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Transition metals as optically active dopants in glass-ceramics

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Abstract

Over the past decades, glass-ceramics doped with transition metals have become promising materials for the development of active and passive optical functional devices, interesting a wide variety of commercial applications due to their unique properties. In this Perspective paper, the intrinsic advantages of these composite materials are outlined and we provide an overview of recent and on-going progress and state-of-the-art knowledges of the main applications: broadband amplifiers, tunable lasers, long persistent phosphors, non-invasive optical temperature sensors, saturable absorbers, high IR emitters and thermal shock-resistant color filters. Finally, the today challenges and future prospects are exposed to provide guidelines for future research.

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Transition metal (TM) ions such as Ni^{2+} or Cr^{4+} are highly promising optically active ions in single-crystalline materials since they show rich electronic transitions in the near infra-red (NIR) region and they have wide applications to gain media for lasers. However, the manufacturing processes of single crystals seriously limit the flexibility in compositions, and the versatility to shape them in fibers or on large-scales. TM ions in glasses only exhibit poor luminescence behavior because the strong nonradiative decay processes dominate the relaxations of the excited state and coordination states are unfavorable.^{1,2,3} The gap between glasses and single crystals can be fulfilled by transparent glass-ceramics (TGCs) as these composite materials can offer optical properties similar to those of single crystals, provided that TM ions are incorporated into a suitable crystalline host. Owing to the enhancement of optical properties resulting from the incorporation of TM ions within nanosized crystals embedded into the glass matrix, TGCs have received significant and continuous attention and can offer promising alternatives to crystals in photoelectronic and photonic areas. This perspective letter focuses on recent advances in developing oxide TGCs doped with 3d TM ions for active and passive optical applications. We discuss the recent improvements, existing challenges and future prospects of these nanocomposite materials, paving the way for new fabrication processes and new type of advanced functional materials.

TGCs relies on the *in situ* growth of nanocrystals (NCs) in a glass upon heating treatment (Figure 1). From the viewpoint of materials design, TMs can be purposely activated if the crystalline phases can provide suitable tetrahedral or octahedral sites. The resultant TGCs retain important advantages of crystals, such as high optical activity, combined with easy and flexible glass-forming manufacturing, making them cost efficient compared to single crystals and ceramics, with outstanding properties among which transparency, superior mechanical strength, tailorable thermal expansion coefficients used for high resistance to thermal shock.^{4,3} Additionally, their optical behavior can be almost completely designed by a high level of composition and processing control. Large scale samples or even fibers can be elaborated and sometimes functional crystals precipitated in TGCs are difficult or impossible to synthesize as single crystals,^{4,5} offering new functionalities.

TGCs are attractive as optical components as long as high transparency is achieved. The development of transparent glass-ceramics (TGCs) can be optimized in two ways:⁶ (1) by minimizing the refractive index difference (<0.01) of the two phases (NCs and residual glass)

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or (2) by controlling the size of the NCs with a critical size much smaller (preferably <30 nm) than the wavelengths of the visible spectrum. The former allows the formation of large crystals up to micrometer scale while maintaining transparency.³ The second method controlling the size limit of NCs is more generally used though it requires a good mastering and understanding of the crystallization processes. The transparency usually requires volume (as opposed to surface) nucleation which is initiated by the addition of nucleation agents (ZrO₂ and/or TiO₂) in moderate amounts.⁷ These agents promote phase separation that is enhanced by a heating treatment at 30-100°C above the annealing temperature of the glass.⁸

Fabrication of TGCs is a major advantage compared to single crystals, owing to the possibility to produce large pieces of arbitrary shapes and sizes adapted for commercialization. Optical GCs can be designed using various methods: traditional melt-quenching followed by thermal heat treatments, sinter-crystallization¹⁰ or low-temperature techniques such as sol-gel¹¹ or modified chemical vapor deposition.¹² The reuse of industrial wastes as raw materials is also an important field that should develop in future years with both ecological and economical importance.¹³

The fabrication of the TGCs is tightly attached with the physical mechanism of nucleation and crystal growth in glass phase. It has been regarded as a challenging fundamental issue and the deep understanding is critical to manipulate the formation of NCs. Over the past years, the existence of mesoscale heterogeneities within glasses has been demonstrated as a determinant parameter in the underlying mechanism of nucleation.^{14,15,16,17} These mesoscale heterogeneities (Figure 2) may be further exploited for mastering the microstructure, the crystalline phase formation or the distribution of TMs.¹⁴ Benefiting from the substantial progress in revealing the structural nature of the parent glass for TGCs, in recent years, new methods of elaboration have emerged. In particular, laser-induced crystallization using TM (Ni²⁺, Cu²⁺) atom heat processing opens new perspectives for localized or oriented crystallization, reshaping of NCs or for patterning, with high potential for new optical active devices.^{18,19} For practical and advanced applications, such as high-capacity telecommunication, biomedical remote sensing or compact light source, TGCs have to be ultimately produced in fiber geometry. The technique of melt-in-tube fiber drawing has stimulated many studies to obtain optical GC fibers.^{20,18,21,22} We can cite the realization of TGC fibers containing various crystals: Cr⁴⁺-Mg₂SiO₄,^{21,23} Cr³⁺:ZnAl₂O₄,²² Ni²⁺-Li(Ga,Al)₅O₈ and

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$\text{Ni}^{2+}:\gamma(\text{Ga,Al})_2\text{O}_3$,^{5,20} that should pave the way for commercially viable devices. Moreover, the material category has also been extended to more complicate systems such as novel multiphases (LiTaO_3 and $\text{LiAlSi}_2\text{O}_6$) TGC and even TGC fiber (Figure 2).¹⁴

Rare-earth (RE) ions show discrete energy levels due to purely $4f-4f$ electronic transitions (zero-phonon lines). These narrow bands yield limited applications for broad flatline-shape absorption and emission bands. On the contrary, the TM ions interact with the vibrations of the crystal lattice (vibronic coupling).²⁴ The overlap between the excitation of an electronic transition and vibrational transitions gives intrinsic broad absorption bands, when TMs are located in specific environments in oxide matrices, e.g. Cr^{4+} and Co^{2+} in tetrahedral sites and Ni^{2+} in octahedral sites. As opposed to the f -level screening in the case of RE ions, the specificity of $3d$ TM ions is that $d-d$ transitions are strongly dependent on their local ligand field because the d -orbitals are only weakly shielded from the surrounding neighbors.

Another prominent feature is that controllable energy transfer can be realized in TM ions doped TGCs. The energy transfer process can be simply described by using two interacting dopants with the energy donor as sensitizer and energy receiver as activator. In this process, an excited state energy is transferred, in whole or partly, from a sensitizer to an activator by nonradiative and radiative processes.²⁵ A high energy transfer is expected when the emission spectrum of the sensitizer widely overlaps the absorption spectrum of the activator and when the sensitizer-activator distance is short (energy transfer rate proportional to r^{-6} , with r the separation distance).^{14,18} The strength of interaction is strong for allowed transitions (broad bands) as opposite to forbidden transitions (narrow lines). Recent progresses have been demonstrated to develop diverse combinations of codoped ions based on this method of energy transfer due to impurity-sensitizers.

On one hand, the energy transfer process can be utilized for improving the luminescence brightness in TMs doped TGCs. Octahedral Cr^{3+} sites have a broad and strong absorption in the visible region and fluoresce in the red and NIR region. Under 532 nm excitation, Cr^{3+} is a desirable sensitizer because its NIR emission overlaps well with the NIR absorption of Ni^{2+} , resulting to an efficient energy transfer from Cr^{3+} to Ni^{2+} ions. In consequence, $\text{Cr}^{3+}/\text{Ni}^{2+}$ co-doping has been investigated in several TGCs: $\text{Cr}^{3+}/\text{Ni}^{2+}$ codoped spinels NCs in $\text{ZnO-Al}_2\text{O}_3\text{-SiO}_2$ GCs and $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ GCs^{25,26} and $\text{Cr}^{3+}/\text{Ni}^{2+}$ codoped LiGa_5O_8 in $\text{Li}_2\text{O-Ga}_2\text{O}_3\text{-SiO}_2$ GCs.²⁷ Compared to Ni^{2+} single-doped materials, co-doping enhances emission intensity by

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approximately 8 times. The energy transfer is confirmed by time-resolved emission spectra with an efficiency that can reach 85%. Similarly, enhancement of NIR luminescence is observed in $\text{Yb}^{3+}/\text{Ni}^{2+}$ -codoped transparent GCs as Ni^{2+} ions are activated by Yb^{3+} sensitizing.^{28,29} Cr^{3+} ions are also competitive energy sensitizers in RE-based laser solids because the visible and NIR emissions of Cr^{3+} significantly overlap with the absorption of RE (Nd^{3+} , Tm^{3+}) ions.^{26,30} Tb^{3+} was also used as an efficient sensitizer for $^{61}\text{Mn}^{2+}$ in ZnAl_2O_4 NCs embedded in a GC, giving intense red photoemission.³¹ The energy transfer process upon 350 nm excitation can be controlled by the crystallization conditions and the dopant concentrations allowing the color of photoemission to be tuned by simultaneous emission of Tb^{3+} and Mn^{2+} centers. A potential application of this material is considered as single or dual-mode emitting phosphor for luminescent lighting.

On the other hand, the rational control of the energy transfer process, with even suppressing the process if unwanted, is also an interesting topic in TMs doped TGCs.³² The partition of the different dopants into the crystalline phases is a major challenge to efficiently manage energy transfers.^{32,33,34} It was demonstrated that an efficient energy transfer results from accumulation of RE (Er^{3+} , Yb^{3+}) ions inside $(\text{Ni}^{2+}, \text{Cr}^{3+})\text{:}\gamma\text{-Ga}_2\text{O}_3$ NCs, enabling different energy transfers $\text{Yb}^{3+} \rightarrow \text{Ni}^{2+}$, $\text{Ni}^{2+} \rightarrow \text{Er}^{3+}$ and $\text{Er}^{3+} \rightarrow \text{Cr}^{3+}$.³⁵ A strategy was recently proposed to control the energy transfer between Er^{3+} and Ni^{2+} in dual-phases GCs by a selective incorporation of these active centers in LaF_3 and Ga_2O_3 NCs.³² A treatment at low temperature allows energy transfer between Er^{3+} and Ni^{2+} in Ga_2O_3 while a treatment at high temperature confines the two ions either in LaF_3 (Er^{3+}) or Ga_2O_3 (Ni^{2+}) and suppresses energy transfer. The latter partitioning can be reproduced with ultra-short laser pulse-induced crystallization giving a composite material with multicolor emissions. The thermometric performances for temperature sensing should also be boosted by temperature-dependent energy transfer based on co-doping between TM, RE and Ln^{3+} ions ($\text{Ln} = \text{Er}, \text{Ho}$).³⁶ Finally, the energy transfer from Cr^{3+} to Yb^{3+} in a YAG GC can be advantageously used to convert the VIS sunlight to NIR emission at 1030 nm with a high efficiency.³⁷

The development of luminescent materials in the near infra-red window has been extensively explored, achieving some promising results in the field of telecommunication and information technology (broadband amplifiers, tunable lasers, smart solid-state lighting)^{38,39}, in medical diagnostic and surgery (bioimaging, photodynamic therapy)^{40,41} and, in general, in

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the area of photoelectronics and photonics.^{14,3} Luminescence phenomenon originates from a wide optical gap present in the electronic band structure or from luminescent centers giving localized electronic states within the gap.^{42,24} The most common centers are TM or RE ions. TGCs doped with TM ions are potential effective candidates due to enhancement of the photoluminescence efficiency and very broad bands, depending on the ion environment and concentration and the excitation. These materials show broadband NIR emissions: for instance, Cr³⁺ ion,⁴³ Cr⁴⁺ and Ni²⁺ ions^{44,45,46} have wide emissions covering the 1200-1600 nm range, which is the region of interest to extend the optical communication transmission window. Indeed, the design of new fiber amplifiers or laser sources with a wide and flat gain bandwidth is a promising perspective to achieve more efficient wavelength division multiplexing transmission network giving higher capacity and faster bit rate to revolutionize future optical communications.^{38,39} Furthermore, novel light sources emitting in the NIR are highly desirable because this is the region of transparency of biological tissues (little autofluorescence and low transmission loss of optical signal).^{47,41}

Ni²⁺ ions are considered as the most promising choice of optical active center, when localized in octahedral coordination (⁶Ni²⁺), as they exhibit a broadband NIR emission with a high quantum yield and a long fluorescence lifetime and nickel has a stable valence state. Promising ⁶Ni²⁺-doped crystals have been selected and precipitated in several TGC systems: β-Ga₂O₃,^{48,49,32,50} different types of spinels,^{46,51,52,11,53,54} hollandite-type BaAl₂Ti₆O₁₆,⁵⁵ mullite (Ga₂O₃)₃(GeO₂)₂,⁴⁷ hexacelsian Ba_{0.808}(Al_{1.71}Si_{2.29})O₈⁴⁷ and perovskite SrTiO₃.⁵⁶ In particular, spinel-like compounds have attracted considerable attention as an appropriate crystalline host to insert ⁶Ni²⁺: AB₂O₄ spinels, in which A can be Mg,^{51,52} or Zn,¹¹ or a mixture of Mg and Zn,⁵³ and B can be Al or Ga, or spinel LiGa₅O₈.⁴⁶ The Ga₂O₃ addition in spinel NCs largely enhances the luminescent intensity of Ni²⁺,^{57,58} which could be ascribed to the strong preference of Ga³⁺ ions for tetrahedral site,⁵⁰ and the decrease of the mean frequency of phonon density of states in the spinel solid solutions.⁵⁷ The parent glass compositions suitable for crystallization of desired crystals are often synthesized with addition of titania and/or zirconia as nucleating agents.^{7,59,60,61,62,63,64} The incorporation of TiO₂, initially to promote volume nucleation, can also play a favorable role by drastically increasing both the luminescence intensity and lifetime. The reason of the enhancement is identified as the substitution of Ga³⁺ by Ni²⁺ + Ti⁴⁺ with Ti⁴⁺ being a charge compensator.⁵⁸

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Compared to state-of-the-art erbium-based optical amplifiers,⁵⁰ effective emission bandwidths are usually large and can reach 400 nm for Ni²⁺:Mg_xZn_{1-x}Ga₂O₄ TGC.⁶⁵ Internal fluorescence quantum efficiency (η) is slightly increased in TGCs compared to crystals (for instance, ~25% for Ni²⁺:ZnGa₂O₄ TGCs compared to ~18% for a pure Ni²⁺-doped ZnGa₂O₄ crystal).⁶⁶ High quantum efficiency are observed in TGCs containing Ni²⁺:ZnAl₂O₄ (~55%),⁴⁴ Ni²⁺:LiGa₅O₈ (~60%)⁴⁶ and Ni²⁺:BaAl₂Ti₆O₁₆ (~65%).^{55,67} Optical amplification can be limited due to low emission efficiency and high scattering loss,³ but a gain coefficient of 0.283 cm⁻¹ at 1300 nm (pumping: 980 nm, 1.12 W) was demonstrated in a Ni²⁺: β -Ga₂O₃ flat plate TGC.⁴⁹ For potential applications, TGCs must also be easily drawn into fibers with embedded ^[6]Ni²⁺-doped crystals. Fortunately, the corresponding fibers have been successfully fabricated and they are highly attractive for high-capacity optical communication devices.^{3,14,20}

An interesting advantage of TGC is the ability to manipulate the composite to tune the optical properties,³² such as the position and shape of the NIR emission band and the decay kinetics. This can be achieved by precise tailoring of the TGC composition to modify the local ligand field symmetry and strength,^{14,47} by controlling the nature and content of nucleating agents, or by adjusting the NiO concentration (typically 0.05-0.1 mol%)^{50,55,56,65,68,69} and heat-treatment conditions to control the nature, quantity and size of NCs.^{54,55,69,70} In the specific case of Ni²⁺:SrTiO₃ GC, the fluorescent lifetime increases with the NiO concentration up to 0.1 wt%. Above this latter value, the performances rapidly decrease due to the fluorescence quenching resulting from the energy transfer between close Ni²⁺ ions.⁵⁶ Interestingly, the Ni-doping level influences the domain size of a Ga-oxide phase, suggesting that Ni plays a relevant role in crystal nucleation and growth of the segregated nanophase.^{50,55}

Unlike trivalent RE ions, the *d-d* transition of Ni²⁺ strongly depends on the interaction of the 3d-electrons with the nearest neighbors and the local symmetry around Ni²⁺ ions, which is measured by the crystal field strength *Dq* determined from the absorption spectra.^{49,3} A long fluorescent lifetime and a broadband optical amplification have been observed only for a high crystal field strength.¹⁸ The effect of ligands on the absorption and emission spectra has been exploited in a TGC containing Ni²⁺: β -Ga₂O₃ NCs, by partial substitution of Ga³⁺ and O²⁻ with In³⁺ or F.⁷¹ By simply manipulating the optically inactive codopants, the emission can be rationally triggered from 1200 to 1400 nm, corresponding to the whole telecommunication window, and the decay rate can also be managed. The lifetimes of the longest component

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were estimated to be around 1537 μs (Ni^{2+}), 1351 μs ($\text{Ni}^{2+}/\text{In}^{3+}$), 639 μs ($\text{Ni}^{2+}/\text{F}^-$) and 332 μs ($\text{Ni}^{2+}/\text{F}^-/\text{In}^{3+}$), which correspond to the order of Dq . Interestingly, a spectral broadening is noticeable exclusively in F-doped samples, which is ascribed to the strong local ligand distortion after F⁻ addition. The IR luminescent band can be also purposely broadened by judiciously localized Ni^{2+} -doped TGCs in multiple octahedral local environments, either in a single crystalline phase with different octahedral sites or in a combination of different crystalline phases offering different octahedral positions.^{47,18} A significant inhomogeneous emission broadening was achieved with a bandwidth up to ~ 480 nm for TGC, associated with an extremely flat spectral shape covering the whole telecommunication low loss window (1260-1675 nm). This opens up new avenues for better engineering the spectral broadening.¹⁴

Cr^{4+} is another TM activator, having a broadband NIR emission in the optical communication window when it occupies a tetrahedral position.³ $^{4}\text{Cr}^{4+}$ ions can be found in substitution of Si or Ge in various crystals precipitated in TGCs like $\text{Ca}_2\text{Al}_2\text{SiO}_7$, Mg_2SiO_4 , $\text{Li}_x\text{Zn}_y\text{SiO}_4$ and Ca_2GeO_4 .^{9,43,45,72,73,74,75} The different ligand fields enable to tailor the NIR luminescence from 1130 to 1350 nm and the lifetime from 6 to 100 μs .⁹ However, the parasitic presence of Cr^{3+} and Cr^{6+} is difficult to avoid and, in practice, these ions will quench the NIR luminescence from Cr^{4+} and limit the observation of optical amplification. Nevertheless, an optical gain of 1.27 cm^{-1} (pumping: 808 nm, 0.8 W) was realized in a $\text{Cr}^{4+}:\text{Li}_2\text{ZnSiO}_4$ TGC, achieving a quantum yield of 17%.^{9,72} Some Cr^{4+} -doped TGCs were considered as an appropriate alternative for an active laser media (for instance $\text{Cr}^{4+}\text{-LiGaSiO}_4$ TGCs)⁷⁶ but no laser action has been demonstrated.

Other fields could benefit of the introduction of TM ions in GCs. Octahedrally coordinated Cr^{3+} ions have been successfully prepared in TGCs as lamp-pump laser active centers and as luminescent solar concentrators by doping various crystalline phases:²⁶ spinels, mullite, β -quartz solid solution, and ZrO_2 .⁶² Finally, a red emission of $^{6}\text{Mn}^{4+}:\text{Li}_2\text{Ge}_4\text{O}_9$ crystals has been obtained in a $20\text{Li}_2\text{O-}80\text{GeO}_2\text{-}x\text{MnO}_2$ GCs.⁷⁷ A red-blue color can be tuned with Mn^{4+} concentration and remarkable quantum yield of 40% has been observed. However, the photoluminescence rapidly drops with temperature around 100 °C.

The design of novel long persistent phosphors (LPPs) stimulates intense research with widespread applications and commercializations, as dark/night environment vision materials for security route signage, identification markers, displays or medical diagnostics.^{78,79,80}

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Several TGCs have been designed with Cr^{3+} and Mn^{2+} ions precipitated in spinel $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ($0 \leq x \leq 1$) or LiGa_5O_8 to realize materials that can emit for multiple hours after the excitation stoppage.^{46,81,82,83,84} Mn^{2+} ions show remarkable emissions from red to orange and green with decreasing crystal fields.⁸⁵ This property has been successfully exploited in $\text{Mn}^{2+}:\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ NCs to obtain controllable, multi-color persistent luminescence, giving the possibility to change the crystal field around Mn^{2+} with different devitrification processes upon annealing.⁸¹ GCs containing $^{61}\text{Cr}^{3+}:\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ NCs have been considered for red phosphors design as they exhibit persistent red-luminescence afterglow and temperature sensing properties.^{46,83} The substitution of Ga^{3+} by Ge^{4+} and Zn^{2+} yields brighter and longer persistence luminescence due to a spinel inversion: Ga^{3+} ions replace Zn^{2+} in tetrahedral sites forming anti-site defects ($\text{Ga}^{\bullet}_{\text{Zn}}$) that are responsible for distortion of $^{61}\text{Cr}^{3+}$ neighborhood and for enhancement of Cr^{3+} emission.⁸² The red long-lasting luminescence properties is further improved (great enhancement of the brightness and decay time) by introducing Ge and Sn to the spinel structure. The substitution creates distorted $^{61}\text{Cr}^{3+}$ sites surrounded by octahedral Ge and Sn positive substitutional defects that likely act as new efficient traps.⁸² Nanocrystalline high-albite $\text{Mn}^{2+}:\text{Na}(\text{Al},\text{Ga})\text{Ge}_3\text{O}_8$ have been precipitated in sodium gallium aluminum germanate glasses.⁴¹ Even with small NC sizes (<50 nm), red to NIR persistent luminescence cover the 600-800 nm region corresponding to that of transparency for biological tissues (650 - 1300 nm) with an afterglow duration lasting more than 100 hours. These materials are envisaged for applications to in vivo bioimaging or photodynamic tumor therapy. The persistent luminescent TGC embedded with $\text{Mn}^{2+}:\text{ZnGa}_2\text{O}_4$ shows an interesting pressure sensitive green luminescence. Based on this unique feature, the new concept of smart active glass has been proposed and TM ions have been demonstrated to be promising candidates for the related applications.⁸⁶

Materials having high temperature dependency of their luminescence lifetime have attracted much attention as candidate optical temperature sensors in electro-magnetically and/or thermally harsh environments.⁸⁷ TGCs are attractive as they can offer continuous real-time reading, high spatial resolution and high temperature sensitivity. Recently, a TGC with a chromium partitioning of a majority Cr^{4+} in a ZnO-SrO-SiO_2 glass and a minority Cr^{3+} in a ZnAl_2O_4 crystalline sub-phase was obtained. A high temperature sensitivity ($1.72\% \text{ K}^{-1}$) was achieved for Cr^{4+} compared to Cr^{3+} ($0.83\% \text{ K}^{-1}$), which is also significantly higher than typical

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Cr³⁺-based optical thermometric sensing materials.^{87,88} Multi-modal temperature sensing is a promising route to generate a large temperature range with high sensitivity. This approach is currently exploited by the selective incorporation of RE, Ln³⁺ or TM ions into different NCs.⁸⁹ For instance, Ln³⁺ and Cr³⁺ ions incorporated into GdF₃ and Ga₂O₃ nanophases via controlled glass crystallization of TGCs leads to a much improve temperature sensitivity (up to 15-22% K⁻¹).⁹⁰

Passive Q-switching (PQS) is an optical component inserted into the laser cavity to generate short laser pulse duration from nano- to subnano-seconds, allowing fabrication of compact solid-state mini-lasers and microchip lasers.^{8,91} It consists of a saturable absorber (SA) for which the absorption decreases with increasing fluence of the incident radiation (photobleaching effect).⁹¹ Eye-safe Er lasers have emission wavelengths in the region 1500-1700 nm, thus requiring a SA having an absorption band that matches the range from visible to Middle-IR (MIR) wavelengths. Additionally, low saturation fluence, fast recovery time of the initial absorption, low non-saturable losses and high laser damage threshold are required.⁴ TGCs containing tetrahedrally coordinated TM ions (Co²⁺, V³⁺, Cr⁴⁺, etc.) have been widely considered as SAs for NIR lasers,^{3,8,91} as they exhibit strong nonlinear absorption of their broad absorption bands in the NIR-MIR region. This is the case of ^[4]Co²⁺ for which the broadband absorption overlaps the ~1540 nm emission of Er³⁺-doped in crystal and glass lasers. TGCs based on different nanosized spinels doped with Co²⁺ were developed in aluminosilicate systems with interesting performances.^{92,93,94,95} For instance, a saturable absorption has been reported for TGCs containing both Co²⁺:β-Zn₂SiO₄ and Co²⁺:ZnO NCs.⁹¹ The absorption characteristics (low saturation fluence of 0.75 J.cm⁻² at 1540 nm, short recovery time of 830 ns, and high laser damage threshold of 14 J.cm⁻²) enable this TGC to be a SA solution for diode-pumped Er,Yb:glass lasers, resulting in the generation of Q-switched pulse of 0.77 mJ energy with a pulse duration of 45 ns. Similar properties were also demonstrated for a TGC containing Co²⁺:γ-Ga₂O₃ NCs, with the shortest (1300 nm) and longest wavelength edge (1780 nm) among the known cobalt-doped TGC materials.^{96,97} However, ultrafast pulse compression into ps or fs range are not possible with TM ions as their 3d level lifetime are typically of the order of micro- to nanoseconds. Quantum-dot glasses are best candidates for such fast response times.³ The idea of optical modulation component has been successfully extended to other types of TM ions or TGCs. TGCs containing Cr⁴⁺:Mg₂SiO₄ NCs were successfully fabricated based on a local chemistry engineering strategy. This candidate helps to achieve pulse laser

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with the shortest wavelength edge (1060 nm, 176 ns) among TM-doped TGC materials. Importantly, a wide frequency range from 800 to 1200 nm can also be expected based on the unique broadband feature of the constructed TGCs.⁹⁸ In addition, co-doping of Co^{2+} with Er^{3+} would be attractive because a gain medium and a SA could be combined, which would appreciably simplify the laser cavity design. A good candidate could be a TGC that selectively incorporates Co^{2+} and Er^{3+} ions in different phases, ZnAl_2O_4 and YF_3 , respectively.⁹⁹ The isolation of the two ions is useful to suppress energy transfer between the ions while maintaining the efficient SA characteristics of $\text{Co}^{2+}:\text{ZnAl}_2\text{O}_4$ and the excellent luminescent performance of $\text{Er}^{3+}:\text{YF}_3$.

The effect of the TM ions doping on the IR emissivity of GCs has been particularly considered for energy saving solutions in architecture.³ Titanium slags and fly ashes were used as raw materials to obtain a GC containing a cordierite solid solution incorporating iron ions.¹³ The presence of $\text{Fe}^{2+}/\text{Fe}^{3+}$ impurities acting as lattice defects improved properties with a high IR irradiance and a low thermal expansion coefficient. Further it was demonstrated that a GC synthesized by using pure oxides as the starting materials improve further the material performances by increasing the waveband IR emissivity.^{100,101}

Lastly, TM-doped GCs can also have significant contributions as thermal shock-resistant color filters for laser systems and high-power light sources.^{92,4} TGCs with a low coefficient of thermal expansion have been developed in the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. By varying the heat-treatment temperature, the TM optically active ions can be favored in different NCs, producing various tints (violet, blue, green, red, purple, and neutral). For instance Ni^{2+} ions in spinel NCs give a green color while, in β -quartz solid solution, these ions give purple and red tints.¹⁰²

Though great successes have been made, challenges and prospects may be addressed in the future for the development of TM activated TGCs:

- (i) Theoretically, various types of crystalline phases can be potentially precipitated inside TGCs. Currently, the matrixes suitable for hosting TM dopants are still highly limited. Therefore, exploration of new categories of TM-doped TGCs is considered as one of the main tasks in future research.
- (ii) The co-doping of TMs and REs ions has promising applications and offer a rich variety of tunable properties for active, passive and up conversion devices, often based on

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energy transfer processes. This combination of active ions still requires important efforts to be developed and explored.

- (iii) As compared with single crystals, the main disadvantage of TGCs is that active ions are not only concentrated within the desired phase, but they can remain in the parent glass or at the glass-crystal interfaces, resulting to optical losses of the material.⁹² Thus, new strategies to confine TM dopants into crystalline phases in TGCs are expected to be highly beneficial for upgrading their optical performance.
- (iv) As a typical composite, the volume ratio of crystalline phase and glass matrix dominates the optical performance of TM activated TGCs. On one hand, the content of crystalline phases should be increased as high as possible to enhance the optical activity of TGCs. On the other hand, the increase of the crystalline volume fraction in glass matrix may cause undesired optical scattering, which may deteriorate the optical quality of TGCs. Thus, finding the optimal balance relies strictly on a deep insight into the fundamental light-matter interactions in TM activated TGCs and a high level of understanding and control of the processing conditions.

All these future directions should stimulate intense fundamental research to discover new systems, have a rational design of these composite materials and develop new functionalities that could improve current performances or initiate novel applications.

AUTHOR'S CONTRIBUTIONS

All authors contributed equally to this work.

DATA AVAILABILITY

Data sharing not applicable – no new data generated

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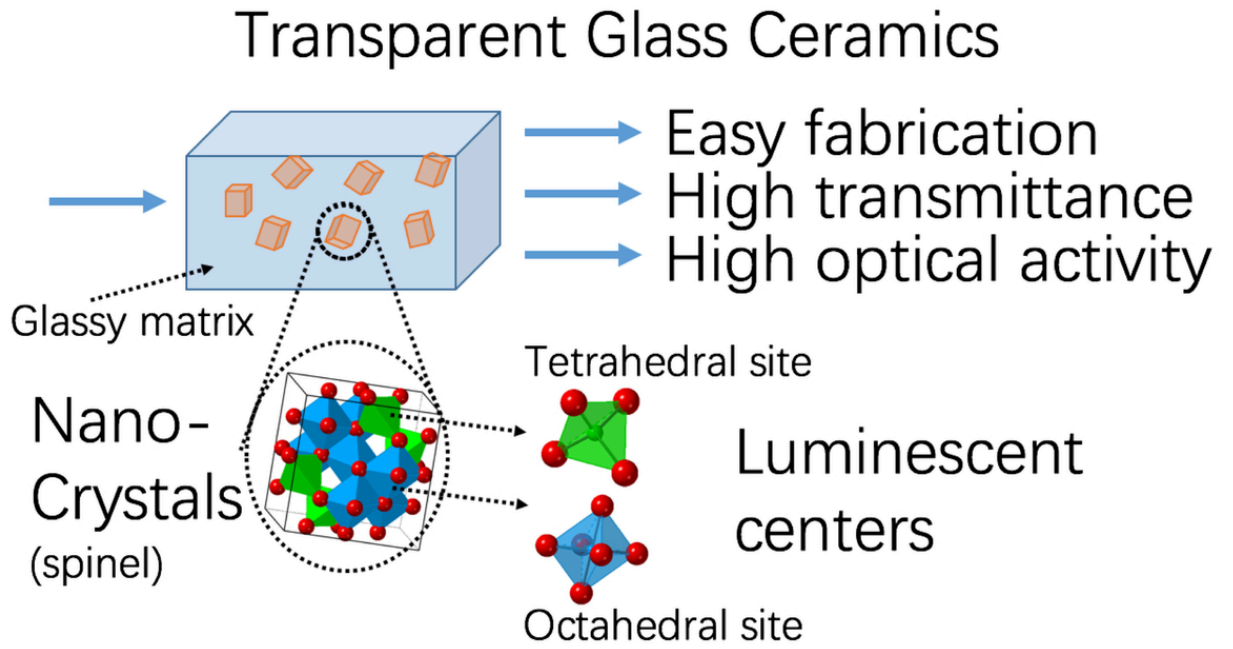
FIGURE CAPTION

Figure 1: Schematic diagram of TGCs containing spinel nanocrystals with octahedral and tetrahedral sites available for doping with TM ions (adapted from Zhuang et al.⁹). Reprinted with permission from Zhuang et al. *NPG Asia Materials* **97**, 3519 (2014). Copyright (2014), John Wiley and Sons.

Figure 2: (a) HAADF-STEM glass micrograph revealing the presence of mesoscale heterogeneities in a $\text{Li}_2\text{O-Ta}_2\text{O}_5\text{-Al}_2\text{O}_3\text{-SiO}_2$ glass. (b) Line profile of the contrast line in a. (c) X-ray Diffraction patterns of the glass, the composite GC containing LiTaO_3 and $\text{LiAlSi}_2\text{O}_6$ crystals. (d) Optical cross-section micrograph of the multiphase fiber. (e and f) Raman mapping in the core region of the fiber for the bands at 593 cm^{-1} and 486 cm^{-1} corresponding to the fingerprints of LiTaO_3 and $\text{LiAlSi}_2\text{O}_6$ crystals, respectively. (g) Photograph of the activated fiber. (h and i) Energy Dispersive X-ray mappings of Ta and Al elements in the core region of the activated fiber. Reprinted with permission from Yu et al. *NPG Asia Materials* **8**, e318 (2016). Copyright (2016) Springer Nature.

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