A Review of Cr$^{2+}$ or Fe$^{2+}$ Ion-Doped Zinc Sulfide and Zinc Selenide Ceramics as IR Laser Active Media

Natalia Timofeeva 1, Stanislav Balabanov 1,∗ and Jiang Li 2

1 G.G. Devyatykh Institute of Chemistry of High-Purity Substances of the RAS, Nizhny Novgorod 603951, Russia; timofeeva@ihps-nnov.ru
2 Transparent Ceramics Research Center, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201899, China; lijiang@mail.sic.ac.cn
∗ Correspondence: balabanov@ihps-nnov.ru

Abstract: Zinc chalcogenides doped with Cr$^{2+}$ or Fe$^{2+}$ ions are of considerable interest as active media for IR lasers operating in the 2–5 µm wavelength range. Such lasers are in demand in various fields of medicine, remote sensing and atmospheric monitoring, ranging, optical communication systems, and military applications. In recent years, however, the rate of improvement in the characteristics of zinc chalcogenide laser sources has slowed considerably. Unwanted thermally induced effects, parasitic oscillations, and laser-induced damage of the active element have hindered the scaling of output power and efficiency. However, the physical and chemical properties of the materials leave ample room for further improvements. In particular, the control of the dopant concentration profile in the active element is of great importance. Zero concentration of Cr$^{2+}$ or Fe$^{2+}$ ions on the radiation input/output surfaces can significantly increase the laser-induced damage threshold; the designed concentration distribution in the element volume allows regulation of heat dissipation and reduction of parasitic oscillations. The zinc chalcogenide ceramic technology seems to be the most suitable to solve this challenge. This review presents and discusses the state of the art in ZnS and ZnSe optical and laser ceramics and the directions for further development of their technology.

Keywords: laser ceramics; zinc chalcogenide; active media; IR lasers

1. State of the Art in Zinc Chalcogenide Active Media

Zinc chalcogenides are wide-bandgap semiconductors belonging to the II-VI group, of which zinc sulfide (ZnS) and zinc selenide (ZnSe) are the most widely used as optical materials. They form mainly two types of crystals: sphalerite with cubic symmetry (sp. gr. $F_4^{3}m$) and wurtzite with hexagonal symmetry (sp. gr. $P_{6_3}mc$), as shown in Figure 1. The Zn$^{2+}$ cations in both structures are fourfold coordinated by S$^2$− (Se$^2$−) anions. The cubic phase is stable at room temperature, and the transition to wurtzite is observed at a temperature of about 1020 °C for ZnS and 1425 °C for ZnSe.

Zinc chalcogenides are known as excellent host media for doping with transition metal ions. As host matrices (with a cubic symmetry), they have low maximum phonon energies (~339 cm$^{-1}$ for ZnS and ~253 cm$^{-1}$ for ZnSe [1]), high thermal conductivity (18 W·m$^{-1}$·K$^{-1}$ at 300 K [2]), and wide transparency range (0.4–12 µm for ZnS and 0.5–22 µm for ZnSe). However, they have large dn/dT coefficients (43 × 10$^{-6}$ K$^{-1}$ for ZnS and 63 × 10$^{-6}$ K$^{-1}$ for ZnSe at 3 µm [3]), which are the main contributors to the thermal lens [4]. Chromium or iron ions replace Zn$^{2+}$ in the crystal lattice of zinc chalcogenides and have a $+2$ oxidation state. Other states, such as $+1$ and $+3$, are possible depending on the presence of compensating defects [5].

Doped zinc chalcogenides—Fe$^{2+}$:ZnS, Cr$^{2+}$:ZnS, Fe$^{2+}$:ZnSe and Cr$^{2+}$:ZnSe—are used to fabricate active elements (AEs) of IR lasers operating in the 2–5 µm spectral range [6–12]. Such laser sources are in demand in various fields of medicine, highly sensitive spectrum analyzers, remote sensing and atmospheric monitoring, ranging, optical communication systems, and military applications.
systems, and military applications [9,13–19]. The traditional methods of dopant (Cr$^{2+}$ or Fe$^{2+}$) introduction into the chalcogenide host matrix are doping during crystal growth (melt growth method [6–8,20–22], physical or chemical vapor transport technique [23–25]) and post-growth high-temperature diffusion doping of single or polycrystals from thin-film metal sources deposited on the sample surface [10,12,26–34]. The latter approach is most commonly used; the matrix is usually a polycrystalline ZnS or ZnSe material synthesized by chemical vapor deposition (CVD). To date, record levels of laser output power have been achieved using such AEs in both pulsed and continuous wave modes [12,29–31].

Figure 1. The crystal structures of ZnS: (a) sphalerite, sp. gr. F3m; (b) wurtzite, sp. gr. P6$_3$mcc.

There are experimental and theoretical justifications for the necessary improvements in AE characteristics that will allow scaling the efficiency and power of zinc chalcogenide lasers [35–41]. However, the objective limitations of traditional AE technologies do not allow these improvements to be realized in practice, and there has been no significant progress in this direction in recent years. To increase the laser-induced damage threshold of AE, which is mainly limited by the surface damage resistance, samples must have a zero activator ion concentration at the surface [36,42], and it is also necessary to limit contamination during doping [43,44]. The control of thermally induced effects (such as thermal lens and thermally induced depolarization) and the suppression of parasitic oscillations are related to the formation of the targeted/desired dopant concentration distribution in the AE volume; for example, by creating alternately doped and undoped multilayer elements [37,39–41,45,46], or a non-uniform distribution of active ions in the transverse direction [38–40].

Diffusion-doped AEs are characterized by a high dopant concentration near the surface and a short active medium length. This is due to the low values of the dopant diffusion coefficients, which decrease in the following order: Cr$^{2+}$:ZnSe, Cr$^{2+}$:ZnS $\leftrightarrow$ Fe$^{2+}$:ZnSe (depending on the starting material and process temperature), Fe$^{2+}$:ZnS [27,32,43,47,48]. If, for Cr$^{2+}$:ZnSe elements in rod geometry, the problem of creating a zero Cr$^{2+}$ ion concentration at the radiation input/output surfaces and distributing it sufficiently uniformly in the volume can be solved, the fabrication of the other media remains a difficult task. Even a significant increase in annealing temperature and time in a hot isostatic press (HIP) does not result in a uniform distribution of iron ions [12,28,30,31,33,40,48,49]. The doping of ZnS is further complicated by a phase transition at 1020 °C; exceeding this temperature leads to the formation of secondary phases and/or cracking due to inhomogeneous density changes, especially for relatively large AEs. It is also challenging when a uniform distribution and
high concentration of Cr$^{2+}$ and Fe$^{2+}$ ions are required in co-doped elements. Such elements can potentially solve the problem of the lack of powerful and convenient lasers for pumping Fe$^{2+}$:ZnS and Fe$^{2+}$:ZnSe [50]. Implementing the excitation transfer from Cr$^{2+}$ to Fe$^{2+}$ ions can make lasers in the 4–5 μm range much simpler, less expensive, and more compact [51].

The ability to control the active ion distribution profile in the AE volume has been demonstrated through the use of additive technologies, in particular layer-by-layer doping during CVD [36,42,52] or solid-state diffusion bonding of doped elements [37,38,46,53]. Despite the improvement of some properties of such AEs (e.g., suppression of parasitic oscillations has been demonstrated [37,46]), these methods did not lead to a qualitative change due to the difficult technical feasibility, the formation of defects in the bonding zone, and probably an increased contamination due to the multi-step fabrication process.

A ceramic approach is a current and promising direction for the fabrication of AEs based on zinc chalcogenides [54]. Over the past two decades, optical ceramic technology has been intensively developed and many laser-quality materials have been created, including compounds that are virtually impossible to produce as single crystals [55,56]. The ability to precisely control the dopant concentration distribution in the AE volume is one of the advantages of this technology.

The first reports on the fabrication of chromium-doped zinc selenide laser ceramics were published 10 years after the achievement of lasing on Cr$^{2+}$:ZnS single crystals [57–59]. However, the ceramic approach was not intensively developed because the other methods provided incomparably higher AE quality. To date, new requirements for AEs are reviving interest in zinc chalcogenide ceramic technology. Although the total number of publications on zinc chalcogenide laser ceramics is not large, there is a clear trend of increase in recent years, as shown in Figure 2.

![Figure 2. Publication activity on zinc chalcogenide laser ceramics by year.](image)

2. Zinc Chalcogenide Optical Ceramic Technology

The use of zinc chalcogenides as optical materials has a long history, and the first mention of their ceramic technology probably refers to the patent filed in 1964 for the hot pressing of zinc sulfide [60]. ZnSe ceramic technology was also developed in the 1960s [61]. ZnS ceramics had relatively high transmittance of ~70% in the 8–12 μm spectral range [62–68] and ZnSe of ~60% in the 11–19 μm range [69,70]. These materials were mainly used as IR optics in military equipment operating in the atmospheric transparency window of 8–12 μm, and were produced in the USA under the trade names IRTRAN-2 (ZnS) and IRTRAN-4 (ZnSe) and in the USSR under the trade names KO-2 and KO-4. Over the next decade, melting, sublimation, and CVD methods were developed to produce these materials, resulting in both higher optical quality and achievable optical element sizes. As a consequence, the industrial technology of ceramics lost its practical importance. Nevertheless, various research organizations continued to work in this direction, improving the key stages of ceramic technology: synthesis of starting powders, their preparation for pressing, and consolidation.
Zinc chalcogenide synthesis from the elements is a simple and productive way to prepare powders for optical ceramics [69,71–74]. The principle of the method is to co-grind Zn and S or Se in a planetary or ball mill. To control the reaction rate, ballast substances, such as ZnCl$_2$ or NaCl, are sometimes introduced and then washed out of the zinc chalcogenide. The synthesis can be carried out in the combustion mode [75–78]. The inhomogeneity of the macro-composition, the quantitative transfer of impurities from the initial elements, including practically uncontrolled oxygen contamination, as well as the polydispersity of the resulting particles and their agglomeration are the disadvantages of this method.

Precise control of the granulometric composition of powders can be achieved by wet chemical methods. These include chemical precipitation from aqueous solutions [62,79–86], hydrothermal synthesis [66–69,87], and synthesis by combustion in an aqueous solution [63,64]. Chemical precipitation methods are based on the selection of suitable zinc- and chalcogen-containing precursors and the precipitation conditions (temperature, time, solution pH, etc.). The sulfide source is usually thioacetamide CH$_3$CSNH$_2$ or Na$_2$S, while the zinc source is ZnCl$_2$ or Zn(NO$_3$)$_2$·6H$_2$O. The synthesized ZnS particles have a spherical shape and a controlled size in the order of tens of nm. The process is well reproducible. However, both the entrapment of the mother liquor during crystallization and the adsorption of chemical reaction products and other impurities are unavoidable. The transmission spectrum of synthesized ZnS particles contains absorption bands of hydroxyl, hydrocarbon, carboxyl, alcohol groups, and oxygen-containing impurity defect centers [62,66–68,80,85,88]. Therefore, various types of thermal treatment of powders have been developed, taking into account the optimal relationship between impurity removal, particle growth, agglomeration, and phase transitions occurring in the process. Annealing is typically performed in the temperature range of 500–900 °C under vacuum [67,80,85], argon [79,83,84,88–90], or hydrogen sulfide H$_2$S/N$_2$ atmosphere [62–64,86]. Effective purification from oxygen-containing impurities begins at ~600 °C [62]. At the same time, treatment at elevated temperatures increases the agglomeration of powders and does not completely remove impurities.

A number of studies show a decrease in the phase transition temperature of zinc sulfide nanopowders up to ~800 °C compared to bulk material (1020 °C) [62,67,68,79,80,83,91,92]. This is usually associated with the high surface energy of nanoparticles. However, it seems more likely that the formation of the hexagonal phase at low temperatures is due to the high impurity content in the nanopowders. The influence of impurities on phase transitions is well known, e.g., the sphalerite structure in ZnS can be stabilized by Cu$^+$ ions or CaF$_2$, while Al$^{3+}$ ions and LiF contribute to wurtzite stabilization [74,93–96]. In [66], it was found that an excess of sulfur contributes to a decrease in the concentration of oxygen atoms and a stabilization of the sphalerite structure.

The fabrication of ZnSe powders by chemical precipitation from solutions is usually carried out using NaHSe as a source of selenium ions [88,89]. Oxygen contamination is also an issue for the ZnS; it is present in the powders in significant amounts and is detected both by XRD analysis and in the transmission spectrum of the synthesized ceramics [88].

Work is underway to obtain nanopowders with an average size of 18 nm by laser ablation of a ZnSe target with a fairly good productivity of 100 g/h [97]. The powders contained ~60 wt% of high temperature hexagonal phase associated with their rapid cooling outside the laser plume. It is known that the evaporation of ZnSe occurs with its dissociation into elements, while zinc and selenium have different vapor pressures [98]. In this context, the issue of maintaining stoichiometry in the resulting powders requires separate studies.

It is well known that the CVD method allows the synthesis of zinc chalcogenides with excellent characteristics in terms of impurity composition and stoichiometry [99,100]. Therefore, the preparation of powders by mechanical grinding of bulk samples of polycrystalline CVD-ZnS or CVD-ZnSe eliminates many of the above problems associated with...
methods of synthesis from elements or wet chemistry [101]. However, grinding does not provide the desired particle morphology and narrow particle size distributions [69,71].

It seems promising to use the CVD method to directly obtain powders with optimal properties for ceramic technology, rather than bulk materials with subsequent grinding. There are data on the CVD of zinc chalcogenide powders by reaction of zinc and sulfur vapors [102] or zinc and hydrogen selenide vapors in a vertical quartz reactor at temperatures of 550–700 °C and pressures of 760–1100 mm Hg [103]. Such powders have a low oxygen content of 10 ppm, but have a rather large size of 5–10 µm [103]. It is mentioned that such powders are intended for the fabrication of optical and phosphor ceramics, but no additional data on the properties of the ceramics are provided. Later, the method was improved to fabricate spherical zinc sulfide powders of 20–100 nm in size [104]. Synthesis conditions can change the ratios of cubic and hexagonal phases, although it is not clear whether the method can be used to obtain ZnS with a pure cubic phase. The powders are intended for use as electroluminescent phosphors; no data are given on the fabrication of optical ceramics from them. In [105], CVD powders were used to fabricate Fe²⁺:ZnSe ceramics, but their morphology was not controlled by the deposition conditions, but by subsequent grinding. A transmission of 67% (≈96% of theoretical) was achieved only in the long wavelength range at 14 µm.

The relatively high vapor pressure of chalcogenides makes it difficult to obtain a dense material by free sintering, so the main methods of consolidating powders are hot pressing (HP) and spark plasma sintering (SPS), in some cases with additional HIP treatment. Optimization of pressing conditions is performed by taking into account possible contamination of the material with carbon from the mold [66], compaction and recrystallization mechanisms [66,68,89,106,107], sublimation of samples of different compositions [68,89], and the influence of sintering additives and dopants present [74,81,94–96,106], as well as a possible phase transition characteristic for zinc sulfide [108]. In order to control the ZnS phase composition, it is preferable to sinter at relatively low temperatures and short holding times, which can be achieved using the SPS method [82,84]. However, high SPS heating rates and nonuniform temperature distribution in the volume of the sintered sample can lead to the formation of an inhomogeneous microstructure and also contribute to the transition of sphalerite to the hexagonal phase [82,90]. These features can be a limitation when using the SPS method to obtain large-size elements. It appears that HP is more suitable for the production of zinc chalcogenide ceramics [64,65,67]. In [109], the SPS and HP of commercial ZnS powder were compared, and in the first case the transmission in the range of 8–12 µm reached 69% and in the second case 75% (close to theoretical). In both cases, subsequent HIP processing of the ceramics was used.

Consolidation processes in chalcogenides can be intensified by the use of sintering additives. The choice of such additives is quite large, unless the aim is to achieve transparency of the ceramics [94,95,106]. They increase the density of ceramics, but at the same time they can change the phase composition [74,94,95] and/or increase the capture of impurities, e.g., oxygen. In [81], wet ZnS powder was mixed with Na₂S, dried under vacuum at 500 °C for 2 h, and then HP was performed at 950 °C for 4 h. The introduction of Na₂S promoted grain growth and reduced porosity. This allowed the sintering temperature to be lowered to prevent wurtzite phase formation, while the transmittance of the sample deteriorated. Additional absorption bands appeared in the transmission spectrum with maxima in the region of 7 and 11 µm due to stretching vibrations of the S-O bond. It can be argued that the use of sintering additives in the technology of optical chalcogenide ceramics requires considerable study.

3. ZnSe- and ZnS-Based Laser Ceramics

The technology of laser ceramics is generally based on the same approaches as optical ceramics, but the requirements for the quality of the material are much higher. This is due to a number of reasons, the most important of which are as follows. First, pores, inclusions, and microinhomogeneities that differ in refractive index lead to passive losses in the active
medium for scattering and absorption. As the wavelength decreases, these losses tend to increase sharply. And while acceptable quality can be achieved in the 8–12 µm range for IR applications of optical ceramics, passive losses in the 2–5 µm wavelength range typically exceed AE requirements (Figure 3). Second, the presence of impurities can increase the non-radiative transition probabilities, reducing the luminescence quantum yield, raising the lasing threshold, or making it impossible to achieve population inversion at all. Therefore, laser ceramics should have both high structural perfection and chemical purity, preferably 99.99% or better; in particular, limited impurities that have electronic transitions in the laser wavelength range should be at the ppm level or less.

Figure 3. Transmittance spectrum of the polished Fe$_{0.01}$Zn$_{0.99}$Se transparent ceramic sintered at 950 °C for 30 min under a pressure of 60 MPa by SPS. Reprinted with permission from [88], © The American Ceramic Society (Westerville, OH, USA) 2019.

To create a laser material, ZnSe or ZnS particles are doped with iron or chromium. The introduction of these metals is possible by solid phase diffusion into prepared zinc chalcogenide powders [80,101,105,110] as well as during synthesis [79,80,88,89,111,112]. In [57], a powder for subsequent consolidation was obtained by mechanical grinding in an agate mortar of pure ZnSe with a ZnSe-CrSe mixture of different concentrations (0.01, 0.03, 0.05, and 0.1 mol%). The particle size did not exceed 10 µm. The green body was formed uniaxially at a pressure of 60 MPa. Initial heating to 900 K was performed in a resistive heating hot press in a graphite mold. Further heating (1400–1500 K) was achieved by applying an electric current through the sample. The applied pressure was 30–35 MPa, the holding time was 10–15 min. The Cr$^{2+}$:ZnSe ceramic laser yielded 2 mJ of output energy with up to 5% slope efficiency. As the chromium concentration increased for the same output energy, the laser efficiency decreased. In cw mode, the output power of the Cr$^{2+}$:ZnSe laser reached 0.25 W with an efficiency of 20% with respect to the absorbed energy. For comparison, the cw laser on diffusion-doped Cr$^{2+}$:ZnSe AE currently achieves ~140 W of power at a wavelength of 2500 nm [29].

In [110], mechanically crushed CrSe and ZnSe powders were annealed together at a temperature of 950 °C in a vacuum of 10$^{-2}$ Pa for 150 h (Figure 4a). HP was performed in a tungsten mold at 950–1200 °C, 150 MPa pressure, and 2 h hold time. Despite a fivefold increase in pressing pressure compared to the technique of [57], pores and inclusions were found in the Cr$^{2+}$:ZnSe ceramics; the quality of the material did not allow laser generation.
In [79], a ZnS powder synthesized by chemical precipitation from an aqueous solution using CH$_3$CSNH$_2$, Zn(NO$_3$)$_2$, 6H$_2$O, and HNO$_3$ precursors was used [83,84]. The prepared ZnS powder was then mixed with Cr$_2$S$_3$ (0.1 mol%) and ground in an agate mortar. The resulting mixture was annealed at 900 °C in argon for 4 h. HP was performed at a temperature of 1000 °C, a pressure of 50 MPa for 2 h. The concentration of Cr$^{2+}$ ions in the Cr$^{2+}$:ZnS ceramic sample was $1.8 \times 10^{18}$ at/cm$^3$, which was lower than the calculated value because some chromium ions remained in the +3 oxidation state. The transmission of the ceramic was ~67% at a wavelength of 11.6 µm and decreased significantly in the short wavelength part of the spectrum.

In [80], different approaches for the preparation of Fe$^{2+}$:ZnS powders were compared. In the first case, doped particles were synthesized by chemical precipitation from a solution of Zn(CH$_3$COO)$_2$, 2H$_2$O, Na$_2$S·9H$_2$O, and FeCl$_2$. The resulting powders were calcined under vacuum for 3 h at a temperature of 800 °C. The second method consisted of solid phase doping by co-annealing ZnS and FeS powders in an evacuated quartz ampoule at a temperature of 950 °C for 5 days. The resulting Fe:ZnS was ground in an agate mortar. Prior to sintering, the powders prepared in the two ways were mixed with commercial ZnS powders (99.99%) in a ratio of 1:9. The green body was obtained at a pressure of 50 MPa, then HP was carried out at a temperature of 900 °C, a pressure of 250 MPa for 2 h. The resulting ceramic was subjected to an additional HIP treatment at 950 °C, a pressure of 150 MPa for 5 h. Using solid-phase doped powders, the maximum concentration of Fe$^{2+}$ ions was 0.565 at%. This is an order of magnitude higher than that of powders synthesized by precipitation and subjected to HIP (0.038 at%), which is associated with the change of part of the iron ions to the +3 oxidation state. However, the sinterability of the particles obtained by precipitation was better; the transmission of the ceramic was ~65% at a wavelength of 4.5 µm, while the same value as that of the ceramic obtained from diffusion-doped powders was ~35%.

In [88,89,112], chemical precipitation from solution was also used to synthesize Fe$^{2+}$:ZnSe powders. Sodium hydroselenide NaHSe was used as the source of Se ions; ZnCl$_2$ and FeCl$_2$ 4H$_2$O were used as the sources of metals. The obtained particles had a good morphology (Figure 4b). A broad particle size distribution of 50–1100 nm was observed, with the major mode of 70% in the range of 300–600 nm. The maximum Fe$^{2+}$ concentration in zinc selenide was 6 at% (~3.3 × 10$^{20}$ cm$^{-3}$), which is 1–2 orders of magnitude higher than that achieved by traditional doping methods. The ceramic samples obtained with different dopant concentrations are shown in Figure 5a. Fe$^{2+}$:ZnSe ceramics fabricated from mechanically crushed powders are also shown (Figure 5b). In this case, the particle size varied from 0.7 to 35 µm, with 90% of the particles having a size within 1.06–14.2 µm [101].
The output energy of the Fe\textsuperscript{2+}:ZnSe (~9.0 × 10\textsuperscript{18} cm\textsuperscript{−3}) ceramic laser at a wavelength of 4.2 μm was 41 mJ with a slope efficiency of 25% with respect to the absorbed energy at a repetition rate of 3 Hz and a pulse duration of 120 ns [112]. To date, this is the best result achieved with a ceramic IR laser. For comparison, the current record for pulsed energy of diffusion-doped CVD Fe\textsuperscript{2+}:ZnSe lasers at room temperature is 1.67 J at the slope efficiency with respect to the absorbed and incident energy of ~43% and ~27%, respectively [30].

### 4. Conclusions and Outlook

This review analyzes data on the fabrication methods of zinc-sulfide- and zinc-selenide-based laser ceramics. Despite the long history of development of chalcogenide optical ceramic technology and more than a decade of laser ceramic technology, the quality of active elements achieved so far is insufficient for practical applications. The comparison of the characteristics of Cr\textsuperscript{2+}:ZnSe and Fe\textsuperscript{2+}:ZnSe lasers obtained by different methods is shown in Table 1. Laser generation data for Cr\textsuperscript{2+}:ZnS and Fe\textsuperscript{2+}:ZnS ceramics are not available in the literature.

<table>
<thead>
<tr>
<th>Reference, Year</th>
<th>Active element</th>
<th>Synthesis method</th>
<th>Effective dopant concentration, at/cm\textsuperscript{3}</th>
<th>Doping</th>
<th>Active element dimensions, mm</th>
<th>Pump laser</th>
<th>Pump diameter, mm</th>
<th>Output energy, J</th>
<th>(\eta_{\text{slope}}), % (with respect to the incident energy)</th>
<th>(\eta_{\text{abs}}), % (with respect to the absorbed energy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[113], 2016</td>
<td>Fe\textsuperscript{2+}:ZnSe</td>
<td>PVD</td>
<td>2.6 × 10\textsuperscript{18}</td>
<td>homogeneous</td>
<td>(d = 27, l = 15)</td>
<td>HF</td>
<td>17</td>
<td>1.2</td>
<td>25</td>
<td>43</td>
</tr>
<tr>
<td>[30], 2017</td>
<td>Fe\textsuperscript{2+}:ZnSe</td>
<td>CVD + HIP</td>
<td>(7−9) × 10\textsuperscript{18}</td>
<td>external, inhomogeneous</td>
<td>(d = 64, l = 4)</td>
<td>HF</td>
<td>14 × 16 (ellip-tical)</td>
<td>1.67</td>
<td>27</td>
<td>38</td>
</tr>
<tr>
<td>[38], 2019</td>
<td>Fe\textsuperscript{2+}:ZnSe</td>
<td>CVD + SSDB + HIP</td>
<td>9.0 × 10\textsuperscript{18}</td>
<td>internal (meniscus), inhomogeneous</td>
<td>(d = 20, l = 7.5)</td>
<td>Er:YAG</td>
<td>8.8</td>
<td>0.48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[112], 2020</td>
<td>Fe\textsuperscript{2+}:ZnSe</td>
<td>Ceramic</td>
<td></td>
<td>homogeneous</td>
<td>(d = 18, l = 3.2)</td>
<td>Er:Glass</td>
<td>2</td>
<td>0.041</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[114], 2012</td>
<td>Cr\textsuperscript{2+}:ZnSe</td>
<td>Ceramic</td>
<td></td>
<td>homogeneous</td>
<td>(d = 15, l = 10.5)</td>
<td>Nd:YAG</td>
<td>6.5</td>
<td>1.1</td>
<td></td>
<td></td>
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<tr>
<td>[57], 2006</td>
<td>Cr\textsuperscript{2+}:ZnSe</td>
<td>Ceramic</td>
<td></td>
<td>homogeneous</td>
<td></td>
<td></td>
<td></td>
<td>0.002</td>
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</table>

* SSDB—solid-state diffusion bonding.

The poor performance of zinc chalcogenide ceramic active elements is due to their high scattering and absorption in the mid-IR region, i.e., in the region of the operating wavelengths of the lasers. There are no studies that demonstrate the existence of fundamental unsolvable problems in the improvement of their quality. Many issues, such as the role of the granulometric composition and morphology of the initial powders, changes
in stoichiometry, the presence of additives, methods of introducing dopants, methods of consolidation, and equipment materials on the functional properties of the resulting material, have been relatively well studied in various works. However, the available information is not sufficient to formulate valid conclusions about the influence of the applied approaches and processing methods on the optical properties and laser performance of chalcogenide ceramics, since the experimental conditions were always different. To determine the factors that deteriorate the optical properties of zinc chalcogenide ceramics, it is necessary to conduct comprehensive physicochemical studies of all stages of their technology. Special attention should be paid to the chemical purity of the samples, including such difficult-to-control impurities as oxygen and carbon, which is extremely rare in published work.

Synthesis of oxygen-free initial powder is one of the major difficulties in zinc chalcogenide ceramic technology. Several methods have been described to remove oxygen-containing impurities from powders, but they are based on exchange processes between the solid phase and an oxygen-free gas atmosphere. These processes cannot be sufficiently effective due to the proximity of the chemical properties of oxygen, sulfur, and selenium, which belong to the same group in the periodic table. Reducing dissolved oxygen in powders to the ppm level or below is probably an unattainable goal with such approaches. In this regard, it seems expedient to synthesize the initial powders in a high-purity state, which can be achieved, for example, by the CVD method; and probably an oxygen-free atmosphere will be required for operations with nanopowders prior to their consolidation. This increases the cost of the already complex laser ceramic technology and raises an important question about the competitiveness of such active elements.

From our point of view, the development of zinc chalcogenide ceramic technology makes sense because solving this problem opens up new perspectives for IR laser design. It will make it possible to create active elements with a targeted distribution of $\text{Cr}^{2+}$ and $\text{Fe}^{2+}$ ions in the volume, which will lead to an increase in the efficiency and power of IR lasers, reducing their size and allowing new pumping schemes. Several groups that have previously demonstrated excellent results with oxide laser ceramics are engaged in scientific research in this area. Therefore, there is little doubt that the existing gaps in chalcogenide ceramic technology will be filled in the foreseeable future.

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