Review of Research on the Rare-Earth Doped Piezoelectric Materials

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The piezoelectric materials, such as ceramics, crystals, and films, have wide applications in the mechanical industry, medical imaging, electronic information, and ultrasonic devices, etc. Generally, adding oxide dopants, or introducing new solid solutions to form the morphotrophic phase boundary of the piezoelectric materials were common strategies to enhance the electric properties. In recent decades, rare-earth elements doped piezoelectric materials have attracted much attention due to their multifunctional performances combining piezoelectric and photoluminescence properties, which has potential applications in ultrasonics, electronics, automatic control, machinery and optoelectronic fields. An overview of the recent investigations and perspectives on rare-earth doped piezoelectric ceramics, single crystals, and films were presented.

Keywords: piezoelectric materials, rare-earth doping, electric properties, photoluminescence properties, multifunctional materials

INTRODUCTION

Rare-earth (RE) elements contain rich structures and energy levels and exhibit excellent optical, electrical, magnetic, and nuclear properties, which were exploited in functional materials to enhance their properties and broaden applications (Singh et al., 2015; Steudel et al., 2015).

As one of the important functional materials, piezoelectric materials play a significant role in the fields of medicine, acoustics, machinery, and electronics due to the ability of mutual conversion between mechanical energy and electric energy. The electric performances of piezoelectric materials are affected by compositions, microstructure, and lattice defects like oxygen vacancies. Thus, extensive investigations have been carried out to enhance the properties of the piezoelectric materials by introducing new solid solutions or adding oxide dopants. The rare-earth ion doping may substitute the original ions and cause the formation of vacancies so that the distortion of the crystal lattices may affect the electric properties due to their unique ionic radius and different chemical valence (Qiu and Hng, 2002; Hagemann and Hennings, 2010; Singh et al., 2011). There are 17 members in the family of rare-earth elements, including 15 lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), Sc, and Y. Figure 1 shows the rare-earth elements doped piezoelectric materials and relative properties based on the reported works. Some piezoelectric materials with certain rare-earth doping can exhibit obvious photoluminescence properties because of the ladder-shaped 4f energy level and relatively long metastable state of some rare-earth ions (Tsonev, 2008; Sun et al., 2011; Pieter, 2013; Pieter, 2017). Figure 2A shows the main energy flow paths during the sensitization of lanthanide (Ln) luminescence. The energy levels of Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$, Eu$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, Ho$^{3+}$, Er$^{3+}$, Tm$^{3+}$, and Yb$^{3+}$ ions are also given schematically in Figure 2B. The electrons in the singlet ($S_0$) ground state absorb energy and then jump to the singlet ($S_1$) excited state. Besides, the excitation energy of ($S_1$) state is transferred to the triplet state ($T_1$) based on intersystem crossing firstly and to the 4f states
subsequently. Finally, the corresponding emission of lanthanide ions can be acquired (Sun et al., 2006; Dang et al., 2008).

Although the rare-earth ion doped piezoelectric materials have attracted much attention owing to their outstanding electric and luminescence performance, there are few reviews reported in this research field. Most reviews are focused on a certain type of piezoelectric material or a fabricating method. Zheng et al. (2018) addressed the lead-free perovskite piezoelectric bulk materials. The relationships among the phase boundaries, domain configurations, and electrical properties in lead-free materials were discussed. Liu (2015) reviewed the progress on lead-free textured piezoelectric ceramics with an enhancement of the piezoelectric property. Chen et al. (2020a) paid attention to textured piezoelectric ceramics with an enhancement of the lead-based ceramics were summarized.

RARE-EARTH DOPED PIEZOELECTRIC CERAMICS

Rare-Earth Doped Lead-Based Piezoelectric Ceramics

Piezoelectric ceramics are a kind of piezoelectric materials with a wide range of applications due to the characteristics of good electric properties, fine optical properties, low production cost, and simple preparation. In the past few decades, lead-based piezoelectric ceramics have dominated the market due to their good properties. In the following section, the rare-earth doped lead-based ceramics were summarized.
et al., 2004; Camargo et al., 2005). These studies indicated that the transparent PLZT ceramics with rare-earth doping were suitable for photonic devices, optic sensors, and multifunctional optic devices, etc.

Furthermore, the Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-Pb(Zr$_{0.51}$Ti$_{0.49}$)O$_3$ (PZN-PZT) system has recently attracted much attention owing to their better piezoelectric properties ($d_{33} = 550$ pC/N, $k_p = 0.69$) compared with traditional PZT ceramics (Vittayakorn et al., 2006; Zheng et al., 2014; Li et al., 2015a). Deng et al. (2010) reported that the piezoelectric coefficient $d_{33}$, dielectric constant $\varepsilon_r$, and electromechanical coupling factor $k_p$ of the La doped 0.3 Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-0.7 Pb(Zr$_{0.51}$Ti$_{0.49}$)O$_3$ can reach 845 pC/N, 4,088, and 0.70, respectively. Wang et al. (2012) reported that La doped 0.25 Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-0.75 Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$ ceramics near the morphotropic phase boundary had good piezoelectric properties ($d_{33} = 570$ pC/N, $k_p = 0.60$). Fan et al. (2014) found that introducing the proper amount of Li$_2$CO$_3$ and Sm$_2$O$_3$ into 0.3PZN-0.7PZT ceramics could not only effectively improve the sinter ability and reduce the sintering temperature ($\sim 900^\circ$C), but also enhance the electric properties ($d_{33} = 483$ pC/N, $\varepsilon_r = 2,524$, $\tan \delta = 0.0178$).

**Rare-Earth Doped PMN-PT Ceramics**

Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (PMN-PT) ceramic is another kind of typical lead-based ceramic, which has been widely applied in multilayer capacitors, actuators, electro-optical modulators,
ultrasonic transducers, and infrared detectors due to the good electric properties \((d_{33} = 663 \text{ pC/N}, \varepsilon_r = 5,260)\) (Choi et al., 1989; Kamzina et al., 2010; Zhang et al., 2014a).

Li et al. (2018) found an ultrahigh piezoelectricity in the Sm doped 0.71 PMN-0.29 PT ceramics. The piezoelectric constant \(d_{33}\) can reach as high as 1,500 pC/N, and the dielectric constant \(\varepsilon_r\) can arrive at about 13,000. But the Curie temperature decreased to 89°C. Guo et al. (2019a) reported the enhancement of electric properties in the 0.72 PMN-0.28 PT ceramics doped with 2.5 mol % Eu. The piezoelectric constant \(d_{33}\), dielectric constant \(\varepsilon_r\), and electromechanical coupling coefficient \(k_{33}\) of the ceramics can reach 1,420 pC/N, 12,200, and 0.78, respectively. Guo et al. (2019b) also developed Sm doped 0.4 Pb(Mg\(_{1/3}\)Nb\(_{2/3}\))O\(_3\)-0.248PbZrO\(_3\)-0.352PbTiO\(_3\) ternary system ceramics. These ceramics possess a high piezoelectric constant \(d_{33}\), good dielectric constant \(\varepsilon_r\), and relatively high Curie temperature \((T_C = 184°C)\). The previous studies also proved that the optical properties of PMN-PT ceramics can be also significantly improved by rare-earth doping. Wei et al. (2010) achieved a much larger Kerr effect in the La doped 0.75 PMN-0.25 PT transparent ceramic. The Kerr effect (second-order electro-optic effect) refers to the phenomenon of inductive birefringence that is proportional to the square of the electric field, providing useful devices such as light valves, deflectors and displays (Uchino, 1995). The quadratic electro-optic coefficient of the ceramics can reach as high as \(66 \times 10^{-6} \text{ m}^2/\text{V}^2\), Wei et al. (2012a) and Wei et al. (2012b) reported that the transparency of the Er doped 0.75 PMN-0.25 PT transparent ceramics can reach 65% from visible light to infrared band. Besides, three broad peaks at 950–1,060, 1,220–1,290, and 1,420–1,560 nm can be observed under the excitation of a 521 nm laser. Liu et al. (2016) acquired a strong yellow-green up-conversion photoluminescence in the Ho/Yb co-doped 0.67 PMN-0.33 PT ceramics under the excited of a 980 nm laser. Ma et al. (2018) reported La doped 0.88 PMN-0.12 PT transparent ceramics. The transparency in the near infrared region increased to 70% with 1.0 mol% La doping. Fang et al. (2021) reported that the transparency and quadratic electro-optic coefficient of the Sm doped 0.88 PMN-0.21 PT transparent ceramics can reach 69.6% and \(35 \times 10^{-6} \text{ m}^2/\text{V}^2\), respectively. Lv et al. (2019) obtained strong visible up-conversion emissions at 491, 529, 539, 649, 685, 710, and 737 nm and near-infrared down-conversion emissions around 1,061 nm and 1,006 nm in the Pr/Yb co-doped 0.75 PMN-0.25 PT ceramics under the excitation of a 980 nm laser. These studies indicate that the rare-earth doped PMN-PT ceramics are promising multifunctional materials due to the improved electric properties, electro-optic effects, and various photoluminescence properties.

**Rare-Earth Doped Lead-free Ceramics**

BNT-BT ceramic is one of the most widely used lead-free piezoelectric ceramics owing to the good piezoelectric constant and high Curie temperature \((d_{33} > 100 \text{ pC/N}, T_C > 280°C)\) (Panda, 2009; Jo et al., 2011). Li et al. (2004) reported the enhancement electric properties of the BNT-6BT ceramics doped with one at% La, showing the piezoelectric constant \(d_{33}\) increased from 117 to 125 pC/N, but the thick electromechanical coupling coefficient \(k_t\) decreased slightly from 0.43 to 0.38. Liu et al. (2008) reported that the BNT-6BT ceramics doped with 0.4 wt% CeO\(_2\) had better performances compared to pure BNT-6BT ceramics. The piezoelectric constant \(d_{33}\) and thick electromechanical coupling coefficient \(k_t\) of the doped ceramics were 120 pC/N and 0.52, respectively. Peng et al. (2010a), Peng et al. (2010b) and Peng et al. (2011c) reported the enhancement of electric properties in the Sm doped BNT-6BT ceramics. The piezoelectric constant \(d_{33}\) and coupling coefficient \(k_p\) of the ceramics increased to 202 pC/N and 0.3, respectively. In the same year, this group found that Nd doping can also improve the electric properties of BNT-6BT ceramics. The piezoelectric constant \(d_{33}\) and planar electromechanical coupling coefficient \(k_p\) of the ceramics can reach 175 pC/N and 0.31, respectively. Besides, this group also fabricated La\(_2\)O\(_3\) doped BNT-6BT ceramics. After 0.6 wt% La\(_2\)O\(_3\) doping, the ceramics with showed good piezoelectric properties \((d_{33} = 167 \text{ pC/N}, k_p = 0.30)\).

**Rare-Earth Doped BNT-BT Ceramic**

The PMN-PT ceramics have good electric properties. However, the low Curie temperature \((159°C)\) limits their applications. By contrast, the Bi\(_{5}\)Sr\(_{5}\)O\(_{15}\)-PbTiO\(_3\) (BS-PT) ceramics exhibit a high Curie temperature \((T_C \sim 450°C)\) and good piezoelectric property \((d_{33} \sim 460 \text{ pC/N})\) near the morphotropic phase boundary (Inaguma et al., 2004; Zhang et al., 2005). Yao et al. (2010) found the enhancement of the electric properties \((d_{33} = 361 \text{ pC/N}, k_p = 0.40)\) in the La doped BS-PT ceramics. The highest Curie temperature can reach 467°C. Politova et al. (2011) reported a large piezoelectric coefficient \((d_{33} = 350 \text{ pC/N})\) and the piezoelectric coupling coefficient \((k_t = 0.68)\) in the Nd doped BS-PT ceramics. Li et al. (2009) reported a high Curie temperature \((T_C = 490°C)\) and good piezoelectric properties \((d_{33} = 147 \text{ pC/N}, k_p = 0.28)\) in the Y doped BS-PT ceramics. The combination of high Curie temperature and good piezoelectric properties suggested that these rare-earth modified ceramics can be a promising candidate for high-temperature actuators and transducers. Table 1 shows the properties of some lead-based piezoelectric ceramics with rare-earth doping.
Chi et al. (2015) observed visible up-conversion luminescence at 532, 540, and 600 nm, as well as near infrared (1440–1660 nm) and mid-infrared (2620–2840 nm) broadband down-conversion luminescence in the Er doped BNT-7BT ceramics under the excitation of 980 nm. Li et al. (2019a) achieved a strong orange luminescence in the Sm doped BNT-12BT ceramics when excited by blue light, and the emission intensity depends largely on the doping concentration.

**Rare-Earth Doped KNN-Based Ceramics**

KNN ceramics with high Curie temperature (Tc ~ 400°C) and good electric properties (d33 ~ 80 pC/N, k33 ~ 0.36) have been deemed as potential candidates for lead-based piezoelectric ceramics (Saito et al., 2004; Birol et al., 2006; Jaeger, 2010).

Du et al. (2017) studied the effect of the KNN ceramics doped with different rare-earth elements (Dy, Er, Eu, and Pr). The piezoelectric constant d33 increased slightly after doping. (KNN-Dy: 95 pC/N, KNN-Er: 91 pC/N, KNN-Eu: 84 pC/N and KNN-Pr: 94 pC/N). Wu et al. (2017) fabricated Er doped KNN based ceramics with the piezoelectric constant of 70–90 pC/N, and the dielectric constant and loss is about 1,400 and 0.03, respectively. Zhai et al. (2019) reported good piezoelectric and ferroelectric properties in the KNN ceramics doped with Tb and Tm. The d33(Tb) and d33(Tm) can reach 140 pm/V and 127 pm/V, respectively.

In addition to studying the electric properties, the optical performances of rare-earth doped KNN ceramics were also investigated extensively. Yang et al. (2017) reported that the transparency of 1.5 mol% La2O3 doped KNN ceramic can reach as high as 74%. Geng et al. (2017) reported that Eu doped K0.47Nd0.47Li0.06Nb0.98O3 ceramics presented high transmittance both in the near-infrared and middle infrared regions (close to 100%). Besides, the ceramics were efficiently excited by near-ultraviolet and blue light to realize strong reddish luminescence. Sun et al. (2012), and Sun et al. (2014) observed strong green (528 nm) and red (617 and 650 nm) emissions in the Pr doped KNN ceramics under the excitation of 450 nm. Two years later, this group found strong green (510–590 nm) and a relatively weak red (645–695 nm) emissions in the Er doped KNN ceramics under the 980 nm excitation, and it is possible to modulate the ratio of red to green emission by adjusting the Er concentration. Similarly, Wu et al. (2013), Wu et al. (2015a), and Wu et al. (2015b) found that the Er doped KNN ceramics fabricated by sol-gel method exhibited luminescent bands at 527, 548, 660, and 487 nm under the excitation of 980 nm. Besides, Er doping is beneficial to the formation of fine and uniform grains, which helps to enhance the up-conversion efficiency and luminous efficiency. Furthermore, seven down conversion emission bands (530, 548, 605, 618, 650, 672, and 740 nm) could be observed in the Er and Pr co-doped KNN ceramics under the excitation of 485 nm. Besides, three up-conversion emission bands (510–537 nm, 537–585 nm, and 640–690 nm), and two down-conversion emission bands (1,400–1700 nm and 2,600–2,850 nm) were found in the Er and Yb co-doped KNN ceramics. Zhang et al. (2014b) also achieved a strong orange emission in the Sm doped KNN ceramics under excitation from 400 to 500 nm. Li et al. (2020a) also observed a bright photoluminescence with a strong orange emission in the Sm-doped 0.96(K0.48Na0.52)(Nb0.95Sb0.05)-0.04Bi0.5(Na0.82K0.18)0.5ZrO3 ceramics under visible light irradiation.

**Rare-Earth Doped BT Ceramic**

BT ceramic has received much attention due to the high dielectric constant, high resistivity and outstanding insulation performance, which has been extensively applied in positive temperature coefficient of resistivity (PTCR) thermistors, multilayer ceramic capacitors (MLCC), piezoelectric devices, optoelectronic elements, and semiconductors (Zhou et al., 2001). Among them, the application of MLCC is extremely wide, for improving the dielectric constant to meet the requirements of high capacitance. It is effective in significantly increasing the dielectric constant of BT ceramics with rare-earth doping (Caballero et al., 2000; Morrison et al., 2001).

Sun et al. (2010) reported the enhancement of dielectric properties in the Sm doped BT ceramics. Sm doping can inhibit the growth of the crystal grains and make the BT ceramics possess semiconductor characteristics. Li et al. (2012) achieved a large dielectric constant (70,000 ~ 80,000) and low dielectric loss (<0.04) in the Tb doped BT ceramics. Zhang et al. (2020a) reported the Yb/Mn co-doped BT ceramic possessed a relatively good performance with dielectric constant εr (~2,600), low dielectric loss tanδ (0.0183) and high insulation resistivity (4.38 × 1014 Ω cm). Zhang et al. (2020b) reported the dielectric constant can reach 5,091.7 for 0.3 mol% La2O3 doped BT ceramic. Kumari et al. (2020) reported that the relative dielectric constant

### TABLE 1 | The properties of some lead-based piezoelectric ceramics with rare-earth doping.

| Composition | d33 (pC/N) | k33 | εr | Tc (°C) | Ref |
|-------------|------------|-----|-----|---------|-----|
| (Eu,La,Nd,Sm, Gd,Dy,Er):PZT | 53–569 | – | 187–3,413 | 156–368 | Shannigrah et al. (2004) |
| Sm,PZT | 172 | 0.42 | 610 | 274 | Pandey et al. (2009) |
| (Pr,Yb,Sm):PZT | – | – | 210.48–7,000 | 314–394 | Samad et al. (2017) |
| Sm: PNN-PZT | 1,510 | 0.78 | 13,000 | 99 | Li et al. (2018) |
| Eu: PNN-PZT | 1,420 | 0.78 | 12,200 | 83 | Guo et al. (2019a) |
| Sm:PMN-PZT | 910 | 0.7 | 4,090 | 184 | Guo et al. (2019b) |
| La: PZN-PZT | 440–845 | 0.63–0.7 | 3,321–4,088 | 206–213 | Deng et al. (2010) |
| La: PZN-PZT | 570 | 0.6 | 3,900 | 204 | Wang et al. (2012) |
| Sm: PNN-PZT | 605 | 0.55 | 5,020 | 128 | Peng et al. (2016) |
| Sm2LiPZN-PZT | 483 | 0.65 | 2,524 | 394 | Fan et al. (2014) |
| LaBS-PT | 361 | 0.4 | 3,500 | 467 | Yao et al. (2010) |
| Y:BS-PT | 147 | 0.28 | – | 490 | Li et al. (2009) |
$\varepsilon_r$ of the BT ceramics doped with Eu can increase to 8,581, and the grains of the ceramics was uniform with average grain size of 800 nm. These studies indicated that BT ceramics doped with rare-earth may be a promising candidate for MLCC applications. Besides, Battisha et al. (2010) reported the up-conversion of infrared light to visible light can be observed in Er/Yb co-doped BT ceramics. Cernea et al. (2013) observed three distinct peaks (483, 660, and 800 nm) in the BT ceramics doped with Tm under the excitation of 460 nm.

Thus, rare-earth doped piezoelectric ceramics can effectively modify the electric properties and introduce excellent photoluminescence properties, which expanded the applications of piezoelectric ceramics greatly, such as actuating devices, ultrasonic transducers, electro-optical deflector, potential phosphor, and multifunctional optoelectronics. Table 2 summaries the properties of some lead-free based piezoelectric ceramics with rare-earth doping.

### Table 2 | The properties of some lead-free based piezoelectric ceramics with rare-earth doping.

| Composition | $d_{33}$ (pC/N) | $k_p$ | $\varepsilon_r$ | $T_c$ (°C) | Ref |
|-------------|----------------|-------|----------------|-------------|-----|
| La: BNT-6BT  | 125            | 0.24  | —              | 250         | Li et al. (2004) |
| Ce: BNT-6BT  | 127            | 0.23  | 851            | 280         | Liu et al. (2008) |
| Sm: BNT-6BT  | 202            | 0.3   | 1,200          | 277         | Peng et al. (2010a) |
| Nd: BNT-6BT  | 175            | 0.31  | 1,400          | 280         | Peng et al. (2010c) |
| Dy: BNT-6BT  | 167            | 0.3   | 1,470          | 272         | Peng et al. (2010c) |
| Dy: BNT-6BT  | 190            | 0.372 | 1,100          | 275         | Jiang et al. (2018) |
| (La, Ho, Yb, Y): BT-Mn | — | — | 2,108-2,613 | — | Zhang et al. (2020a) |
| (Dy, Er, Eu, Pr): KNN | 84-95 | — | — | — | Du et al. (2017) |
| Sm: KNN-LS | 176            | 0.35  | 1,372          | 328         | Hao et al. (2015) |
| (Nd, Dy, Ho): KNN-Li | 68-128 | — | 247-807 | 400-433 | Zhou et al. (2014) |
| Er: KNN-Li | 89             | —     | 1,350          | 350         | Wu et al. (2017) |

**RARE-EARTH DOPED PIEZOELECTRIC SINGLE CRYSTALS**

**Rare-Earth Doped Lead-Based Single Crystals**

In order to further improve the properties of the piezoelectric materials, the growth of piezoelectric single crystals has drawn wide concern. The discovery of relaxor-based ferroelectric single crystals represented by Pb(Mg(1/3)Nb(2/3))O$_3$-PbTiO$_3$ (PMN-PT) and Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (PZN-PT) are considered as a revolutionary breakthrough of piezoelectric materials, which tremendously improved the electric properties ($d_{33} = 1,780$ pC/N) of piezoelectric materials compared to commercial piezoelectric PZT-5H ceramics (590 pC/N) (Kim et al., 2010).

Li et al. (2019b) reported a large piezoelectric constant $d_{33}$ in the Sm doped PMN-PT single crystals, and the values (exceeding 3,400 pC/N) increased more than double compared with the Sm doped PMN-PT ceramics (1,510 pC/N). The Sm doped single crystals also showed improved compositional uniformity along the crystal boule. Furthermore, the electric field-induced strain can reach 30%, which is almost 90% higher than that of undoped PMN-PT single crystals. This study provided commercial opportunities for high-performance piezoelectric applications. Besides, PZN-9PT piezoelectric single crystal showed excellent electric properties ($d_{33} > 1,500$ pC/N, $k_{33} > 90$%) near the morphotropic phase boundary (Kuwata et al., 1982). However, the low coercive field ($Ec \sim 3.5$ kV/cm) and low Curie temperature ($T_c \sim 170$ °C) limit the application of PZN-PT single crystal in high-power and high-temperature environments (Rajan et al., 2007). Xi et al. (2016a) and Xi et al. (2016b) reported a significantly enhanced coercive field $E_c$ (11.6 kV/cm) in the Er doped PZN-9PT crystal. The Curie temperature $T_c$ was around 178°C. Furthermore, the green and red up-conversion emission bands can be obtained in the ceramic under the 980 nm excitation. The group also reported the enhancement of the coercive field ($E_c = 5.9$ kV/cm), remnant polarization ($P_r = 38.40 \mu$C/cm$^2$) and Curie temperature ($T_c = 175^\circ$C) in the Ho doped PZN-9PT crystal. Li et al. (2019c) also prepared Tm/Yb co-doped PZN-9PT crystal with large coercive field $E_c$ of 12.1 kV/cm, and the value is nearly four times higher than that of PZN-9PT crystal. The Curie temperature $T_c$ was increased to 182.5°C. Under a 980 nm laser excitation, the modified crystals produce up-conversion with three colors [blue (480 nm), strong near-infrared (804 nm), and weak red (652 nm)].

### Rare-Earth Doped Lead-free Single Crystals

Na$_{0.5}$Bi$_{0.5}$TiO$_3$ (BNT)-based lead-free crystals were reported to have superior electric properties, large band gap and high near-visible light absorption coefficient (Hiruma et al., 2010; Li et al., 2015b). In recent years, the electric and optical properties of...
the rare-earth doped BNT single crystals have been studied. Zhang et al. (2014c) prepared an Eu doped BNT single crystal by top-seeded solution growth, and observed that the crystal presented orange and red emissions under the excitation of 611 nm. The piezoelectric constant $d_{33}$ and remnant polarization $P_r$ of the crystal increased to 86 pC/N and 7.38 μC/cm², respectively. Jiang et al. (2018) achieved an extremely strong green emission in the Er doped BNT single crystal under the 980 nm near-infrared excitation. But Er doping led to a slight decreasing of dielectric constant, dielectric loss and transmittance. He et al. (2013) reported high transparency Nd doped NBT single crystal by a top seeded solution growth method. The transparency reached more than 50% above 450 nm, and a strong emission band around 1,066 nm was found under laser excitation at 808 nm. These research results may help to extend various biomedical applications including intravascular imaging, photoacoustic imaging, and microbeam applications.

RARE-EARTH DOPED PIEZOELECTRIC FILMS

Compared to piezoelectric crystal and ceramics, piezoelectric films can greatly improve the operating frequency due to unlimited size. Currently, piezoelectric films such as PZT and Bi$_4$Ti$_3$O$_12$ (BIT) thin films are widely applied in ferroelectric dynamic random-access memory, room temperature infrared detectors, piezoelectric motors, ultrasonic detectors, film capacitors and integrated optical waveguide devices (Xie et al., 2006).

Rare-Earth Doped PZT Films

Majumder et al. (2001) investigated rare-earth (Nd, Gd, and Ce) doped PZT (53/47) thin films by sol-gel technique, realizing an improvement of ferroelectric and dielectric properties of the PZT thin films with Ce and Gd. Nd doping was effective to increase the retained switchable polarization of PZT from 63 to 84%. Yu et al. (2003) fabricated the Eu doped PZT (52/42) thin films with an improved polarization and low leakage current by a sol-gel method. Nakaki et al. (2004) studied the effect of the PZT (40/60) thin films doped with various rare-earth elements (Y, Dy, Er, and Yb). The remnant polarization $P_r$ of the films increased to 26 (PZT-Y), 25 (PZT-Dy) and 26 μC/cm² (PZT-Er), respectively, while Yb doping degraded the remnant polarization $P_r$ down to 16 μC/cm². Pandey et al. (2007) reported the remnant polarization and dielectric constant of the Sm substituted PZT (65/35) thin films can reach about 52 μC/cm² and 1,220, respectively. Moreover, the transparency of the film was close to 80% at 1200 nm. Rath et al. (2019) reported the enhancement of piezoelectric constant $d_{33}$ (more than 130 pm/V) in La doped PZT film. Zhang et al. (2021) achieved a large remnant polarization (22.73 μC/cm²) in the 2 mol% Dy doped PZT (60/40) thin films. Moreover, the films also exhibited a significantly reduced leakage current density. All these studies indicated that rare-earth doping is one promising technique for improving the ferroelectric property of PZT film to meet a wide range of application requirements.

Rare-Earth Doped Lead-free Films

Due to the fatigue-free characteristics, the BIT films have been widely used in special applications, typically like nonvolatile ferroelectric random access memory. Kim et al. (2002) reported the enhancement of ferroelectric properties in the Eu doped BIT films. The remnant polarization $P_r$ of the films was about 30 μC/cm². Zhang et al. (2003) reported that the remnant polarization of Nd doped BIT films increased double (8.8 μC/cm²) compared to the pure BIT films. Ruan et al. (2008) reported a high optical transparency (>80%) in the Eu doped BIT films, and the emission spectra of the films presented two peaks at 594 and 617 nm under the excitation of 350 nm. Moreover, the films exhibited high fatigue resistance after $10^{10}$ switching cycles. Gao et al. (2009) observed two strong green emission bands centered at 524 and 545 nm and a weak red emission band centered at 667 nm in the Er/Yb co-doped BIT films under the excitation of 980 nm. Ding et al. (2011) observed two emission bands centered at 546 and 656 nm in the Ho/Yb co-doped BIT thin films under the excitation of 980 nm.

In addition to the research of rare-earth doped piezoelectric thin films, Xu et al. (2020) have also made remarkable achievements in the thick films. They obtained high $d_{33}$ (343 pC/N), large $P_r$ (12.45 μC/cm²) and low $Ec$ (0.63 kV/mm) in the Er doped Ba$_{0.95}$Ca$_{0.05}$Ti$_{0.95}$Zr$_{0.05}$O$_3$ textured thick films. Besides, two strong green emission bands centered at 525 and 550 nm and one weak red emission band of 660 nm were acquired under the excitation of a 980 nm laser. These results showed that rare-earth doped films significantly enhanced the electrical properties as well as the photoluminescence performances, which has high potential for multifunctional film devices applications.

DISCUSSIONS

Electrical Properties

The rare-earth doping may influence the electrical and optical performances of the piezoelectric materials significantly. Two tables (Tables 1, 2) and Figure 3 summary the piezoelectric properties of the rare-earth doped piezoelectric ceramics with perovskite (ABO$_3$) structure. It can be found that Sm doped PMN-PT ceramics exhibited the highest piezoelectric constants (1,510 pC/N) among the rare-earth doped ceramics listed, which may be due to the addition of aliovalent Sm$^{3+}$ dopant on A-site of the perovskite structure with similar ion radius. It is noting that Sm$^{3+}$ is the smallest ion among all the lanthanide rare Earth ions, which may completely occupy the A-site of PMN-PT solid solution and then replace the Pb ion (Li et al., 2020b). The significant effect on electric properties of Sm doping PMN-PT is mainly due to the local structure disorder. Besides, Eu$^{3+}$ doped PMN-PT ceramics also exhibit excellent piezoelectric properties ($d_{33}$~1420pC/N). As we know, the Eu$^{3+}$ have similar ionic radius and valence states to Sm$^{3+}$ ions, which also proved that the rare
Earth ions with a similar ionic radius to the A-site ions of the perovskite ferroelectric materials can be used to improve piezoelectric performance. Nevertheless, Sm doping reduced the Curie temperature of PMN-PT (89°C) that would limit their high temperature applications. The RE doped lead-based (PMN-PZT and BS-PT) and lead-free based (BNT and KNN) materials with relatively high Curie temperature were studied for enhancing piezoelectric constant. Therefore, it is difficult to obtain the samples with both excellent piezoelectric constant and high Curie temperature and more research works will be needed in the future to improve performances by regulating the local structure disorder of piezoelectric materials with a stale Curie temperature.

**Optical Properties**

Except for the electric properties, the optical performances were discussed. On the one hand, the rare-earth doping can obtain transparent samples with high transmittance. Figure 4 gives the transmittance of some piezoelectric materials with rare-earth doping. It can be found that the transparency of the listed piezoelectric materials exceeds 60% in a specific wavelength range. For the ceramics, the grain boundary scattering loss is the main factor affecting the transmittance. Without exceeding the solubility limit, rare-earth can dissolve into the perovskite lattice homogeneously, meanwhile enhance the ceramic density, transparency, and other properties. However, excessive rare-earth ions may accumulate at the grain boundaries with increasing rare-earth content, which will lead to Rayleigh scattering loss due to the different refractive indices between grain boundaries and matrix. Besides, ion vacancies and crystal defects as well as the defect-induced poor crystallinity may decrease the transparency. Therefore, optimizing these factors to further improve the transparency of rare-earth doped piezoelectric materials may promote the development of multifunctional optical devices greatly.

One the other hand, the rare-earth doped piezoelectric materials can get characteristic emission spectrum after being
excited due to the ladder-shaped 4f energy level of rare-earth ions (Figure 2). Under the excited of 300–500 nm, some sharp down-conversion emissions can be achieved in the rare-earth doped materials. Typically, Eu$^{3+}$ doping can acquire red (617 nm, $^5D_{0} \rightarrow ^7F_{2}$) emission, and Sm$^{3+}$ doping can get red (645 nm, $^7G_{5/2} \rightarrow ^{5}H_{4/2}$) and orange (563 nm, $^6G_{5/2} \rightarrow ^{6}H_{5/2}$) emissions. Pr$^{3+}$ doping can obtain green (545 nm, $^3P_{0} \rightarrow ^3H_{2}$) and red (617 nm, $^3P_{0} \rightarrow ^3H_{2}$) emissions. Besides, some sharp up-conversion emissions can be also achieved in the rare-earth doped materials under the excitation of 980 nm. Green (500 nm, $^5G_{11/2}, ^4S_{3/2} \rightarrow ^4I_{15/2}$) and red (670 nm, $^4I_{15/2} \rightarrow ^4I_{11/2}$) emissions can be found for Er$^{3+}$ doped samples, and blue (480 nm, $^1G_{4} \rightarrow ^3H_{6}$) and red (652 nm, $^3G_{4} \rightarrow ^3F_{2}$) emissions can be observed in Tm$^{3+}$/Yb$^{3+}$ co-doped samples. Green (529 nm $^3P_{0} \rightarrow ^3H_{2}$), orange (623 nm $^3P_{1} \rightarrow ^3H_{4}$) and red (649 nm $^3P_{0} \rightarrow ^3H_{2}$) emissions were found in Pr$^{3+}$/Yb$^{3+}$ co-doped materials. The introduced photoluminescence performance can significantly expand the application range of piezoelectric materials. Especially, the materials can achieve up-conversion emissions with converting long-wavelength light (invisible to the naked eye) into visible light, which will have important application in the information science and technology fields such as laser, display, anti-counterfeiting, and will also open up new research fields in biomedicine or photoacoustic multi-mode images. However, some conditions including doping concentration, sintering temperature, chemical composition and preparation process have a great influence on the electrical performance and luminescence performance of the rare-earth doped piezoelectric materials. Adjusting these conditions to obtain both good electrical and optical properties is of great significance for the development of multifunctional devices and materials.

**CONCLUSION AND PERSPECTIVE**

The electric and photoluminescence properties of piezoelectric materials can be significantly modified by rare-earth doping. Consequently, rare-earth doping is an effective method to fabricate multifunctional materials. The research and development trend of rare-earth doped piezoelectric materials are prospected as follows. 1) With the needs of environmental protection and sustainable development of human society, it is urgent to develop environmental friendly lead-free piezoelectric materials with excellent performance to replace traditional lead-based ceramics. The future development trend is to find an appropriate concentration of rare-earth oxide and proper lead-free piezoelectric materials to achieve excellent electric properties. 2) For the large strain and high energy conversion efficiency applications, rare-earth doped piezoelectric single crystals are superior to traditional piezoelectric ceramics due to their great electric properties. The future development trend is to optimize the growth conditions and properties of single crystals to meet increasingly demanding applications. 3) The rare-earth doped piezoelectric materials are a type of optical-mechanical-electric integrated multifunctional material. Due to the unique properties of rare-earth ions and piezoelectric materials, this type of new material has great advantages in sensing, detection, and information transmission.

**AUTHOR CONTRIBUTIONS**

YC and DZ wrote and edited the manuscript. ZP, MY, and XJ conceived the project and edited the manuscript.

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