

Effect of Fe impurity on the optical loss of Nd-doped phosphate laser glass

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The optical loss coefficient at 1053-nm wavelength, influenced by Fe ions in N31-type Nd-doped phosphate laser glass, was determined precisely and analyzed in detail. It is found that the optical loss coefficient per unit of Fe concentration ($\text{cm}^{-1}/\text{ppmw}$) increases with Fe concentration in the range of 0–300 ppmw, but it approaches a constant as the Fe concentration is larger than 300 ppmw. Such a concentration effect is due to a shift in the redox equilibrium between Fe^{3+} and Fe^{2+} ions in the glass. The effect of oxygen pressure, temperature, and variable valence states of other metal ions in glass samples on the optical loss is also discussed.

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The Nd^{3+} -based laser at about 1053 nm is one of the interesting laser systems due to its high efficiency and large number of applications. Nd-doped phosphate laser glasses are used in all major high-energy solid-state laser systems in the US, Europe, and Asia as the gain medium. For example, the 1.8 MJ, 500 TW solid-state laser currently under construction at Lawrence Livermore National Laboratory (LLNL) requires over 3000 meter-size Nd-doped phosphate glasses. Nd-doped phosphate glasses are widely used because they have excellent energy storage and extraction characteristics and can be made in large sizes, with high optical quality and free of inclusions^[1].

Nowadays, N31-type Nd-doped phosphate glasses are used in high-energy solid-state laser systems in China. It is well known that the impurities can degrade the laser performance of Nd-doped phosphate glass by increasing its optical loss. The optical loss of Nd-doped phosphate glass is mainly due to the strong absorption loss of transition metal ions at laser wavelength of 1053 nm, even at contaminant concentrations in ppmw level. Currently, spectroscopic properties of Nd-doped phosphate laser glasses influenced by impurities including OH, transition metal ions and rare earth ions are reported in detail by LLNL^[1–6]. In this work we investigate the influence of Fe ions on the optical loss at 1053 nm of N31-type Nd-doped phosphate glass because Fe contamination exists in raw materials and melting process. It is found that the higher optical loss of N31-type Nd-doped phosphate laser glasses is mainly due to Fe impurity widely existing in the glasses. Therefore, Fe impurity should be kept carefully under control in the raw materials used and melting process. It is an important way to increase the finished product probability.

The net gain of a glass laser amplifier is a function of the gain coefficient and the combined passive transmission losses in the glass due to impurity absorption. The total optical loss, α , in laser glass at 1053 nm is a sum of contributions

$$\alpha = \alpha_{\text{Nd}} + \alpha_{\text{scatter}} + \alpha_{\text{Fe}} + \sum_{i=1}^n \alpha_{\text{impurities}}, \quad (1)$$

where α_{Nd} is the absorption loss coefficient (cm^{-1}) due to Nd^{3+} ion, α_{scatter} is the optical loss coefficient (cm^{-1}) due to scattering by defects and inclusions (such as bubbles and Pt particles), α_{Fe} is the absorption loss coefficient (cm^{-1}) due to Fe impurity, and $\sum_{i=1}^n \alpha_{\text{impurities}}$ is the absorption loss coefficient (cm^{-1}) due to other transition metal ions and rare earth ions impurities. Scatter losses can be negligible because of highly polished surfaces and free of inclusions or bubbles in the glass samples. Generally the scatter loss $< 10^{-5} \text{ cm}^{-1}$ ^[2,3]. Thus, the total optical loss is mainly due to Nd^{3+} ion and impurities. Nd^{3+} absorption loss coefficient for ${}^4I_{11/2}$ to ${}^4F_{3/2}$ transition at room temperature in phosphate glasses can be described using the empirical expression^[2,3]

$$\alpha_{\text{Nd}}(T) = 1.03 \times 10^{-20} [\text{Nd}^{3+}] \exp\left(\frac{-2576}{T}\right), \quad (2)$$

where $\alpha_{\text{Nd}}(T)$ is the temperature-dependent absorption coefficient (cm^{-1}) and $[\text{Nd}^{3+}]$ is the Nd ion concentration (ion/cm^3). In this study, Nd^{3+} absorption loss is nearly a constant, because the Nd^{3+} concentration remains constant in all glass samples. The optical loss of the sample without Fe doping, which remains nearly a constant, is caused by Nd^{3+} ion, other transition metal ions and rare earth ions impurities. Because the glass samples are melted with the same melting condition and the same raw materials. The absorption loss from other transition metal ions and rare earth ions impurities in all glass samples also remains a constant. Thus, the optical loss coefficient of Fe at 1053 nm can be determined for samples with various Fe concentrations, taking the sample without Fe as a standard.

The N31-type laser glass samples were prepared from high purity raw materials (Cu, Co, Ni, Cr, $V < 0.5$ ppmw) with the following weight (%) composition: (60–70) P_2O_5 -(9–10) Al_2O_3 -(7–8) K_2O -(11–12) BaO -3 Nd_2O_3 - $x\text{Fe}_3\text{O}_4$, $x = 0$ –1000 ppmw.

In brief, the glass samples were melted in Pt crucible and homogenized by stirring. The melting processes were bubbled with both O_2 and Cl_2 to remove OH groups from the raw materials. The samples were first melted at 1100

°C and then refined for 5 hours at 1380 °C to remove bubble. The liquid was then cooled to 900 °C and cast into a mold. The samples were annealed to reduce residual stress at a rate of about 30 °C/h starting from about 500 °C and ending near room temperature.

The Nd concentration and Fe concentration of each sample were determined by analysis of fully dissolved glass solutions with inductively coupled plasma (ICP) emission spectrometry (Thermo Iris Intrepid). After acid cleaning, the samples were dissolved by perchloric acid (HClO₄) and hydrofluoric acid (HF). The measured Nd concentration is in close agreement with the mean composition (±5%). The measured Fe concentration can quantify in 10 ppmw range.

Absorbance measurements were carried out with a spectrophotometer (Perkin-Elmer 900UV/VIS/NIR) using polished samples with 50-mm thickness.

Static optical loss measurements were carried out by a self-built device using polished round stick samples with $\phi 8 \times 190$ mm. The samples without striae and bubbles were used for measurement. The measurement error is $\leq \pm 1 \times 10^{-4}$ (cm⁻¹).

The measured absorbance spectra between 500—1100 nm for 4 typical samples containing various Fe concentrations are shown in Fig. 1. It shows that 5 characteristics of Nd³⁺ absorption bands at about 870, 800, 750, 580, 530 nm are due to the Nd³⁺ transition from the ⁴I_{9/2} ground state to states of ⁴F_{3/2}; ⁴F_{5/2}, ²H_{9/2}; ⁴F_{7/2}, ⁴S_{3/2}; ²G_{7/2}, ⁴G_{5/2} and ²K_{13/2}, ⁴G_{7/2}, ²G_{9/2}, respectively. It is found that the optical absorption cross-section of Nd³⁺ is hardly influenced by Fe concentrations. However, the absorption near 1053 nm corresponding to the ⁴F_{3/2}-⁴I_{11/2} transition is influenced sharply by Fe (see Fig. 2). Figure 2 shows absorbance spectra near 1053 nm of 4 typical N31 samples containing various Fe concentrations. It is found that the absorption near 1053 nm increases rapidly with increasing Fe concentration. Nevertheless, the relations of various Fe doping concentrations to the absorption at 1053 nm are qualitative.

The optical loss at 1053 nm can be quantified by using static optical loss measurement. The results from static optical loss data of the samples with various Fe concentrations are summarized in Table 1. In this work, it is considered that the optical loss of the sample 1 without Fe doping is only caused by Nd³⁺ ions and impurities such as other transition metal ions and rare earth

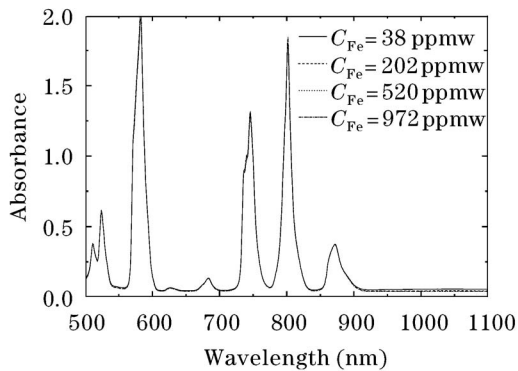


Fig. 1. Absorbance spectra of N31 samples with various Fe concentrations.

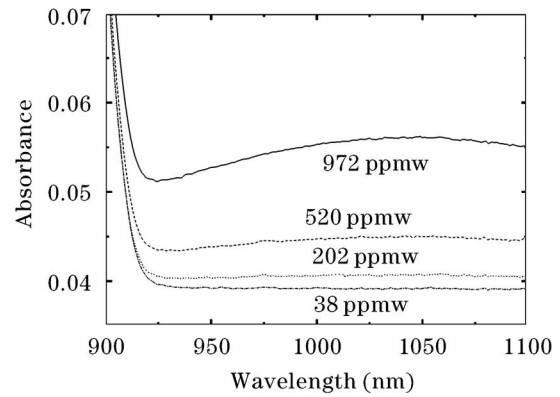


Fig. 2. Absorbance spectra of N31 samples with various Fe concentrations.

Table 1. Optical Loss at 1053 nm Corresponding to Various Fe Concentrations

N31 Samples	C _{Fe} (ppmw)	α (×10 ⁻² cm ⁻¹)	α _{Fe} (×10 ⁻² cm ⁻¹)	ε _{Fe} (×10 ⁻⁵ cm ⁻¹ /ppmw)
1 (undoped)	0	0.12	0	0
2	38	0.19	0.07	1.8
3	58	0.30	0.18	3.1
4	67	0.33	0.21	3.1
5	73	0.37	0.25	3.4
6	94	0.55	0.43	4.6
7	202	1.32	1.20	5.9
8	264	1.70	1.58	6.0
9	520	3.52	3.40	6.5
10	747	5.45	5.33	7.1
11	972	7.37	7.25	7.5

ions, and the optical loss of Fe in sample 1 is nearly zero. Therefore, the optical loss caused by various concentrations of Fe doping in the samples can be modified, taking sample 1 as a standard. These modified optical loss coefficients per unit of Fe (cm⁻¹/ppmw) at 1053 nm are fitted by

$$\varepsilon_{Fe} = \varepsilon_{max}[1 - \exp(-C_{Fe}/129)], \quad (3)$$

where ε_{Fe} is the optical loss per unit of Fe (10⁻⁵cm⁻¹/ppmw), C_{Fe} is the Fe concentration (ppmw), and ε_{max} is the limiting optical loss per unit of Fe at 1000 ppmw concentration. The measured ε_{max} is 7.5 × 10⁻⁵ cm⁻¹/ppmw (see Fig. 3). It is found that the fitting constant is different from the results in LHG-8 and LG-770^[3].

Figure 3 shows the modified optical loss per unit of Fe (cm⁻¹/ppmw) in samples as a function of Fe-doping concentrations. The solid line is the calculated results from Eq. (3). It is found that the optical loss per unit of Fe (cm⁻¹/ppmw) at 1053 nm increases rapidly from 0 to 300 ppmw of Fe, but it remains almost constant as the Fe concentration larger than 300 ppmw. The behavior of the optical loss is caused by changes in the Fe²⁺/Fe³⁺ ratio for different Fe total doping concentrations^[3]. It indicates that the Fe²⁺/Fe³⁺ ratio increases with the concentration below about 300 ppmw, and the Fe²⁺/Fe³⁺

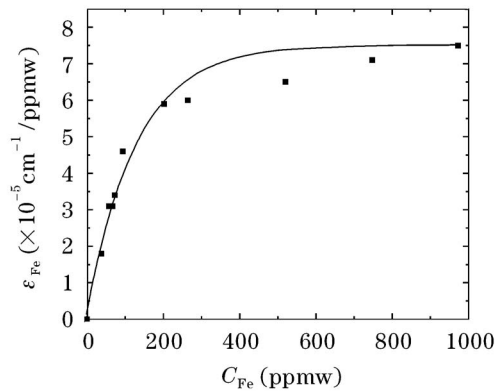


Fig. 3. Optical loss coefficient per unit of Fe at 1053 nm as a function of Fe concentration.

ratio approaches to be a constant as the concentration above 300 ppmw.

The region of interest in this study is the optical loss per unit of Fe ($\text{cm}^{-1}/\text{ppmw}$) with below 100-ppmw Fe, because the optical loss control is important in our melting process. N31-type Nd-doped phosphate laser glasses used in high-energy solid-state laser systems require the optical loss $< 1.5 \times 10^{-3} \text{ cm}^{-1}$. In this experiment, the optical loss of the sample 1 undoped with Fe is $1.2 \times 10^{-3} \text{ (cm}^{-1})$. Therefore, at low ppmw Fe doping range ($< 100 \text{ ppmw}$), the changes of the optical loss at 1053 nm should be more important to our investigation. It is found that the correlation between the optical loss per unit of Fe and Fe concentration below about 100 ppmw is considered to be nearly linear (see Fig. 3). To analyze our data more completely, we fit the modified optical loss coefficient data as a function of Fe concentration up to 100 ppmw to an equation of the form

$$\alpha_{\text{Fe}} = 5.0 \times 10^{-5} (C_{\text{Fe}})^2. \quad (4)$$

In Fig. 4, the solid line is calculated results using Eq. (4). The optical loss at 1053 nm increases quadratically with Fe concentration below 100 ppmw. This unusual behavior of the optical loss plays a very important rule in our melting process. As a result of Fe impurity widely existing in the glasses, quite a few glasses whose optical loss exceed $1.5 \times 10^{-3} \text{ cm}^{-1}$ are not up to the quality standard. From Eq. (4), it is required not more than 20 ppmw of Fe contamination in N31-type Nd-doped phosphate laser glasses which used in high-energy solid-state laser systems. Therefore, Fe concentration in raw materials and Fe contamination in melting process must be carefully controlled. It is well known that Fe in glasses exists in the states of both Fe^{2+} and Fe^{3+} . The optical loss at laser wavelength of 1053 nm is due to Fe^{2+} [3,4]. Therefore, the changes of optical loss at 1053 nm are due to Fe^{2+} concentration. Figure 3 shows that the optical loss per unit of Fe ($\text{cm}^{-1}/\text{ppmw}$) increases almost linearly with Fe concentration below about 100 ppmw. It indicates that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio increases rapidly as Fe doping in low ppmw range. This behavior is considered that the optical loss per unit of Fe ($\text{cm}^{-1}/\text{ppmw}$) at 1053 nm is concentration dependent below about 100 ppmw. This concentration dependence is due to a shift in the redox equilibrium between Fe^{3+} and Fe^{2+} [3]. Therefore, the unusual changes of the optical loss are caused by

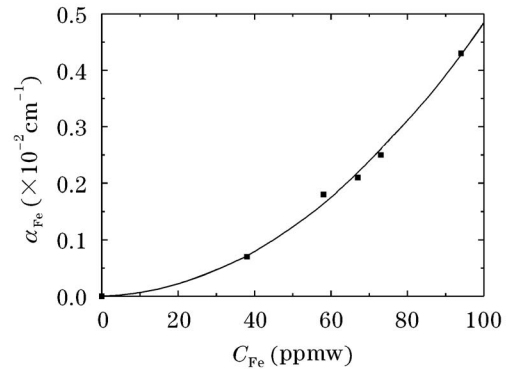
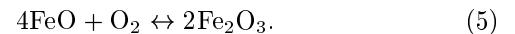


Fig. 4. Optical loss caused by Fe at 1053 nm as a function of Fe concentration below 100 ppmw.

changes in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio for different Fe total doping concentrations[3]. In fact, although Fe contamination in N31 glasses can be controlled under 20 ppmw, the optical loss per unit of Fe ($\text{cm}^{-1}/\text{ppmw}$) will also increase rapidly if the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio is not carefully controlled in melting process. Fe in glasses is distributed in the states of Fe^{2+} and Fe^{3+} and this distribution depends on the redox state of the glasses. The oxidation-reduction reaction in glass could be represented as



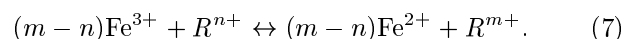
From Eq. (5), the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio changes with the fugacity of oxygen in the melt. The oxidation-reduction equilibrium in glass melt moves towards the oxidizing side with increase of oxygen fugacity. A number of workers have studied the effect of the fugacity of oxygen on the oxidation-reduction equilibrium in glass forming melts, and the relationship expected from Eq. (5) has always been observed[7]. In this study, glass samples are melted in O_2 condition and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio always changes with the fugacity of oxygen in the furnace atmosphere.

The $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio changes with melting temperature. The oxidation-reduction equilibrium in an oxide melt moves toward the reduced side with increasing temperature of liquid. At one constant oxygen pressure and constant composition, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio changes with melting temperature as the following equation[7]

$$4 \log(\text{Fe}^{3+}/\text{Fe}^{2+}) = -\Delta H/(4.575T) + \text{constan } t, \quad (6)$$

$\log(\text{Fe}^{3+}/\text{Fe}^{2+})$ versus $1/T$ is expected to be linear. This expression is applicable in N31 glass system in this study.

The variable valence states of other metal ions in glass samples can not be negligible. The oxidation-reduction reaction between metal ions with variable valence states and Fe can be written as



Thus, the oxidation-reduction reaction moves towards the oxidizing side with variable valence states of other metal ions such as Sb, Ce, and Mn, etc..

Therefore, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in our melting process can be controlled sufficiently by changing the melting condition. It is found that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio can be decreased by increasing the fugacity of oxygen, decreasing

the melting temperature, and doping the variable valence states of other metal ions in glasses. It is an important way to decrease the optical loss of Fe in N31-type Nd-doped phosphate laser glasses. However, the change of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio is difficult to determine in N31 glass samples. LLNL reported the measurement result about $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in LG-770 and LHG-8^[3]. They suggest that the change in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio can be measured from the change in intensity ratios for bands 415 and 1053 nm associated with Fe^{3+} and Fe^{2+} . However, the absolute magnitude of the changes of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio should be viewed with caution because of the lack of a numerical band fitting analysis.

At laser wavelength of 1053 nm, the optical loss from Fe increases with Fe concentration in N31-type Nd-doped phosphate laser glasses, ranging up to 1000 ppmw. The quantitative relations about various Fe doping concentrations to the optical loss at 1053 nm are determined precisely and analyzed in detail. The fitting constant in Eq. (3) is different from the results in LHG-8 and LG-770. At low ppmw Fe doping range (< 100 ppmw), the optical loss at 1053 nm increases quadratically with Fe doping. It is found that Fe contamination in N31-type Nd-doped phosphate laser glasses is required under 20 ppmw and that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio can be controlled in melting process. The unusual changes of the optical loss

is caused by changes in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio for different Fe total doping concentrations. Therefore, Fe contamination in N31-type Nd-doped phosphate laser glasses and the changes of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in melting process must be carefully controlled. It is the direction to improve our melting process and the qualities of N31-type Nd-doped phosphate laser glasses.

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