

Impurities in large scale produced Nd-doped phosphate laser glasses. II. Pt ion and Pt inclusion

Si Chen, Youkuo Chen, Jimeng Cheng, Qinling Zhou, Wei Chen, Lili Hu,

Georges Boulon

► To cite this version:

Si Chen, Youkuo Chen, Jimeng Cheng, Qinling Zhou, Wei Chen, et al.. Impurities in large scale produced Nd-doped phosphate laser glasses. II. Pt ion and Pt inclusion. Optical Materials: X, 2019, 2, pp.100032. 10.1016/j.omx.2019.100032. hal-04461923

HAL Id: hal-04461923 https://hal.science/hal-04461923

Submitted on 16 Feb 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés. Contents lists available at ScienceDirect

Optical Materials: X

journal homepage: www.journals.elsevier.com/optical-materials-x

Invited Article

(INVITED) Impurities in large scale produced Nd-doped phosphate laser glasses. II. Pt ion and Pt inclusion



Optical

Si Chen^{a,b}, Youkuo Chen^a, Jimeng Cheng^a, Qinling Zhou^a, Wei Chen^{a,*}, Lili Hu^a, Georges Boulon^c

^a Key Laboratory of Materials for High Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai, 201800, China

^b Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, 100049, China

^c Institut Lumière Matière (ILM), UMR5306 CNRS-Université Claude Bernard Lyon 1, Université de Lyon, 69622, Villeurbanne, France

ARTICLE INFO

Keywords: Nd-Doped phosphate laser glass Pt ion Pt inclusion Spectrophotometry Selective adsorption for Pt ion EPMA

ABSTRACT

Platinum is a special kind of impurity in Nd-doped phosphate laser glasses. Firstly, its presence in the glass depends on the production processes, rather than the purity of the raw materials used. Secondly, there coexist Pt ion and Pt inclusion in the glass, which one is the oxidized and the other is the reduced. The detection for these two kinds of Pt impurities in the large-scale produced Nd-doped phosphate laser glasses can reflect the control level and stability of the processes. To determine more accurately the content of Pt ion in the glass, a hemicyanine dye, instead of SnCl₂ previously used, is utilized to color Pt ion solution by dissolving the glass. On the basis of such a new hemi-cyanine spectrophotometric analysis, the factor of proportionality between Pt ion content and its absorption coefficient at 400 nm is determined and discussed. To avoid the interference from other cations in the multi-cation solution by dissolving the glass, when doing ICP-MS analysis for Pt, a magnetic poly-ionic liquid is synthesized successfully by bonding an ionic liquid to nano-Fe₃O₄ particles covered by C. Such a new magnetic poly-ionic liquid can adsorb Pt ions with a better selection. The element distribution of Pt, O and P for differently sized Pt inclusions in the glass is analyzed by EPMA.

1. Introduction

It is a complicated work to control the impurities in Nd-doped phosphate laser glasses [1]. In view of their sources, there are two kinds of impurities in the glass. The first kind, mainly Cu, is introduced via the raw materials, and even by contamination in the production processes. The second kind, mainly Pt, is an inherent impurity resulting from the Pt crucible and Pt stirrer which must be used in the laser glass production under present technique condition. Since these Pt impurities cannot be eliminated fully, their detection will be carried out through the whole processes to produce the glass.

Pure platinum metal, with relatively high chemical stability and excellent ductility, can be recycled after being purified [2–4]. In order to produce high quality Nd-doped phosphate glass with excellent optical and laser properties, a large amount of platinum and its alloys will be used in high temperature melting processes [5,6].

Generally, the high temperature resistance of platinum makes Pt inert to molten glass. However, the physical and chemical erosion of Pt still can occur to some extent, especially when melting phosphate glasses at a high temperature. The main sources of Pt impurities in Nd-doped phosphate laser glass are as follows [7–10]: 1. Reaction of Pt

crucible with atmospheric O_2 . When heated at a lower temperatures, the surface of Pt crucible does not show obvious change, but actually a thin layer of PtO₂ is formed. As the temperature increases, solid phase PtO₂ undergoes sublimation to the gaseous phase. When the partial pressure of PtO₂ tends to be saturated, PtO₂ transfers into glass melt, forming Pt ions or being reduced to metal Pt. 2. Reaction between Pt crucible and oxides in the glass melt. The raw materials are mainly in the form of metaphosphate, and metal Pt will be oxidized to Pt(PO₃)₄ in an oxidizing atmosphere. The reversibility of this reaction results in the presence of both Pt ions and metal Pt in the melt and glass.

Pt inclusions in Nd-doped phosphate laser glasses will be heated and vaporized when subject to an intense laser irradiation [7], even those on-line laser disks have to be replaced only after several shots. By using an oxidizing atmosphere to eliminate Pt inclusions, which oxidizes Pt^0 to Pt^{n+} in the glass melt, such a process avoids laser damage due to Pt inclusions as possible, but results in a higher content of Pt ions in the glasses, compared to those of Cu and Fe [1,11]. In the large-scale production involving thousands of meter-scale Nd-doped phosphate laser glasses [12], it is a key issue to control the chemical states of Pt to ensure product quality and consistency [13,14]. It is necessary to develop efficient test and grading methods to determine Pt impurities.

https://doi.org/10.1016/j.omx.2019.100032 Received 24 July 2019; Accepted 13 August 2019 Available online 30 August 2019 2590-1478/ © 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(http://creativecommons.org/licenses/by-nc-nd/4.0/).



^{*} Corresponding author. Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai, 201800, China. *E-mail address:* weichen@siom.ac.cn (W. Chen).

In this paper, two kinds of Pt impurities in Nd-doped phosphate laser glass are detected and discussed. For spectrophotometry, a hemicyanine dye that can color Pt ion solution is developed. It can replace that previously used $SnCl_2$ spectrophotometry. The factor of proportionality between Pt ion content and its absorption coefficient at 400 nm is determined and discussed. For ICP-MS, a magnetic poly-ionic liquid is developed on the basis of nano-Fe₃O₄ particles covered by C. It can selectively adsorb Pt ions and avoid the interference of other cations. For Pt inclusions in the glass, EPMA presents an element distribution analysis for Pt, O and P, respectively.

2. Experimental

Two kinds of Nd-doped phosphate laser glasses, N31-type and N41type, are produced in our institute by pot melting and continuous melting. Although two melting techniques, the final products remain almost unchanged compositions. The main composition of N31-type and N41-type is $(58-62)P_2O_5-(8-12)Al_2O_3-(12-16)K_2O-(8-12) BaO-(1-2)Re_2O_3$ and $(58-62)P_2O_5-(6-10)Al_2O_3-(20-25)K_2O-(8-12)MgO-(1-2)Re_2O_3$, in which Re represents rare earth oxides except Nd₂O₃.

A PerkinElmer Lambda 950 UV-VIS-NIR spectrophotometer was used for absorbance measurements in the range of 250 nm–1200 nm. Its instrument parameters: resolution: UV/Vis < 0.05 nm; NIR < 0.20 nm, wavelength accuracy: UV/Vis < 0.080 nm; NIR < 0.300 nm, wavelength repeatability (10 times of standard deviation): UV/Vis < 0.005 nm; NIR < 0.020 nm.

After acid cleaning, the glass samples were dissolved by perchloric acid (HClO4) and hydrofluoric acid (HF). A Thermo Scientific iCAP TQ ICP-MS was used to determine the ion content in the glasses and raw materials. The working parameters: Rf power: 1550W; Plasma gas flow rate: 14L/min; Auxiliary gas flow rate: 0.8L/min; Nebulizer gas flow rate: 1.0L/min; Collision gas: He; Collision gas flow rate: 4.8 mL/min; Sampler/Skimmer diameter orifice: Ni 1.1mm/0.5 mm; Scanning mode: Peak-hopping; Isotopes: ¹⁹⁵Pt; Internal standard isotope: ¹⁰³Rh, ¹¹⁵In.

A JXA-8230 EPMA microanalyzer was used for surface scanning analysis of compositions on the sample surface. The acceleration voltage of the electron beam is 15 kV and the current is 1×10^{-8} A. The glass was ground close to the particulate inclusion, polished and coated with C before analyzing.

3. Results and discussion

3.1. Pt ion in Nd-doped phosphate laser glass

Fig. 1 is the transmittance spectrum of N31-type Nd-doped phosphate laser glass, and the embedded figure is the absorption spectrum of N31-type Nd-free phosphate glass. From the absorption spectrum, it is obvious that the absorption band of Pt ion in the N31 matrix is very wide, covering 350–430 nm wavelength range. From the transmittance spectrum of Nd-doped phosphate laser glass, the absorption bands of Nd³⁺ do not interfere in the range from 370 to 420 nm. The two peaks observed at 350 and 356 nm correspond to $^{2}L_{15/2}$ and $^{2}I_{11/2}$ mixing with ^{4}D states of Nd³⁺, respectively. The weak peak at 429 nm corresponds to $^{2}D_{5/2}$ excited state of Nd³⁺.

The valence states and coordination of Pt ions in Nd-doped phosphate and silicate glass systems were investigated by XAFS [15,16]. Pt²⁺ was neither found in both the phosphate matrix nor the silicate matrix. Pt ion exists predominantly as Pt⁴⁺ and forms a six-coordinated structure with O. Therefore, the absorption intensity at 400 nm can be used to determine Pt⁴⁺ content in Nd-doped phosphate laser glass [11]. However, the 400 nm absorbance of glass samples measured by spectrophotometry may be affected by varying light sources, monochromators, detectors, and filters. In addition, the intensity of the ultraviolet absorption edge near 300 nm, as shown in Fig. 1, is much stronger than that of Pt⁴⁺ at 400 nm. This indicates that the strong absorption edge in near-UV will affect the absorption intensity at



Fig. 1. Transmittance spectrum of N31-type Nd-doped phosphate laser glass. Absorption spectrum of N31-type Nd-free phosphate glass is shown in the middle.

400 nm. In fact, the embedded figure in Fig. 1 also shows that absorption of Pt ion in N31 glass matrix is a wide but very weak absorption band superimposed on the stronger absorption edge.

It is essential to dissolve the glass sample in high purity non-platinum containers for an accurate determination of Pt ion content. $SnCl_2$ spectrophotometry [17,18] is previously used to detect Pt in the Ndglass. $SnCl_2$, which is widely used as a reductant and complexing agent, will reduce Pt^{4+} to Pt^{2+} and then combine Pt^{2+} to form a complex anion group. This group shows an absorption band at 400 nm, as shown in Fig. 2(a). The peak wavelength of the absorption band is basically stable at 400 nm with different Pt contents, as shown in the embedded figure of Fig. 2(a). But there are two shortcomings of this method. Firstly, the absorption band of such a yellow-complexed Pt ion is too close to the ultraviolet absorption edge. Thus, the high-intensity absorption edge of the solution will enhance the absorption intensity of the complex Pt. Secondly, a lower absorbance of complex Pt ion limits the sensitivity of $SnCl_2$ spectrophotometry method.

A hemi-cyanine dye (2-[2-[4-[(2-Cyanoethyl) methylamino] phenyl] vinyl]-1,3,3-trimethyl-3H-indolium chloride, simplified as CPVTI) is used as chromogenic agent, and butyl acetate is used as an extracting agent. In this detection system, Pt^{4+} ions will be surrounded by I⁻ ions and become anionic groups. These anionic groups and those hemi-cyanine dye molecules produce counterion pairs, which can be transferred to butyl acetate phase. The counterion pairs in the butyl acetate phase, containing Pt ion, result in an absorption band at 530 nm shown in Fig. 2(b), and its intensity corresponds to Pt⁴⁺ ion content. Fig. 3 shows main detection procedure to determine Pt ion content in the laser glass by this new hemi-cyanine spectrophotometry method.

The embedded figure in Fig. 2(b) shows that the peak wavelength of this new detection system is stable at 530 nm with the change of Pt^{4+} content. Compared with previous $SnCl_2$ spectrophotometry of Fig. 2(a), this new method has two advantages. Firstly, the peak wavelength is red-shifted from 400 nm to 530 nm, which will be free of the interference from the absorption edge. Therefore, the absorption intensity at 530 nm can accurately represent the Pt ion content. Secondly, compared to that 400 nm absorbance, this 530 nm absorbance is increased by an order of magnitude. Such a new hemi-cyanine spectrophotometry has a better accuracy and sensitivity to detect Pt ion.

Moreover, this new method involves a liquid phase transfer process from water phase to butyl acetate phase. Such a liquid-liquid extraction process would eliminate matrix interference. In principle, the hemicyanine spectrophotometry does not change the valence state of Pt⁴⁺ ion in the solution, while SnCl₂ reduces Pt⁴⁺ to Pt²⁺. It implies such a



Fig. 2. Absorption spectra of the complex ion of Pt ion by adding $SnCl_2$ into the solution from N31-type phosphate laser glass (a), and of the dye molecule containing Pt ion by adding hemi-cyanine into the solution (b). The embedded figure shows a variation of the peak wavelength with different content of Pt in the solution.

spectrophotometry has the possibility to distinguish different valence states of Pt ions in the dissolved solution [19].

Table 1 lists the determined contents of Pt ion in pot melting N31type phosphate laser glass, by hemi-cyanine spectrophotometry, $SnCl_2$ spectrophotometry and ICP-MS. The results by the hemi-cyanine spectrophotometry method are almost same as those by ICP-MS, while the results by $SnCl_2$ spectrophotometry method are on the higher side.

Table 2 lists the factor K of proportionality, a ratio of Pt ion content to its absorption coefficient at 400 nm, which is determined by the hemi-cyanine and SnCl₂ spectrophotometry, respectively. K is a constant, which corresponds to the reciprocal value of the absorption cross section at 400 nm for Pt ion.

By SnCl₂ spectrophotometry, the K of N31-type Nd-doped phosphate laser glass is about 625 \pm 28 ppm• cm. It is almost same as the reported

Table 1

Pt content in Nd-doped phosphate laser glass determined by hemi-cyanine
spectrophotometry, $SnCl_2$ spectrophotometry and inductively coupled plasma
mass spectrometry.

Sample	[Pt]by hemi-cyanine ppm (wt)	[Pt]by SnCl ₂ ppm (wt)	[Pt]by ICP-MS ppm (wt)
1	102	140	96
2	100	138	98
3	95	127	92
4	94	127	93
5	93	141	90



Fig. 3. Spectrophotometric analysis to determine Pt content in Nd-doped phosphate laser glasses by hemi-cyanine method.

Table 2

The factor K of proportionality about Pt ion content in N31-type Nd-doped phosphate laser glass, determined by $SnCl_2$ and hemi-cyanine spectro-photometry.

Method	No.	Absorption coefficient at $400 \text{ nm}, \text{ cm}^{-1}$	[Pt] ppm (wt)	K ([Pt]∝K•Absorption coefficient) ppm•cm	
SnCl ₂ spectrophotometry	1	0.231	144	623	625 ± 28
	2	0.222	138	622	(Average)
	3	0.212	133	627	
	4	0.205	127	620	
	5	0.19	124	653	
	6	0.195	122	626	
	7	0.227	138	608	
	8	0.228	141	618	
Hemi-cyanine	1	0.234	102	434	449 ± 20
spectrophotometry	2	0.221	100	452	(Average)
	3	0.217	95	438	
	4	0.207	94	455	
	5	0.211	93	442	
	6	0.206	92	449	
	7	0.208	92	445	
	8	0.194	92	476	

value, 637 ppm• cm (Page 59 of Ref 21 in Ref. [14]), but still lower than the value, 855 ppm• cm for LHG-8, LG750 and LG770 [14]. By converting 625 \pm 28 ppm• cm of N31-type laser glass, the absorption cross section of Pt ion is approximately 52×10^{-20} cm², which is close to the value of \sim 50 $\times 10^{-20}$ cm² [20]. On the other hand, it is reported that K of LG770 is 526 ppm• cm [20]. By the hemi-cyanine spectrophotometry, the K of N31-type laser glass is about 449 \pm 20 ppm• cm, lower than the reported. It should be noted that, such a value is also supported by ICP-MS analysis, since the results for Pt content by the hemi-cyanine spectrophotometry are almost the same as the results by ICP-MS, as shown in Table 1.

Table 3 lists the factor K for pot melting and continuous melting N31-type and N41-type phosphate laser glasses, determined by the hemi-cyanine spectrophotometry. For N31-type, the K (436 \pm 9 ppm·cm) of the continuous melting is slightly lower than that (449 \pm 20 ppm·cm) of the pot melting. For N41-type, the K (295 \pm 20 ppm·cm) of the continuous melting is slightly higher than that (286 \pm 12 ppm·cm) of the pot melting. It should be pointed out that, the K of N31-type is obviously higher than that of N41-type, as the K of LHG-8 is much more higher than that of LG770 [1,14,20]. Generally, the same trend occurs for these two series.

An indispensable part to the large-scale production of Nd-doped phosphate laser glasses is the accurate detection of Pt content in the glass. The resulting loss of platinum during the processes of melting glasses can be determined. If accurately detecting Pt ion content in the glass for the whole course of the pot or continuous melting, the stability of Pt ion content in the glass, as well as a comparison between the total Pt ion content and platinum loss, they can reflect not only the quality of the laser glasses, but also the stability of large scale production for Nddoped phosphate laser glasses.

3.2. Selective adsorption of Pt ion in multi-cation solution

If only from the point of view of detection limit, the current techniques such as ICP-OES and ICP-MS are sufficient to detect trace metal impurities. However, for N31-type and N41-type Nd-doped phosphate laser glasses, their complex composition and various impurities will cause multi-cation and matrix interferences.

The adsorption behavior for Pt ions was investigated by different adsorbents, such as ionic liquid-coated magnetic nanomaterial containing thiol and sulfonyl group [21], pyrrole and thiophene co-coating magnetic nanomaterial [22], polypyrrole-coated magnetic nanomaterial [23] and cysteine modified silica gel [24]. These adsorption

Table 3

The factor K of proportionality for Pt ion content in N31-type and N41-type Nddoped phosphate laser glasses, determined by hemi-cyanine spectrophotometry.

Type No.		Absorption coefficient at $400 \text{ nm}, \text{ cm}^{-1}$	[Pt] ppm (wt)	[Pt]∝K•Absorption coefficient ppm•cm	
Pot melting N31-	1	0.234	102	434	$K = 449 \pm 20$
type phosphate	2	0.221	100	452	(Average)
laser glass	3	0.217	95	438	-
-	4	0.207	94	455	
	5	0.211	93	442	
	6	0.206	92	449	
	7	0.208	92	445	
	8	0.194	92	476	
Continuous melting	1	0.061	26	431	$K = 436 \pm 9$
N31-type	2	0.063	27	429	(Average)
phosphate laser	3	0.063	27	429	
glass	4	0.069	30	443	
	5	0.070	30	437	
	6	0.071	31	437	
	7	0.072	32	446	
	8	0.077	34	439	
Pot melting N41-	1	0.193	56	291	$K = 286 \pm 12$
type phosphate	2	0.193	55	285	(Average)
laser glass	3	0.185	51	274	
	4	0.180	51	281	
	5	0.181	50	276	
	6	0.175	49	282	
	7	0.179	49	275	
	8	0.153	45	294	
Continuous melting	1	0.145	44	301	$K = 295 \pm 20$
N41-type	2	0.151	42	282	(Average)
phosphate laser	3	0.151	41	275	
glass	4	0.147	41	278	
	5	0.134	41	305	
	6	0.136	40	297	
	7	0.133	40	303	
	8	0.128	40	315	

methods are simple way to overcome the problems related with the complex matrix. However, these adsorbents are mainly for water samples, only with a small amount of impurities and without high-content ion interference, not entirely suitable for a complex matrix.

A magnetic nanomaterial for selective adsorption of Pt ions from complex matrix solution by dissolving Nd-doped phosphate laser glass is successfully synthesized. Pt ions can be separated from the original solution and eluted into the detected solution. Thus, most of cations will be left in the original solution, and the detected solution will remain enough Pt ions to be detected, without so many cations and matrix interference.

Firstly, the carbon-coated magnetic particles were prepared by the hydrothermal method with nano-Fe₃O₄ particles and glucose solution. C-coating is designed to protect Fe₃O₄ particle from being eroded by acid in solution while maintaining magnetism during adsorption. Secondly, an ionic liquid monomer is synthesized by the reaction of 1allyl-3-cyanoimidazole chloride with lithium bis(trifluoromethanesulphonyl)imide. There are three task-specific sites for nitrogen atom, located in nitrile group, imidazole, bistrifluoromethylsulfonamide. These nitrogen atoms have unbounded electron pairs and can adsorb Pt ions in the solution based on hard and soft acid-base theory [21]. Thirdly, ionic liquid monomer is immobilized on the carbon layer surface of Fe₃O₄ nano-particle to obtain the ionic liquid coated magnetic nanomaterial (simplified as FCASIL) by in situ polymerization. The magnetism of Fe₃O₄, the adsorbability of ionic liquid monomer to Pt ion, and the acid-base corrosion resistance of carbon layer are all on it. FCASIL is a magnetic poly-ionic liquid with triple task-specific sites adsorbing Pt.

Mixing such a magnetic adsorbent with the solution by dissolving Nd-doped phosphate laser glass, magnetic adsorbent with the adsorbed



Fig. 4. ICP-MS analysis to determine Pt content in Nd-doped phosphate laser glasses by selective adsorption method.

Pt ions will be collected by a magnet. Finally, Pt ions will be eluted into a solution by nitric acid, but magnetic adsorbent will be separated by a magnet. Thus, Pt ion content in the eluent solution can be determined by ICP-MS without multi-cation interference, as shown in Fig. 4.

Fig. 5 is the full range mass analysis and detail mass spectra around Pt mass number, for the solution by dissolving N31-type Nd-doped phosphate glass, which is without treated by FCASIL. From Fig. 5(a), it is clear that there are too many kinds of ions in the solution. Their high count corresponds to their high content. In Fig. 5(b), there are still many spectral lines closer to the mass number of Pt. Ions or polyatomic ion groups with high content or closer to Pt mass number, all of them will cause the mass interference leading to a large bias of Pt signal intensity.

As shown in Fig. 6(a) and especially Fig. 6(b), after the detected solution is treated by FCASIL, ICP-MS presents more clearer mass spectra. Besides Pt-related lines, there are still some spectrum lines such as polyatomic interference $^{16}O^{16}O$, Ar lines produced by ICP, internal standard elements 103 Rh and 115 In. Especially, the signal intensity of Pt remains, almost the same as the intensity before treating. These facts prove that, when doing ICP-MS analysis to detect Pt ion content in the solution by dissolving Nd-doped phosphate laser glasses, that newly developed FCASIL selective adsorption method can significantly reduce the multi-cation interference to avoid matrix effects, but most of Pt ions

can be remained in the solution for the determination of Pt ion content in the glass.

3.3. Pt inclusion in Nd-doped phosphate laser glass

If without implementing the processes to dissolve Pt metal atoms into Pt ions, Pt inclusions will most probably occur in the produced Nddoped phosphate laser glasses. By a self-built laser scan system, with repetition rate of 10 Hz and pulse width of 10 ns, even when the energy density is only higher than $\sim 2 \text{ J/cm}^2$, metallic Pt inclusions will be heated and then vaporized because of its much more stronger absorption for 1 µm laser. Such a laser damage is actually the fracture of the glass surrounding Pt inclusion. Even if a micron-sized Pt inclusion in the meter-scale Nd-doped phosphate laser glass will result in a damage site beyond a few dozens of microns [25–27]. Optical inspection and microscopy can be used to detect these grown defect sites, and accordingly the laser slabs will be graded [11]. Such a scan is not only for the inspection of Pt inclusions [25], but also for the stabilization of the growth of Pt inclusions [27] in online laser slabs.

By electron probe micro-analysis (EPMA), Fig. 7 shows the element distribution of Pt, O, P for Pt inclusions in N31-type Nd-doped phosphate glasses. The left is three secondary electron photos corresponding to differently sized inclusions, respectively.



Fig. 5. ICP-MS analysis for the solution from N31-type Nd-doped phosphate laser glass. (a) full range; (b)Pt mass number detail.



Fig. 6. ICP-MS analysis for the solution from N31-type Nd-doped phosphate laser glass, which the solution treated by selective adsorption method. (a) full range; (b) Pt mass number detail.

In Fig. 7(a), there is an inclusion with a size larger than $200 \,\mu\text{m}$. However, in view of the distribution of Pt, there are only three very small Pt microparticles with a size only in the order of several microns. These three Pt microparticles should be metallic platinum, because there is no corresponding oxygen in the microparticle region. But obviously, the main composition of such an inclusion is not Pt. The inclusion is as large as $200 \,\mu\text{m}$, but Pt microparticles are as small as only several microns. It implies that, a very small Pt particle may create a large inclusion in the glass, and it even can result in a much more larger damage site.

Fig. 7(b) shows an inclusion with the size of about $150 \,\mu\text{m}$. In view of the distribution of Pt element, the central $100 \,\mu\text{m}$ region is covered fully and almost uniformly with Pt. Especially, there still remains a

several-micron-sized Pt particle with a very strong Pt signal. This indicates that most of metal Pt have been vaporized, but there is still a micron-sized Pt particle left, that has not been completely vaporized.

Fig. 7(c) shows an inclusion only with the size of about 60 μm . In view of the distribution of Pt element, the inclusion only contains a ${\sim}10\,\mu m$ Pt particle in the central region. Most of the region of this inclusion is without any Pt distribution, which means that ${\sim}10\,\mu m$ Pt particle remains unvaporized. However, the heat absorbed by such a small Pt particle is enough to result in a damage region larger than itself.

Besides the distribution of Pt discussed above, Fig. 7 shows the characteristic that there exists an enriched zone of O element for all of three Pt inclusions, while P element is non-enriched to the glass

Fig. 7. EPMA analysis of variant Pt inclusions in N31-type Nd-doped phosphate glass. The left is secondary electron micrograph for the inclusions of (a), (b), (c), respectively.

background. Such a phenomenon about O enriching also occurs for those non-Pt inclusions in Nd-doped phosphate laser glasses. It implies that the presence of O in the inclusions is not related directly to the presence of Pt, but most probably related to the oxidation atmosphere. That is to say, Pt appears in the inclusion most probably as its metallic state without oxidized.

From the above analysis, the size of Pt inclusion or the size of its damage site may be positively related to Pt content in the Pt inclusion, but more often there seems no clear and proportional relation between the size and the content of Pt inclusions. The number and the size of Pt inclusions can be as an estimation to grade the laser slabs.

4. Conclusion

Pt impurities in Nd-doped phosphate laser glasses, including both Pt ion and Pt inclusion, must be detected and controlled through the whole processes for the large scale production. A new hemi-cyanine spectrophotometry method is developed to determine Pt ion content in the glasses. By combining hemi-cyanine molecule with Pt⁴⁺ ion group in the solution by dissolving Nd-doped phosphate laser glass, 530 nm absorption band of the combined hemi-cyanine in butyl acetate phase is utilized to test Pt ion. Compared to previous SnCl2 spectrophotometry, in which Pt^{2+} is utilized, such a new method has a much more better accuracy and sensitivity to detect Pt ion. A new magnetic poly-ionic liquid material is developed to adsorb selectively Pt ion in the multication solution by dissolving Nd-doped phosphate laser glass. It is based on Fe₃O₄ nano-particle covered by carbon layer, and then further bonding with an ionic liquid. Such a selective adsorption for Pt ion is utilized to avoid the interference from other cations and test Pt ion by ICP-MS. According to EPMA for Pt inclusions in the glass, Pt appears in the inclusion most probably without oxidized, and there seems no clear and proportional relation between the size and the content of Pt inclusions. To control the product quality and the process stability of the large scale production, it is more important to detect accurately Pt ion content in the glasses and Pt loss in the production.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The research work was financially supported by Nd-glass projects from National Major Science and Technology Project of China and National High Technology Research and Development Program for Inertial Confinement Fusion of China.

References

- J.H. Campbell, T.I. Suratwala, Nd-doped phosphate glasses for high-energy/highpeak-power lasers, J. Non-Cryst. Solids 263 (2000) 318–341.
- [2] D. Morris, R. McGrath, ZGS platinum materials for improved glass manufacturing equipment and laboratory ware, Platin. Met. Rev. 57 (2013) 230–232.
- [3] J. Merker, B. Fischer, R. Völkl, D.F. Lupton, Investigations of new oxide dispersion hardened platinum materials in laboratory tests and industrial applications, Mater. Sci. Forum 426–432 (2003) 1979–1984.
- [4] B. Fischer, New platinum materials for high temperature applications, Adv. Eng.

Mater. 3 (2001) 811-820.

- [5] T. Akai, J. Nishii, M. Yamashita, H. Yamanaka, Chemical behavior of platinumgroup metals in oxide glasses, J. Non-Cryst. Solids 222 (1997) 304–309.
- [6] A. Borisov, H. Palme, Experimental determination of the solubility of platinum in silicate melts, Geochem. Cosmochim. Acta 61 (1997) 4349–4357.
- [7] J.H. Campbell, E.P. Wallerstein, J.S. Hayden, D.L. Sapak, D.E. Warrington, A.J. Marker, Effects of melting conditions on platinum-inclusion content in laser glasses, Glastechnische Ber. - Glass Sci. Technol. 68 (1995) 11–21.
- [8] N.R. Bennett, J.M. Brenan, K.T. Koga, The solubility of platinum in silicate melt under reducing conditions: results from experiments without metal inclusions, Geochem. Cosmochim. Acta 133 (2014) 422–442.
- [9] Z. Jiang, L. Hu, Y. Yu, Thermodynamic explanation of eliminating platinum inclusions in laser glass by POCl3 gas bubbling, Proc. SPIE-Int. Soc. Opt. Eng. 2633 (1995) 775–779.
- [10] Q.Y. Zhang, L.L. Hu, Z.H. Jiang, Thermodynamic study on elimination of platinum inclusions in phosphate laser glasses for inertial confinement fusion applications, Chin. Sci. Bull. 44 (1999) 664–668.
- [11] T.I. Suratwala, J.H. Campbell, P.E. Miller, C.B. Thorsness, M.O. Riley, P.R. Ehrmann, R.A. Steele, Phosphate laser glass for NIF: production status, slab selection and recent technical advances, Proc. SPIE-Int. Soc. Opt. Eng. 5341 (2004) 102–113.
- [12] X.M. Zhang, X.F. Wei, Review of new generation of huge-scale high peak power laser facility in China, Chin. J. Lasers 46 (2019) 0100003.
- [13] P.R. Ehrmann, J.H. Campbell, Nonradiative energy losses and radiation trapping in neodymium-doped phosphate laser glasses, J. Am. Ceram. Soc. 85 (2002) 1061–1069.
- [14] J.H. Campbell, T.I. Suratwala, C.B. Thorsness, J.S. Hayden, A.J. Thorne, J.M. Cimino, A.J. Marker, K. Takeuchi, M. Smolley, G.F. Ficini-Dorn, Continuous melting of phosphate laser glasses, J. Non-Cryst. Solids 263 (2000) 342–357.
- [15] F. Farges, D.R. Neuville, G.E. Brown, Structural investigation of platinum solubility in silicate glasses, Am. Mineral. 84 (1999) 1562–1568.
- [16] M. Karabulut, G.K. Marasinghe, C.A. Click, E. Metwalli, R.K. Brow, C.H. Booth, J.J. Bucher, D.K. Shuh, T.I. Suratwala, J.H. Campbell, XAFS investigation of platinum impurities in phosphate glasses, J. Am. Ceram. Soc. 85 (2002) 1093–1099.
- [17] L.K. Shpigun, N.V. Starushko, Flow-injection study and analytical applications of the reactions of palladium(II) and platinum(IV) with tin(II) chloride in hydrochloric acid solutions, J. Anal. Chem. 58 (2003) 186–190.
- [18] F. Pantani, G. Piccardi, Spectrophotometric determination of noble metals with Tin (II) in bromide solutions, Anal. Chim. Acta 22 (1960) 231–236.
- [19] Y.R. Bazel, T.A. Kulakova, Y.I. Studenyak, R. Serbin, S. Rednik, V. Andruch, Extraction of platinum with Astrafloxin FF from aqueous-organic solutions: separative extraction-spectrophotometric determination of platinum(II) and platinum (IV) species, J. Anal. Chem. 67 (2012) 519–526.
- [20] C.A. Click, R.K. Brow, P.R. Ehrmann, J.H. Campbell, Characterization of Pt4+ in alumino-metaphosphate laser glasses, J. Non-Cryst. Solids 319 (2003) 95–108.
- [21] S. Zhou, N. Song, X. Lv, Q. Jia, Magnetic dual task-specific polymeric ionic liquid nanoparticles for preconcentration and determination of gold, palladium and platinum prior to their quantitation by graphite furnace AAS, Microchimica Acta 184 (2017) 3497–3504.
- [22] N. Jalilian, H. Ebrahimzadeh, A.A. Asgharinezhad, K. Molaei, Extraction and determination of trace amounts of gold(III), palladium(II), platinum(II) and silver(I) with the aid of a magnetic nanosorbent made from Fe3O4-decorated and silicacoated graphene oxide modified with a polypyrrole-polythiophene copolymer, Microchimica Acta 184 (2017) 2191–2200.
- [23] A. Mehdinia, M. Asiabi, A. Jabbari, Trace analysis of Pt (IV) metal ions in roadside soil and water samples by Fe3O4/graphene/polypyrrole nanocomposite as a solidphase extraction sorbent followed by atomic absorption spectrometry, Int. J. Environ. Anal. Chem. 95 (2015) 1099–1111.
- [24] E. Mladenova, I. Dakova, I. Karadjova, M. Karadjov, Column solid phase extraction and determination of ultra-trace Au, Pd and Pt in environmental and geological samples, Microchem. J. 101 (2012) 59–64.
- [25] S. Schwartz, R.T. Jennings, J.F. Kimmons, R.P. Mouser, C.L. Weinzapfel, M.R. Kozlowski, C.J. Stolz, J.H. Campbell, Vendor-based laser damage metrology equipment supporting the National Ignition Facility, Proc. SPIE-Int. Soc. Opt. Eng. 3492 (1998) 933–938.
- [26] D.I. Dmitriev, V.I. Arbuzov, K.V. Dukelsky, A.A. Zhilin, I.V. Ivanova, V.N. Pasunkin, Y.I. Pestov, V.S. Sirazetdinov, A.V. Charukhchev, V.S. Shashkin, Testing of KGSS-0180 laser glass for platinum micro-inclusions, Proc. SPIE-Int. Soc. Opt. Eng. 6594 (2007) 65940N.1-65940N.8.
- [27] G. Raze, M.A. Josse, H. Bercegol, Growth of damage sites due to platinum inclusions in Nd-doped laser glass irradiated by the beam of a large-scale Nd:glass laser. Laser-Induced Damage in Optical Materials, 7th Int. Workshop Laser Beam Opt. Char. 4932 (2003) (2002) 415–420.