =410 μW K⁻² m⁻¹ ZT = 0.15 (@950 K) | 38   |
| (La₀.₉₅S₀.₉₅)₁₋ₓNbS₂ |            |                    |           | Thermoelectric S²/lρ =460 μW K⁻² m⁻¹ ZT = 0.2 (@950 K) | 38   |
new Nd precursors, namely, Nd(dpdmg)$_3$ and Nd(dpamd)$_3$. It was noted that the thickness and growth rate of the films were greatly affected by the precursors. As shown in Figure 1, Nd(dpdmg)$_3$ can lead to the smallest thickness of 60 nm with the lowest growth rate, which was the most uniform among the prepared films. Furthermore, the precursors of RECs are reported to be important and many other studies have been concentrated on the exploration of new precursors. Cyclopentadienes, diketones, amidines, and mixed compounds have been developed and applied. Apart from MOCVD, traditional CVD methods can also be applied to achieve the main structure of RECs. Crystalline $\alpha$-Sm$_2$S$_3$ nanowires have been synthesized by the CVD method. Besides, the structures of the crystal and energy band were thoroughly investigated by various characterizations and density functional theory. As shown in Figure 1-1, the nanowire structure was about 60 nm in diameter and the growth direction of crystal nanowire was [001], which can match the result of selected area electron diffraction (SAED). Furthermore, the band gap of the $\alpha$-Sm$_2$S$_3$ was found to be ~1.7 eV, which can be reduced to ~1.3 eV by modulating the vacancy sites according to the theoretical calculation.

Sputtering is the process in which particles are bombarded onto a solid surface to allow atoms or molecules near the surface to escape from the solid surface. RECs have been synthesized as the host of thin films by the sputtering method. As shown in Figure 1-K, SmSe thin films have been fabricated by the cosputtering process of Sm and Se at different temperatures. The effects of growth conditions on the crystallinity of SmSe is striking, such as the narrower peaks of growth at 300°C compared to deposition at room temperature. As shown in the transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images, the obtained SmSe films showed the bubble-like grains on the surface of both samples with a thickness of 50 nm and 8 nm. Due to the use of independent Sm and Se sources, the SmSe layers exhibited spatially varying stoichiometry. Besides, SmS thin films have been developed by a dual-target magnetron sputtering at room temperature.

**FIGURE 1** The RE-incorporated low-dimensional chalcogenides as host type. A, B, SEM images of the Nd$_2$S$_3$ films deposited on Si (100) with different precursors of Nd(dpdmg)$_3$ and Nd(dpamd)$_3$ (above list, the top-view; bottom list, the side-view). Copyright 2019, The Royal Society of Chemistry. C-G, TEM images of the $\alpha$-Sm$_2$S$_3$ nanowire bundle: C, TEM image of a separated $\alpha$-Sm$_2$S$_3$ wire; D, SAED of the $\alpha$-Sm$_2$S$_3$ wire at the selected area shown in C; E, High-resolution TEM (HRTEM) image of the wire; F, crystal structure from the [001] view direction built by extended CrystalMaker; G, the simulated SAED spectra based on the crystal orientation indicated in F. Copyright 2013, Elsevier B.V. H-K, Structural characterization of the SmSe thin films: H-I, AFM images of 50 and 8 nm thick films; J-K, TEM images of 50- and 8-nm SmSe films. Copyright 2013, American Chemical Society. L-M, Lorentz microscopy images of EuS and Gd-doped EuS, respectively. Copyright 2014, The Japan Society of Applied Physics.
MBE is another new technology for the preparation of thin films. With this technique, it is possible to prepare a single-crystal thin film as thin as several tens of atomic layers, and an ultrathin layer microstructure formed by alternately growing different compositions and differently doped thin films. EuS and Gd (2%)-doped EuS thin films have been fabricated on Si/SiO₂ substrates by MBE with e-beam evaporation, showing in Figure 1.M. The thickness of the obtained EuS films is ~60 nm. Furthermore, the Al₂O₃ layer was deposited in situ to prevent surface oxidation. The thin film of EuTe is reported to have been fabricated on BaF₂ by MBE, which has a NaCl-type crystal structure with a thickness of 1.5 μm. The magnetic properties were further studied, and it was found that the Neel temperature (T₉) is 9.6 K with an antiferromagnetic structure if below T₉.19 Besides, Gd-doped EuTe thin films were also fabricated and investigated on the electronic and magnetic properties.20-23 With Gd doping, the EuTe can be transformed into ferromagnetic n-type semiconductor or semi-metal, according to the results of high-energy XPS and superconducting quantum interference.

2.2.2 Doping type

Owing to the proper band structure and unique luminescence properties, the RECs have been applied as dopants in the chalcogenide glasses. The chalcogenide glasses exhibit excellent optical properties, including a high IR transparency and refractive index, as well as a wide transmission window from visible wavelengths up to 10 μm. Thus, the chalcogenide glasses are extensively used in optoelectronic applications with RECs doping, which have been reported to improve the optical properties of these glasses for their optoelectronic applications as glass fiber lasers and waveguide amplifiers.24 Additionally, RE elements were recently suggested as dopants for the emerging class of TMD materials to fabricate p-type semiconducting MoS₂. Thus far, the common methods to inject REs into the host materials are CVD, MOCVD, PLD, and sputtering. After RE doping, the crystal textures and physical properties can be adjusted to improve the performance in many applications.

CVD is also the approach to synthesizing layered materials, including metal, alloy, refractory materials, semiconductors, and so on. Furthermore, the properties of the layered materials can be optimized via adjusting the parameters of CVD process such as temperature, pressure, flow velocity, and so on. Various TMDs with different structures and sizes have been developed by the special method. Hao et al first reported that the nanoscale RE-doped TMDs with 2D layered structure.25 The predeposited Er-doped Mo thin film was sulfurized to MoS₂:Er by the element sulfur in the CVD furnace (Figure 2-G). According to the results of energy dispersive X-ray spectroscopy, the ratio of Er/Mo atom was about 3%. And the XPS and TEM results clearly proved that Er atoms were not adsorbed or decorated on the surface but rather incorporated in the MoS₂ lattice through the substitution of cation, which greatly modified the luminescence property of MoS₂ layers. To obtain better crystal structures, optimized CVD growth methods have been applied. A quasi-closed process in a three-zone CVD furnace can produce the large-scale Er-doped MoS₂ with atomic thickness on the sapphire (0001) substrate. On the basis of the results of systematic characterizations, the thickness of the doped MoS₂ films was only ~0.7 nm and the diameter was micrometer scale, indicating the large monolayer structure of the doped films. Furthermore, the Er-doped MoS₂ films not only exhibited the uniform and high crystalline quality but also showed the clean surface of the samples, which were superior for the device application. For the mechanism of Er doping and film growth, during the process, the Er³⁺ vapor can help the reaction vapors of Mo⁴⁺ and sulfur transfer and nucleate on the substrate. Additionally, the Er atom with a smaller electronegativity (1.24 eV) is easier to incorporate with S than Mo atom (2.16 eV). Hence, Er atoms can be doped in the MoS₂ lattice during the formation MoS₂ by the stepwise reaction of MoO₃ and sulfur.

Fu et al have synthesized the Er³⁺-doped monolayer 2D MoS₂ single crystals with high anisotropy by the matrix-assisted sustained release CVD (MASR-CVD).26 Apart from the precursor of Eu₂O₃, MoO₃, and sulfur powders, the NaCl and SiO₂ were employed by melting-assisted media in MASR-CVD (Figure 2-2). By the special preparation method, the crucial sustained release of the Eu precursor can be achieved with help of NaCl and SiO₂. Although the covalent radius of Eu (198 pm) is much larger than that of Mo (139 pm), the Eu³⁺-doped high-quality 2D MoS₂ single crystals can be obtained because of the slow and steady supply of Eu. The fact that 0.3% Eu was introduced into the lattice of the MoS₂ single crystals was clearly confirmed with evidence from the results of HRTEM, XPS, and Raman.

For polycrystalline materials, Ma et al reported that the Er-doped²⁷ and Eu-doped⁹ MoS₂ films were deposited on p-Si substrates by CVD method. The morphology and structure of RE-doped films have been studied and compared to those of pure MoS₂ films synthesized under the same conditions. It was found that, after doping the RE of Er and Eu, the thickness of the films obviously increased from 20 nm to about 50 nm, owing to the promoted nucleation and growth rate of deposited films. XRD patterns showed the enhanced diffraction
intensity of RE-doped samples, indicating the improved crystallinity of MoS$_2$ films. Furthermore, the growth process of the films was deduced from the results of experiments. For the doped films, the Eu$^{3+}$ ions are chemically active, so they can be easily adsorbed on the surface of substrate and then adsorb MoS$_2$ molecules by van der Waals force, resulting in the more rapid nucleation process on the substrate surface. As for undoped MoS$_2$ films, the electrically neutral MoS$_2$ molecules adsorbed and nucleated by a slow natural process. By analyzing the growth process of different films, they proposed that the growth mode of doped MoS$_2$ initially conformed to the 3D island growth and then followed the 2D film growth, in line with the larger thickness of the obtained films. Many efforts have been also devoted to the development of the larger-scale and thinner 2D TMDs with RE dopants.\cite{9,24-28}

High-brightness Ce-doped SrS films have been prepared by the MOCVD method.\cite{28} The crystal structure of films prepared by MOCVD is polycrystalline, and the anisotropy of films is rather poor. Similar to the case in CVD, the structures and properties of the prepared materials can be optimized by varying the preparation conditions of the preparation process. The Sr(tmhd)$_2$-trimer, Ce(tmhd)$_4$, and hydrogen sulfide (H$_2$S) were used as precursors and reactants. The preparation conditions of synthesis were studied to optimize the structure, morphology, and property of the Ce-doped SrS. The best result was achieved for the doped SrS films with predominantly (200) orientation, 1.0 $\mu$m grain size, and 0.14 at. % Ce dopant concentration. It was found that the H$_2$S reactant flows greatly influenced the size and structure of SrS:Ce films: low flows led to the (200) exposed texture and large grain size grown, whereas higher flows led to (111) exposed films with smaller grain size.

As for the physical method, MBE and PLD are both applied to obtain the RE-doped TMDs. Yb-doped ZnTe layers have been fabricated using MBE on GaAs substrates.\cite{29} The 1-$\mu$m ZnTe buffer layer was deposited before the introduction of 1.5 $\mu$m Yb-doped ZnTe layers.
Via the PLD method, Hao et al reported the promising approach to fabricating wafer-scale Yb/Er codoped WSe$_2$ layered nanosheets. The size of the uniformly high-quality 2D WSe$_2$:Yb/Er thin films can be up to 1 cm$^2$. Furthermore, Pb$_{1-x}$Eu$_x$Te$^{31,32}$ and Pb$_{1-x}$Sn$_x$Te$^{31}$ have been prepared on the (111) BaF$_2$ and (111) Si substrates by MBE.

The chalcogenide glass of thin films has received considerable attention for the optical and optoelectronic applications as waveguides for photonic integrated circuits. Besides dopants, amorphous RECs thin films have been also investigated.$^{33-35}$ The Pr$^{3+}$-doped Ga-Ge-Sb-Se, Er$^{3+}$-doped Ga-Ge-Sb-S (Figure 3-C) and Tm$^{3+}$-doped Ga-Ge-Sb-S thin films have been successfully prepared by the sputtering method. The thickness of the above layered materials was in the micrometer scale, which was applied for the optical devices. Gurlui et al reported that the GaLaS,$^{36}$ Er-doped GaLaS,$^{37}$ and Er/Pr codoped GaLaS$^{38}$ glass thin films with the thickness in the micrometer scale have been prepared by the PLD approach (Figure 3-F). These glass films were all amorphous chalcogenides, and the increased temperature of substrate enhanced the crystallinity of the films. Moreover, Dy can be introduced the Ga–Ge–Sb–S films by PLD.$^{39}$ (Figure 3-E).

**FIGURE 3** The RE-doped chalcogenides thin films synthesized by PLD, sputtering and MBE. A-C, Characterization of the Ga-Ge-Sb-S multilayer films: A, SEM image of Ga-Ge-Sb-S films; B, NanoSIMS analysis of Ga-Ge-Sb-S films; C, the scheme view.$^{34}$ Copyright 2016, Elsevier B.V. D-F: D and E, SEM images of SiO$_2$ and Ge$_{28.1}$Sb$_{6.3}$Se$_{65.6}$; F, energy level diagram of Pr$^{3+}$ ions.$^{33}$ Copyright 2017, Elsevier B.V. G-I: SEM images of Tm-doped Ga$_{5}$Ge$_{20}$Sb$_{10}$Se$_{65}$ sputtered thin films: G, oblique view, H, top view, I, side view.$^{35}$ Copyright 2010, Elsevier B.V.
2.2.3 | The misfit-layer-compound type

Apart from being main composition and dopants, the misfit layer compounds are one significant variety of the RECs of low dimension, which have drawn considerable interest and been applied in the research of thermoelectricity. The misfit layer compounds containing RE can be denoted by a general formula \([(REX)_{1+n}]_m[TX_2]_y\) (T = Ti, V, Cr, Nb, and Ta; X = S and Se; \(m = 0.08-0.28; x = 1, 1.5, \text{ and } 2; y = 1, 2, 3, \text{ and } 4\)). The family of these compounds with an incommensurate layer structure is large. They can be synthesized by the chemical vapor transport (CVT) method. By this simple and powerful method, the high-quality single crystal with rare defects can be obtained. The well-synthesized compounds are composed of two sublattices of host TX2 layers and guest MX layers alternately along the c-axis. The guest REX layer is formed by unit-cell-thick RECs with the distorted NaCl structure, and the host TX2 layer is identical to the single layer of TMDs. Therefore, although these compounds can exhibit long-range ordering in the plane, they lack three-dimensional periodicity. Besides, the charge transfers between the layers of MS and TS2 can stabilize the entire layered structure. However, RE-S based misfit layer compounds are mechanically much harder than the other REX, owing to the stronger interlayer bonding of the RE-X. Many efforts have been devoted to the research of crystal and electronic structure.42-52

The groups of Ohno et al and Cario et al have both reported that they synthesized the EuS-NbS2-based compounds by the CVT method. The valence state of Eu and valence transfer from Eu to S were investigated by XPS, and results indicated the coexistence of the Eu2+ and Eu3+. In addition, a surface rearrangement was brought from the valence transfer of the Eu-S. Miyazaki et al reported that the ionic radius of the RE elements can produce a striking variation of the lattices in the c-axis.40 According to previous work, TiS2, NbS2, and TaS2 layered structures can exhibit the metallic conductivity, whereas VS2 and CrS2 compounds present semiconducting properties. In addition, the Yb-Nb-S-based misfit-layered compound has been synthesized, and their thermoelectric properties were measured below 300 K.22

In recent years, the unique thermoelectric properties of these misfit layer compounds have drawn great interest.44,49,53 The physical properties of misfit compounds are significantly dependent on variations of microstructure due to their anisotropic valence bonds. Thereby, a variety of the RE-based misfit layer compounds have been developed to study the structures and properties. Herein, Johnson et al have reported that the well-ordered \([(\text{CeSe})_{1.14}\text{In}[\text{NbSe2}_2]\text{In} \text{ compounds was synthesized by the}}\) PVD methods. Grippa et al have attempted to introduce Sr element into the Sm- and Tb-layered compounds to improve the thermoelectric property.51 Actually, the misfit layer structures are the natural superlattice structures, which can present prominent properties in many respects.53 Hence, the n-type (LaS)1.20CrS2 and p-type (LaS)1.14NbS2 with randomly and highly oriented lattices have been achieved to investigate the high-temperature thermoelectric properties (Figure 4-4).

Furthermore, many progresses on the RE-layered compounds with novel nanostructure have been exploited. Remarkably, Tenne and Arenal et al have reported the refined preparation and structural studies of single-crystalline nanotubes of TbS-CrS2 and LnS(Se)-TaS (Se)2 (Ln = La, Ce, Nd and Ho). By high-quality TEM techniques, the regular nanotube and wavy nanotube with different crimping types was found to achieve the TbS and CrS2 with alternating arrangements of sublattices (Figure 4-4). For LnS(Se)-TaS(Se)2 nanotubes, these nanostructures of quaternary misfit layered compounds are identified to have a double superstructure of S/Se and La/T. Additionally, amorphous layers can be clearly observed on the nanotubes surface, attributed to the Se deficiency for La-based NTs and oxidation of the Ho-based NTs (Figure 4-4). Another nanotube of LaS-TaS2 was reported to be easily synthesized, and the mechanism of preparation was thoroughly investigated to understand the relationship between the concentration of Nb precursor and the completeness of nanotubes. Moreover, thin flakes of (LaS)1.20CrS2 have been synthesized and fabricated into a field-effect transistor with prominent performances. All of these aforementioned studies can help us to understand the structures and properties of these well-constructed misfit layer compounds thereof. However, the high temperature and long reaction time of the CVT methods limit the progress of RE-based misfit layer compounds in the future. The promising methods such as modified CVD and MBE have emerged to improve the synthesis process for further development of these compounds.

3 | APPLICATIONS

3.1 | Optical applications

REC, regardless the RE component acting as dopants or hosts, have been extensively studied as a potential material system for optical applications due to their abundant 4f electronic energy levels, variable ionic valences, and the proper band gap, which bring the RE superior optical properties.
3.1.1 | Luminescence

Hao et al have reported Er-doped MoS$_2$, and Yb/Er codoped WSe$_2$ layered semiconductor materials with the optimized photoluminescence (PL) properties. Typically, after introducing Er$^{3+}$ to the layer of MoS$_2$, the PL emissions of upconversion (UC) and downconversion (DC) in the near-infrared (NIR) region (1.5 $\mu$m) were first observed, pumped by the single-wavelength NIR excitation source (980 nm), attributed to the energy transfer of $^4$I$_{9/2} \rightarrow ^4$I$_{15/2}$ and $^4$I$_{13/2} \rightarrow ^4$I$_{15/2}$, respectively (Figure 5-5). Moreover, the results also indicated that the Er dopants can affect the density of states of MoS$_2$, from which the NIR luminescence of 1550 nm arose. As for the Yb/Er codoped WSe$_2$ nanosheets with great uniformity and high crystallinity, the PL emissions of the WSe$_2$ thin films pumped by a single laser at 980 nm is reported to be extended to approximately 1540 nm, even when the film was fabricated to an atomic layer structure. The observed emissions of monolayer WSe$_2$: Yb/Er was attributed to both the codoping Yb$^{3+}$ sensitizer and the prominent optical properties of the WSe$_2$ host with a suitable optical bandgap.

It is well known that the 4-5d transition for PL of RE ions is very sensitive to the local crystal field, but the effect of crystal field of monolayer MoS$_2$ on the RE ions had never been investigated until Fu et al reported the crystal-field tuning of PL in monolayer MoS$_2$ with Eu$^{3+}$ doping. The striking red-shift of the PL peaks for the Eu$^{3+}$ arose, compared with the bulk or nanoparticle materials containing Eu$^{3+}$, indicated that the crystal field surrounding Eu ions in the 2D single layer of MoS$_2$ with a higher anisotropy can efficiently distort the degenerate orbitals (Figure 5-5). High-quality ZnTe layers with Yb doping were prepared and the Yb dopant showed optically active if it was associated with other impurities.
The oxygen probably took part in the energy transfer process. It seemed that other impurities like C or S reacted with Yb ions not only to provide the trivalent charge state for Yb ion but also to retain the latter one in this charge state (Figure 5-I).

3.1.2 Optical telecommunication

Amorphous glass of chalcogenide thin films has been widely applied as optical storage media or waveguides. The most commonly used RE dopants for the application are Er and Pr.33,34,37,55-57 Pr³⁺-doped selenide thin films were fabricated by sputtering, and the device of ridge waveguides were fabricated by photolithography and dry etching method.33 With a pumping laser of 1.55 μm, mid-infrared luminescence can be obtained with wavelengths above 4 μm. Under a laser with pumping wavelength of 980 nm, the PL spectra of thin films of Er³⁺-doped Ga-La-S (GLS) glass at different temperatures also exhibited strong emission peaks at 1.53 μm.37 Several PL peaks of Er³⁺ ions within the range of the visible to the mid-infrared spectral region were clearly shown, and Er³⁺-doped chalcogenide waveguide was demonstrated to be excited at 2.76 μm. For the optical storage, the amplifier based on the Pr³⁺-doped chalcogenide microdisk was fabricated.55 In the laser test, the slope efficiency was achieved with a maximum of $S = 8.1 \times 10^{-4}$ with an input pumping power of 2 mW. The results were almost six times higher than that of the Er-doped microdisk.
3.2 | Electronic and optoelectronic applications

Electronic and optoelectronic devices, including photodetectors, solar cells, logic devices, and transistors, are considered the electric devices that can interact, generate, and control light with electricity. The performance of the above-mentioned devices is highly dependent on not only the electronic structure and microstructure, but also the physical property of the functional materials. The RECs have suitable electronic and optoelectronic properties with the bandgap and crystal structure.

3.2.1 | Electronic devices

The obtained misfit layer compound of (LaS)$_{1.20}$CrS$_2$ was fabricated as the field-effect transistor (FET). The optical image of the fabricated back-gate FET device is shown in Figure 6. For investigating the performance of the FET device, drain-to-source current $I_{ds}$ was measured as a function of drain-to-source voltage ($V_{ds}$) and gate voltage ($V_g$). Figure 6 showed that the on/off ratio of the device was 12 at room temperature and ~250 at 120 K. Besides, the mobility of the FET was 0.3 cm$^2$ V$^{-1}$ second$^{-1}$ according to the calculation of the value from Figure 6, which exhibited better performance than reported MoS$_2$ thin flakes. As shown in Figure 6, the SmSe was demonstrated that RE in the form of thin films could modulate a current over 1000 times because of the transition from insulator to metal induced by pressure. Moreover, films with a thickness of 8 nm exhibited a piezoresistive response. The prominent performance and scalability make them promising candidates for nanoscale applications. Thin LaS films were grown on Si substrates with a sheet resistance below 1 $\Omega \cdot$ cm$^{-1}$ that should have potential applications in vacuum microelectronics. The obtained SrS:Ce thin films with predominantly (200) orientation, grain size of 1.0 $\mu$m, and 0.14 atom % Ce dopant concentration exhibited an electroluminescent emission for the device stack of 51 cd m$^{-2}$ measured at 40 V above the threshold voltage. This performance was ascribed to the large grain size of the film, in line with earlier models that a larger grain size was necessary for accelerating the electrons to a sufficient energy before their scattering at the grain boundaries.

**FIGURE 6** The performance of electronic and optoelectronic applications of (LaS)$_{1.20}$CrS$_2$ compounds, SmSe thin films and MoS$_2$:Er thin films. A-C: Field-Effect transistors tests of (LaS)$_{1.20}$CrS$_2$ on SiO$_2$: A, the optical image of field-effect transistors made of (LaS)$_{1.20}$CrS$_2$ compounds; B and C, $I_{ds}$-$V_g$ curves in logarithmic scale and linear scale measured at 290 and 120 K for $V_{ds} = 1$ V. Copyright 2017, WILEY-VCH. D, Pressure-dependent resistance voltage of piezotronic transistor built up by SmSe films. Copyright 2013, American Chemical Society. E, F, The surface I-$V$ curves and photocurrent I-$V$ curves of the doped and undoped MoS$_2$ films and MoS$_2$/Si heterojunction. Copyright 2017, Elsevier B.V
3.2.2 | Optoelectronic devices

Recently, the TMDs and other 2D materials have been applied in the optoelectronic application as photodetectors. However, the efficiency of light absorption of TMDs is still not sufficient for achieving performance. Thus, the RE dopants with excellent properties are usually introduced to improve the performance. Ma et al. reported the Er\(^{3+}\) and Eu\(^{3+}\) doping in the MoS\(_2\) thin films to study the photovoltaic property (Figure 6).\(^9,27\) It was found that with RE doping the carrier mobility and current-voltage features of MoS\(_2\) films can be greatly promoted. Besides, the optical absorption and PL emission of the RE-doped MoS\(_2\) was highly enhanced, resulted in a significant increase of the values of the short circuit current and open-circuit voltage. The application has been studied that the Er\(^{3+}\)-doped Ge\(_{25}\)Ga\(_5\)Sb\(_5\)S\(_{65}\) chalcogenide glass as an upconversion material with improved efficiency of silicon solar cells.\(^{58}\) The chalcogenide glass exhibits good thermal, chemical, and physical properties, owing to the proper energy offset between bands. As shown in Figure 6, the energy of bandgap is \(\sim 2.23\) eV, which can excite green and red luminescence, respectively, from \(^4S_{3/2} \rightarrow ^4I_{15/2}\) and \(^2F_{9/2} \rightarrow ^4I_{15/2}\) \(4f-4f\) transitions of Er\(^{3+}\) ions under 800 nm pumping with Ti-sapphire tunable laser.

3.3 | Magnetic applications

RE elements (Gd, Sm, Tb, Ho, etc.) have unique electronic orbital and spin properties, which further brings the RECs materials some excellent magnetic properties. Those magnetic materials are of great significance in the research of magnetic devices and spintronic devices. The critical behavior near the ferromagnetic phase transition of Eu- and Gd-doped films has been studied by using magnetization measurement and a low-temperature Lorentz microscopy.\(^{15}\) As shown in Figure 7, the doping of 2% Gd brings the significant enhancement of ferromagnetic s-f interaction. In addition, the Curie temperature and magnetic phase transition critical index of Gd-doped EuS are 86.3 \(\pm\) 0.2 K, \(\beta = 0.43 \pm 0.01\) and \(\gamma = 1.20 \pm 0.05\), respectively; for pristine EuS, the Curie temperature and critical index are 14.6 \(\pm\) 0.1 K, \(\beta = 0.39 \pm 0.01\) and \(\gamma = 1.20 \pm 0.05\), respectively. These materials have different domain structures near Curie temperature, and thus the long-range ferromagnetic ordering based on the average field model leads to the formation of large domains. In addition to the doping materials, the magnetic materials with hetero-structure or super-lattice were studied.\(^{59-61}\) Superlattice structure of strained metamagnetic EuSe intercalated with nonmagnetic PbSe\(_{1-x}\)Te\(_x\) have been prepared and studied.\(^{59}\) Through

![Figure 7](image-url)
detailed structural and magnetic characterization, the phase transition temperatures and the magnetic phase diagrams of strained EuSe were determined. Thereby, it was demonstrated that introducing biaxial strain on EuSe in superlattice structures can significantly change the magnetic properties of the materials. Then, the configuration of spin in strained metamagnetic EuSe was investigated. The nearly perfect 2D EuSe/PbSe\(_{1-x}\)Te\(_x\) multilayers with 100 periods was achieved. It was demonstrated that the strain of nonmagnetic PbSe\(_{1-x}\)Te\(_x\) interlayer on thin EuSe layer can change the magnetism properties of EuSe. Furthermore, in the complex H-T phase diagram of strained EuSe, the different magnetic phases can be related to specific spin configurations (Figure 7-7).

### 3.4 Thermoelectric application

With the increasing interest in space exploration, advances in medical physics, and the growing difficulty in resource exploration and exploration on Earth, there is a need to develop a power system that can supply itself without care, and thermoelectric power generation is very suitable for these applications. Recently, the RE-incorporated misfit layer compounds have received considerable attention in the thermoelectric community for their PGEC behavior, because of the potential increase of conductivity and reduction of thermal conductivity.

Whall and Parker first reported that the 2D multilayer superlattice can improve ZT value, owing to the quantum well effect of the materials. Obviously, the synthesized misfit layer compounds present the natural superlattice structure. Ohta et al studied the influence of microstructural control on the thermoelectric properties of the LaS-CrS\(_2\) and LaS-NbS\(_2\) compounds. They found that the randomly and highly oriented natural superlattice showed ultralow lattice thermal conductivities. More importantly, the highly oriented structure exhibited the highest thermoelectric figure of merit ZT of 0.14 at 950 K for LaS-CrS\(_2\) system. For LaS-NbS\(_2\) system, the randomly oriented structure showed the highest ZT of 0.15 at 950 K. The LaS-CrS\(_2\) and LaS-NbS\(_2\) misfit layer compounds displayed the electron crystal-phonon glass behavior of excellent thermoelectric materials (Figure 8).
The kinds of RE have different effects on the thermoelectric property. The thermoelectric properties of [RES]$_1$ + $m$TS$_2$ (RE = La, Yb; T = Cr, Nb) have been studied. The NbS$_2$ systems exhibited p-type S (seebeck coefficient), whereas CrS$_2$ systems exhibited n-type S. In all series of REX compounds, [Yb$_2$S$_2$]$_{0.62}$NbS$_2$ shows the highest ZT of 0.10 at 300 K, because $S^2/\rho$ is the highest. The S of the Yb-containing sample was about 60% higher than those of samples containing other RE elements at 300 K, owing to a lower n value ($\sim 5 \times 10^{20}$ cm$^{-3}$).

There are generally two ways to increase the ZT values of a thermoelectric material, by increasing its conductivity ($\sigma$) or decreasing its thermal conductivity ($\kappa$). Herein, the resistivity anisotropy of (SmS)$_{1.25}$ TiS$_2$ has been investigated, as shown in Figure 7-7. The in-plane resistivity displayed an anomaly at 202 K, and the interlayer resistivity also exhibited anomalies at 202 and 222 K as well as an upward curvature between 100 and 222 K. Therefore, the resistivity anisotropy indicated peculiarities, with a leap at 222 K, which was attributed to a probable magnetic ordering or anisotropic lattices distortions. Phuoc et al have also studied the relation between structural distortions and thermoelectric properties of the (LaS)$_{1.196}$ VS$_2$ compounds. No noticeable abnormality was found in the temperature-related transport measurement. However, a large spectral weight transfer of about 1 eV was detected. The result indicated that structural distortion had an important influence in the resistivity of (LaS)$_{1.196}$ VS$_2$.

4 | SUMMARY AND PERSPECTIVES

The REC materials prepared by the dry methods, including chemical and physical methods, have demonstrated promising applications in optics, electronics, and magnetics. In past decades, various RECs with different structures, including crystalline, amorphous, host and doping, have been studied to some extent. In this review, we summarize the existing progress on REC materials with contents covering synthesis methods, structures, and applications.

Up to now, a range of challenges still exists for the low-dimensional REC materials, demanding prompt solutions. According to the above-mentioned studies in this review, the RECs with multiple components and micrometer-scale sizes have been achieved in the form of host, doping, and misfit layer. However, there are only a few parts of RECs that have been synthesized by the dry methods. A large amount of other promising materials with new compositions and structures have not been obtained. In other words, we still need to develop the REC materials by dry method. For example, the single-crystal RECs of few layers with high anisotropy and unique properties have not been successfully prepared, which still needs more effort to exploit. Furthermore, it is necessary to exploit the applications of RECs, besides the aforementioned photoluminescence, optoelectronics, magnetics, and thermoelectricity. There are a variety of emerging fields with considerable attention, including topological crystalline insulators, photoelectric catalysis as well as energy conversion and storage, completely absent in the work on RECs, which is the great opportunity for us. In spite of all challenges, striking opportunities can be also found in the research area. Along with the popularization of the dry methods, the studies of the specific materials and the technologies will be systematic and thorough. Furthermore, the low-dimensional RECs with unique structures and properties can be investigated and understood, which will promote the development of these materials.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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