OPTOELECTRONICS LETTERS Vol.13 No.5, 1 September 2017

Nd^{3+} doped fluorochlorozirconate glass: 3.9 μm MIR emission properties and energy transfer*

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(Received 11 May 2017; Revised 14 June 2017)

The Nd^{3+} doped fluorochlorozirconate (FCZ) glass was prepared by melt-quenching method. The 3.9 μm emission from Nd^{3+} ions is attributed to the two-photon absorption process. The strong emission transition at 3.9 μm fluorescence peak intensity, corresponding to the $^4G_{11/2}\rightarrow{}^2K_{13/2}$ transition, is directly proportional to the NaCl concentration. With the increase of the Cl^- ions amount, the mid-infrared (MIR) luminescent intensity is significantly enhanced. Additionally, the Judd-Ofelt (J-O) parameter Ω_2 is larger than that of the fluorozirconate (FZ) glass, which indicates the covalency of the bond between RE ions and ligand is stronger as Cl^- ions substitution of F^- ions in chloride FZ glass. The X-ray diffraction (XRD) patterns show that the amorphous glassy state keeps the FZ glass network structure. In brief, the advantageous spectroscopic characteristics make the Nd^{3+}-doped FCZ glass be a promising candidate for application of 3.9 μm emission.

Document code: A **Article ID:** 1673-1905(2017)05-0344-5

DOI https://doi.org/10.1007/s11801-017-7107-5

Mid-infrared (MIR) lasers have attracted tremendous scientific and technological interests owing to their wide applications in medicine, military counter-measures, light detection and ranging, and sensing[1,2]. MIR lasers can be achieved by many methods, such as the nonlinear laser[3], semiconductor[4], gas and rare earth doped material[5]. Particularly, the rare earth doped fluoride and sulfide glasses have served as the gain media for MIR emission[6,7]. Fluorozirconate (FZ) glasses have many inherent advantages of low phonon energy, high solubility of rare earth ions, high transmittance from the visible to MIR region[8,9]. The substitution of chloride or bromide for fluorine in FZ glasses around the rare earth ions can change the glass properties due to the ligand field symmetry difference in F-Cl/F-Br mixed-anion glasses. The presence of chlorides or bromides helps to improve the fluorescence emission efficiency because the phonon energy of chlorides or bromides is smaller than that of the fluorides[10]. Hence, the substitution of chloride or bromide for fluorine in FZ glass can obviously improve the MIR luminescent properties of the material[11].

There are multiple absorption levels of Nd^{3+} in the near infrared (NIR) region, corresponding to 1 052 nm, 1 064 nm and 1.3 μm. For this reason, Nd^{3+} ion doped crystals and glasses were studied extensively under 808 nm and 793 nm laser diode excitation in order to develop high power NIR solid state lasers[12]. The effect of Nd^{3+} ion doping on the NIR properties of rare-earth-doped silica-phosphates, germanates, vanadates, tellurite and fluoride glasses has been reported. M. Klimczak et al[13] reported the orange and IR to violet up-conversion processes in Nd:ZBLAN glasses. Bingchu Mei et al[14] reported Nd, Y: CaF_2 transparent ceramics and found three main emission bands of 850—950 nm, 1 000—1 100 nm and 1 300—1 400 nm correspond to $^4F_{3/2}\rightarrow{}^4I_{9/2}$, $^4F_{3/2}\rightarrow{}^4I_{11/2}$ and $^4F_{3/2}\rightarrow{}^4I_{13/2}$ transitions, respectively. However, few investigations have been reported about the MIR emission of the Nd^{3+} ion doped fluorochlorozirconate (FCZ) glass.

In this paper, the Nd^{3+} doped FCZ glass at 3.9 μm emission is proposed. We investigate its MIR luminescent behavior and energy transfer characteristics. The Nd^{3+} ions doped FCZ glass was prepared by melt-quenching method. By introducing the Cl^- ions in the FZ, the emission intensity centered at 3.9 μm can be effectively improved. As the Cl^- ions amount increases, the MIR luminescent intensity of Nd^{3+} doped FCZ glass enhances, but the NIR luminescent intensity declines.

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* This work has been supported by the National High Technology Research and Development Program of China (No.2013AA014201), the Natural Science Foundation of Tianjin (Nos.11JCYBJC00300, 14JCZDJC31200, 15JCYBJC16700 and 15JCYBJC16800), the National Key Foundation for Exploring Scientific Instrument of China (No.2014YQ120351), and International Cooperation Program from Science and Technology of Tianjin (No.14RCGHGX00872).

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Moreover, the Nd^{3+} local symmetry decreases due to the increased intensity parameter Ω_2. The MIR fluorescence intensity enhances significantly when the Nd^{3+} concentration is 1.5% in molar ratio.

The compositions of the samples are listed in Tab.1. The FCZ glasses have the following compositions in molar ratio: $53ZrF_4$-$20BaF_2$-$4LaF_3$-$3AlF_3$-$(20-x)$NaF-xNaF-$y NdCl_3 \cdot 6H_2O$, where x=0, 5, 10, 15 and 20, and y=0.5, 1, 1.5 and 2. The FCZ glasses were prepared by melt-quenching technique with high-purity powder. They were firstly heated in muffle furnace under 800 °C for 30 min. Then, the samples were annealed for about 2 h at 200 °C to remove the thermal stress before cooling down to room temperature. At last, the annealed samples were polished to the size of 10 mm×10 mm×2 mm for spectroscopic property measurement. The crystal structure of the samples was measured using a Rigaku 2500/PC X-ray diffractometer with Cu-Kα radiation source (0.154 2 nm) at 40 kV and 150 mA. The absorption spectra were obtained by a Hitachi UV-4100 type ultraviolet visible NIR fluorescence spectrophotometer. The intermediate infrared emission spectra were captured using an Acton Advanced SP2500A spectrometer (Princeton Instruments). The emission intensity of the samples was detected by a liquid nitrogen cooled detector upon excitation at the wavelength of 793 nm (OPX-MMLD-1500). There is a 1.75 μm and 2.9 μm filter (BP1750/60K, BP2900/60K, transmittance>80%).

Fig.1 shows the XRD patterns of the samples, and all the samples have two dispersion peaks at 26° and 47°, respectively, indicating that all the samples are amorphous glassy state. This shows that all the FCZ glasses have good glass-forming ability and do not show devitrification tendencies[15]. Soga K[16] previously reported that the Cl^- ions mainly replace F^- ions related to the network modifier in the FZ, and will not affect the FZ glass network structure. So the FCZ glass has similar network structure to the FZ glass.

Tab.1 Compositions of glass samples

Number of samples	ZrF_4 (%)	BaF_2 (%)	LaF_3 (%)	AlF_3 (%)	NaF (%)	NaCl (%)	$NdCl_3 \cdot 6H_2O$ (%)
S0	53	20	4	3	20	0	0
S1	53	20	4	3	5	15	0.5
S2	53	20	4	3	5	15	1
S3	53	20	4	3	5	15	1.5
S4	53	20	4	3	5	15	2
S5	53	20	4	3	20	0	1.5
S6	53	20	4	3	15	5	1.5
S7	53	20	4	3	10	10	1.5
S8	53	20	4	3	0	20	1.5

The absorption spectra of the samples at room temperature in the wavelength region from 400 nm to 1 800 nm are indicated in Fig.2. They correspond to the transitions starting from the $^4I_{9/2}$ ground state to the higher levels of $^4I_{15/2}$, $^4F_{5/2}$, $^4F7_{/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{9/2}$, $^4G_{5/2}$, $^4G_{7/2}$, $^4G_{9/2}$ and $^2K_{13/2}$, respectively. The absorption band centered at 793 nm indicates that the FCZ glasses can be efficiently excited by 793 nm pump.

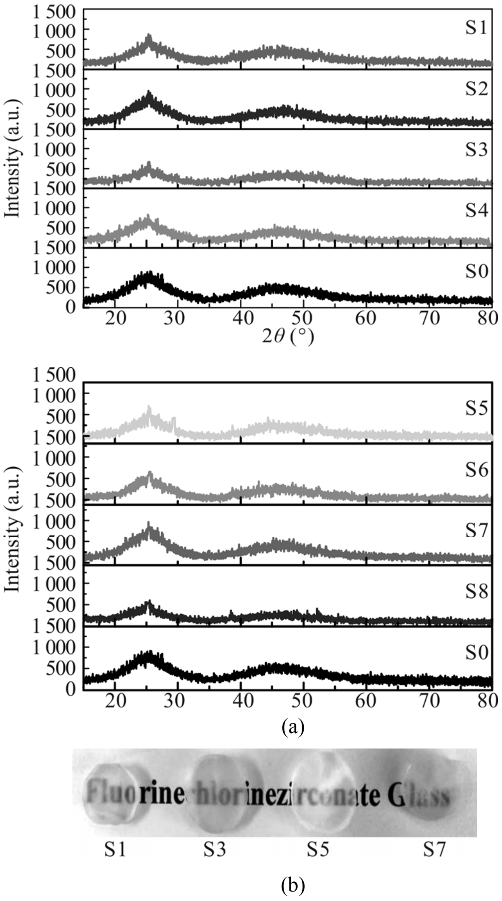


Fig.1 (a) XRD patterns of S0 to S8 glasses; (b) Photograph of the transparent glasses (10 mm thick)

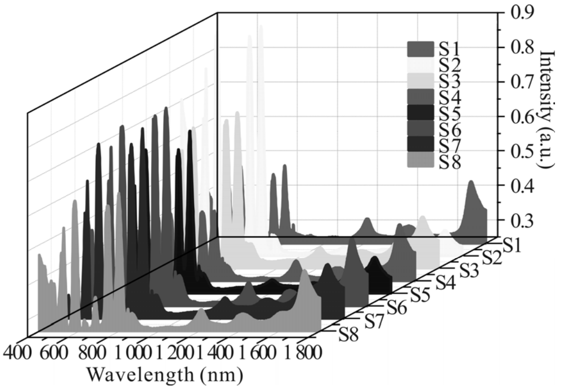


Fig.2 Absorption spectra of the samples at room temperature

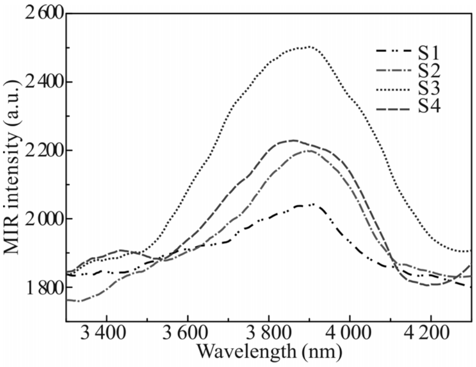
The radiative transition parameters with the $4f^n$ configuration of the Nd^{3+} ions can be analyzed using the Judd-Ofelt (J-O) theory and the measured absorption spectra[19,20]. Tab.2 shows the J-O parameters for the Nd^{3+}:$^4G_{11/2} \rightarrow {^2K_{13/2}}$ transition of the samples. Ω_2 indicates that the amount of the covalent bond is strongly dependent on the local environment of the ion sites, Ω_6 depends less on the environment than Ω_2, but is more dependent on the overlap integrals of the 4f and 5d orbits[21]. In FCZ glass, J-O parameters are higher than those of FZ glass, which indicates a higher covalency and lower symmetry. Weber et al[22] have reported that the increase of J-O parameters is attributed to the replacement of the F^- ions by the Cl^- ions in glass due to the higher polarization ability of Cl^- ions than F^- ions. Additionally, the J-O parameters depend on the host matrix and can provide information on the local structure for bonding in the vicinity of RE ions[23]. The Ω_2 is larger than that of FZ glass, which indicates the covalency of the bond between RE ions and ligand is stronger as Cl^- ions substitution of F^- ions in chloride FZ glass. The values of Ω_6 for the chloride FZ samples are higher than those of the unmodified FZ, which indicates that the local basicity of the modified FZ glasses is lower. The spectroscopic quality factor X ($=\Omega_4/\Omega_6$) is important in predicting the behavior of various lasing transitions in a given matrix[24,25]. In Tab.2, the prepared FCZ glass has the largest value of X, which is favorable for good optical and laser materials.

Tab.2 J-O parameters Ω_t of Nd^{3+} doped FCZ glasses

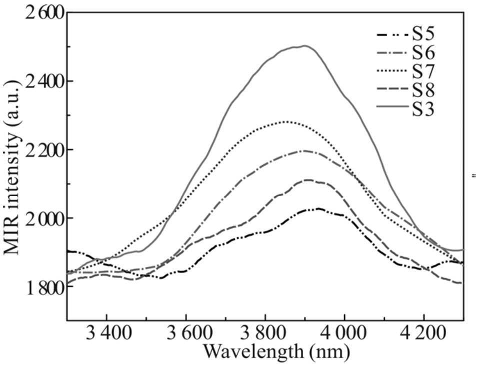
Samples	Ω_2 ($\times10^{-20}$ cm^{-2})	Ω_4 ($\times10^{-20}$ cm^{-2})	Ω_6 ($\times10^{-20}$ cm^{-2})	X	Reference
S1	3.73	1.70	1.08	1.57	This study
S2	3.82	1.73	1.20	1.44	
S3	4.32	1.78	1.33	1.34	
S4	3.75	1.65	1.27	1.30	
S5	3.21	1.61	1.01	1.59	
S6	3.58	1.76	1.25	1.41	
S7	3.96	1.85	1.30	1.42	
S8	9.92	1.79	1.21	1.48	
Silicate	4.23	1.04	0.81	1.28	[17]
Phosphate	3.87	1.27	1.11	1.14	[18]

Fig.3(a) shows the MIR spectra of S1, S2, S3 and S4 doped with 15% (molar ration) Cl^- ions and the luminous intensity change under different Nd^{3+} ion concentrations. It shows that the intensities of the $^4G_{11/2}\rightarrow{}^2K_{13/2}$ transitions change as a function of Nd^{3+} concentration. The fluorescence intensity reaches the maximum when the Nd^{3+} concentration is 1.5 mol. However, the intensity dramatically decreases as the Nd^{3+} concentration is 2 mol, because the luminescence will be quenched by energy transfer processes due to the interactions between Nd^{3+} ions at higher Nd^{3+} concentration. The peak position has a slight shift, which indicates the interactions of ions between Nd^{3+} sites.

Fig.3(b) shows the MIR spectra of S5, S6, S7, S3 and S8 doped with 1.5 mol Nd^{3+} ions. As can be seen, the luminous intensity excited at the wavelength of 793 nm changes with the variation of the Cl^- ions concentration. For the samples of S5, S6, S7, S3 and S8, the emission bands are inhomogeneously broadened, and the fluorescence peaks do not show small shift, due to the site-to-site variation in the local ligand field. It is worth noting that the strong emission transition at 3.9 μm fluorescence peak intensity and the $^4G_{11/2}\rightarrow{}^2K_{13/2}$ transition of the Nd^{3+} ions are far different, which is directly proportional to the NaCl concentration. There is a 1.75 μm and 2.9 μm filter. The strong enhancement of fluorescence after doping Cl^- ions clearly demonstrates that Cl^- ions change the local environment around Nd^{3+} ions. Doping Cl^- ions is available to accommodate the Nd^{3+} ions in a more energetically favorable environment. It indicates the addition of Cl^- ions will not change the absorption of the matrix in MIR region. The intensity of 3.9 μm radiation is improved with increasing the Cl^- ions concentration. Moreover, its tendency is the same as Ω_2 calculated by J-O theory. Hence, the J-O theory can be used to explain the luminescence mechanism of the FCZ glass in MIR region sufficiently.



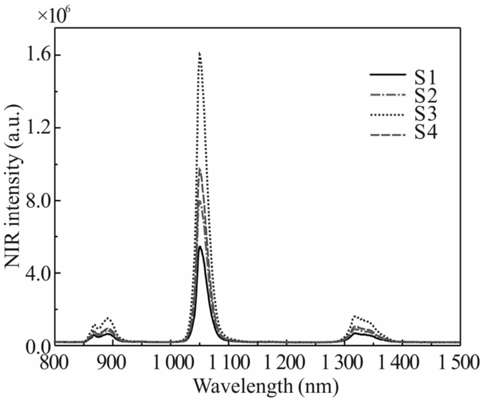
(a) S1—S4



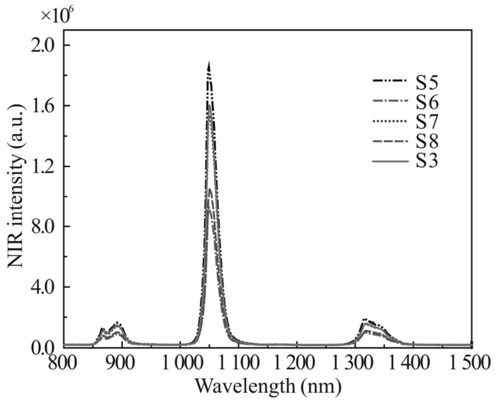
(b) S3, S5—S8

Fig.3 3.9 μm emissions of the FCZ samples under 793 nm excitation

Fig.4(a) shows the NIR emission spectra of the Nd^{3+} doped FCZ glass samples with different Nd^{3+} doping molar concentrations under 793 nm excitation. The strong NIR emission intensities of Nd^{3+} doped bands centered at 890 nm, 1 049 nm and 1 330 nm are observed in the FCZ glass. As can be seen from Fig.4(a), with the increase of Nd^{3+} ion concentration, the NIR luminous intensity increases at first and then decreases. The fluorescence intensity reaches the maximum when the Nd^{3+} concentration is 1.5 mol. Here the decrease of the luminous intensity is caused by the concentration quenching. Fig.4(b) shows that the photoluminescence (PL) spectra doped with 1.5 mol Nd^{3+} ions and the luminous intensity change under different Cl^- ion concentrations. With the increase of the Cl^- ions concentration, there is no obvious difference in the emission location, but the emission intensity obviously declines, which demonstrates that the introduction of Cl^- ions does not promote the near infrared emission. Additionally, we can see from the absorption spectra, the sample of S5 does not contain Cl^- ions, so the absorption intensity is less than that of the others. Hence with the increase of the Cl^- ions, the NIR emission is weakened.



(a) S1—S4



(b) S3, S5—S8

Fig.4 NIR emissions of the FCZ samples under 793 nm excitation

In the MIR and NIR fluorescence spectra, the samples of S1, S2, S3 and S4 have the same fluorescence tendency, which have the same trend with the J-O fitting to get the value of Ω_2. It is noted that Ω_2 enlarges with the increase of the Cl^- ions concentration, which results in the decrease of the Nd^{3+} local symmetry.

On the basis of energy level diagram of Nd^{3+}, the NIR and MIR mechanisms are analyzed and illustrated in Fig.5. For the MIR emissions, the Nd^{3+} ions pumped by a 793 nm laser are excited to the $^4F_{7/2}$ level through the ground state absorption (GSA). When it is excited to the $^2P_{3/2}$ state, some of the Nd^{3+} ions are relaxed nonradiatively to lower level of $^4G_{11/2}$, and the other Nd^{3+} ions are relaxed radiatively to $^2K_{13/2}$ level, resulting in the emission spectra centered at 3.9 μm. Based on the excited state absorption (ESA) mechanism[26], Nd^{3+} ions are firstly pumped to $^4F_{7/2}$ level by absorbing 793 nm photons, and some of the Nd^{3+} ions are relaxed radiatively to lower levels of $^4I_{13/2}$, $^4I_{11/2}$ and $^4I_{9/2}$ with relatively stable states. It has a quite long lifetime and thus the electron has a great chance to absorb a second 793 nm photon before the electron further decays downwards.

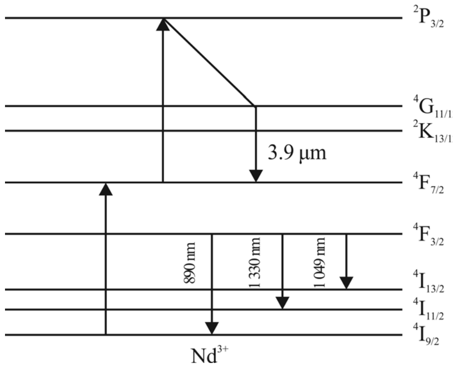


Fig.5 Energy-level scheme describing the NIR and MIR emissions from the Nd^{3+} doped FCZ glasses upon an excitation at 793 nm

The Nd^{3+} ions doped FCZ glass has been successfully fabricated by melt-quenching technique. All the samples are amorphous glassy state with two dispersion peaks at 26° and 47°, respectively. The addition of Cl^- ions does not affect the FZ glass network structure, but decreases the local symmetry of Nd^{3+} ions. We find that the introduction of the Cl^- ions can strengthen the MIR luminous intensity of the FCZ glass, especially at 3.9 μm emission, but will weaken the NIR luminous intensity.

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