APPLICATION OF PULSED GLOW DISCHARGE TIME-OF-FLIGHT MASS SPECTROMETRY FOR ELEMENTAL ANALYSIS OF OPTICAL MATERIALS

#glow discharge #mass spectrometry #optical materials #fluorine #direct analysis #hollow cathode #elemental analysis #depth profiling #KTP

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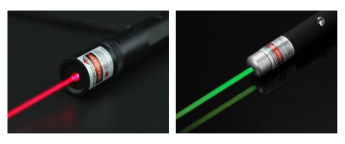
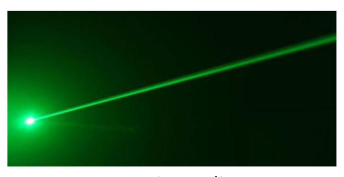
Highlights

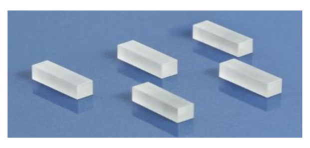
- A procedure of direct elemental analysis of the main components and dopants in optical materials based on pulsed GD TOF MS was developed.
- A new approach to the determination of high-ionization energy elements (O, F), which pose the greatest difficulties in the analysis of solid materials due to its high reactivity, volatility and high ionization energy, is proposed
- The possibility to control the stoichiometric composition and distribution of doping elements over the crystal volume (including depth profiling) is shown
- Pulsed GD MS allows for rapid and effective quality control of nonlinear optical crystals and to establish correlations between their growth conditions, composition and structure, and electrical and optical properties.

Introduction


Second harmonic generators


Laser gain medium


Optical crystals


Electro-optical modulators


Mirror/antireflection coatings

Crystal materials are widely used in laser optics. They are applied as second harmonic generation elements, electro-optical modulators or laser gain medium. Optical and nonlinear optical properties of these materials depend on their stoichiometric composition and distribution of main components and dopants in crystal volume. Therefore, a versatile analytical technique for the quality control of these material is essential.

Currently, glow discharge mass spectrometry is widely and successfully used for the direct elemental analysis of various conducting and dielectric solids. The work considers perspectives of pulsed glow discharge mass spectrometry for elemental analysis of optical materials.

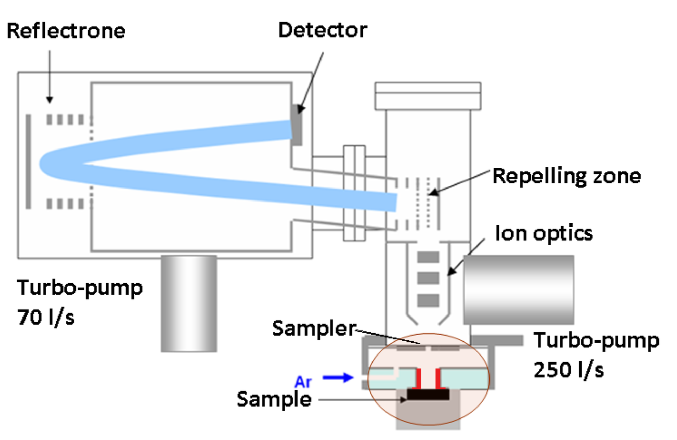
Materials and Methods

Instrumentation

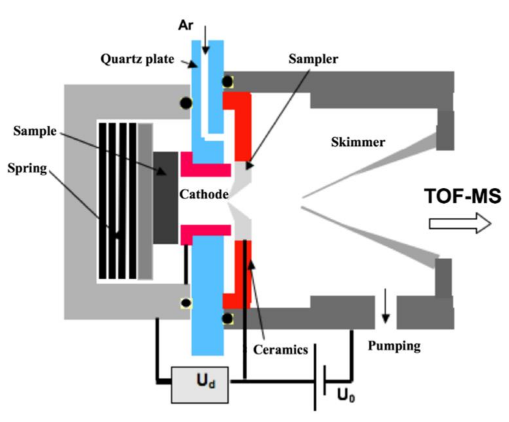

Lumas-30 Pulsed GD TOFMS

Operating parameters

Parameter	Value
Auxilliary cathode	Ta, Al
Sample aperture diameter	1.5 mm
Discharge pulse voltage, V	-900 to -1800
Discharge current	up to 3A
Pulse duration, µs	2-5
Discharge frequency, kHz	1-4
Pressure, Pa	35-1150
Repelling pulse delay, µs	1-300



Ion-optic scheme

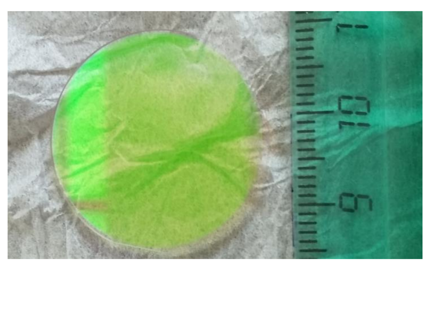


Combined hollow cathode discharge cell

Samples

KTP single crystals (dielectric, used for second harmonic generation elements, electro-optical modulators):
$KTiOPO_4$
$KTiOPO_4$:KF (0.2 – 1.24 mass % F)
$K_{(1-x)}Rb_xTiOPO4$ (0.2 – 25 %)

LaF_3SrF_2:Gd crystals (dielectric, used as laser gain medium)
LaF_3SrF_2:Gd (0.01 – 16 mass % SrF_2, 0.05 mass % GdF_3)

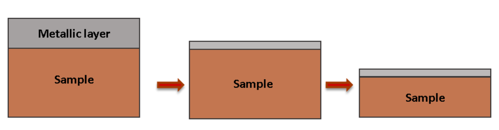


Coatings
350 nm Ni on silicon
Multilayer mirror coating
100 nm SiO_2-(200 nm TiO_2-200 nm SiO_2)x15 on glass

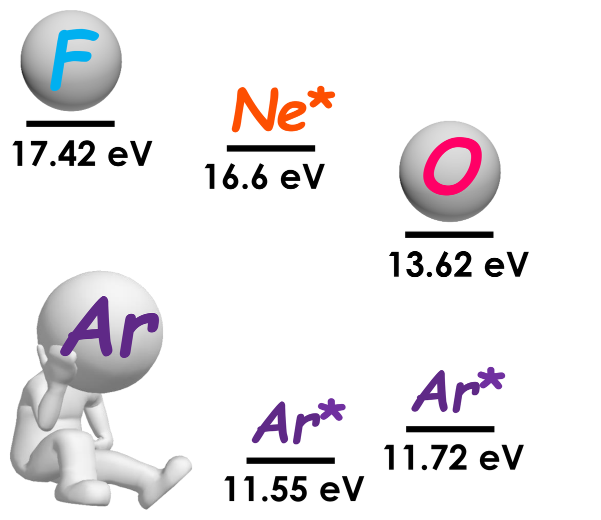
Sample preparation:

Covering with silver suspension in 2-propanol, drying with a technical fan (150°C, 2 min)

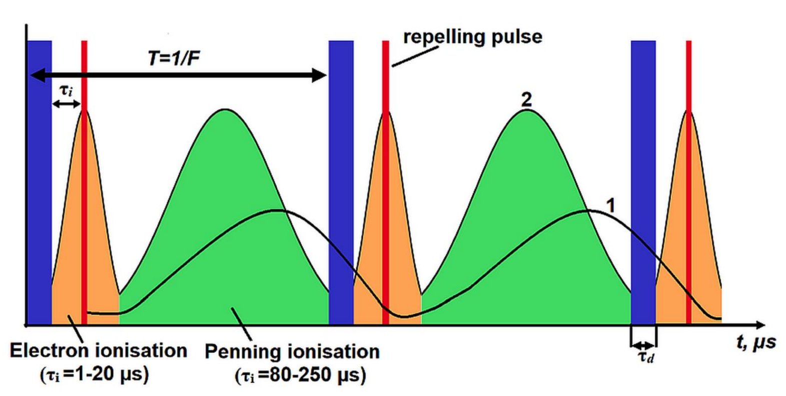
For depth profiling vacuum deposition of silver layer (100-600 nm thickness) is used



High ionization energy elements



Electron ionization at low repelling pulse delays



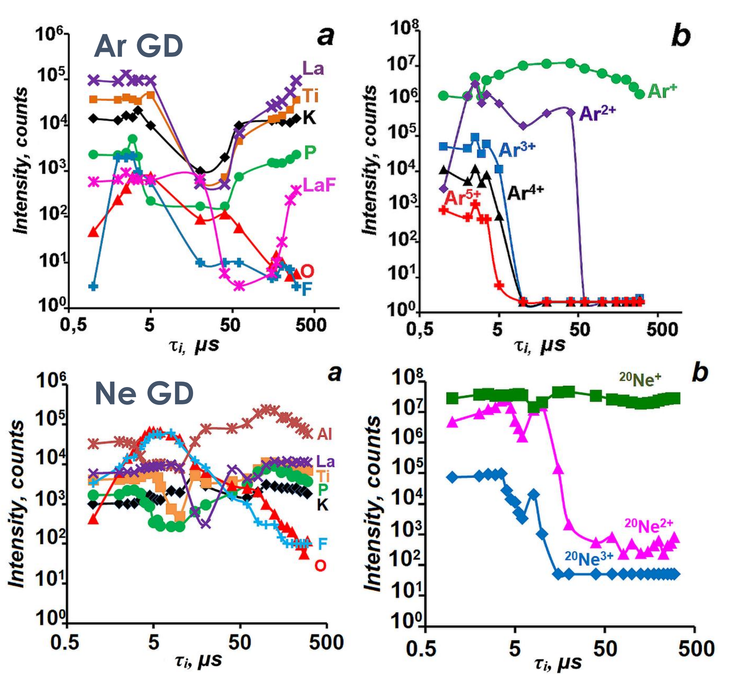
Ionization processes and ion extraction in PGD. 1 –atom flux, 2 – ion flux; T – period of discharge pulses, τ_i – repelling pulse delay.

F, O in KTP crystals

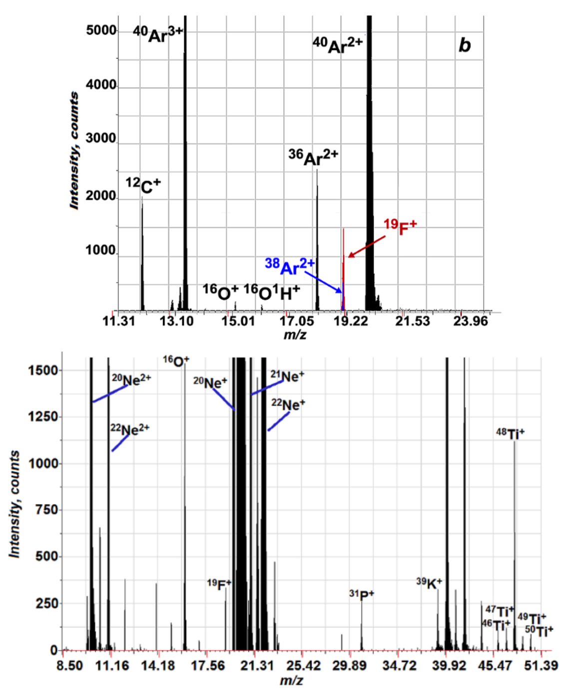
Optimized parameters of O, F determination

Parameter	Ar		Ne
	F quant	O quant	F,O quant.
Auxilliary cathode	Ta	Ta	Ta
Repelling pulse delay, µs	3	4	4
Pulse duration, µs	4	4	4
Discharge voltage, V	1300	1300	1800
Pressure, Pa	37	40	1150
Discharge frequency, kHz	3.2	3.2	3.2

Dependencies of intensities on repelling pulse delay (τ_i)



Mass spectra of KTP:KF (C_F = 0.23 mass %)



Fluorine concentration of KTP:KF crystal and reference material SGD-1A (GDMS, SEM EDX)

Sample	C_F, mass %	C_F, mass % GDMS	C_F, mass % SEM EDX
KTP1	0.20 [a]	0.16±0.06	< 0.5
KTP2	0.22 [a]	0.23±0.07	< 0.5
KTP3	0.45 [a]	0.36±0.09	< 0.5
KTP4	0.45 [a]	0.39±0.11	< 0.5
KTP5	1.24 [a]	1.35±0.33	1.3±0.6
SGD-1A	0.12±0.01[b]	0.11±0.04	< 0.5

a – Putative value calculated from the crystallization charge,
b – Certified value.

KTP elemental content (GDMS, GFA ,SEM EDX)

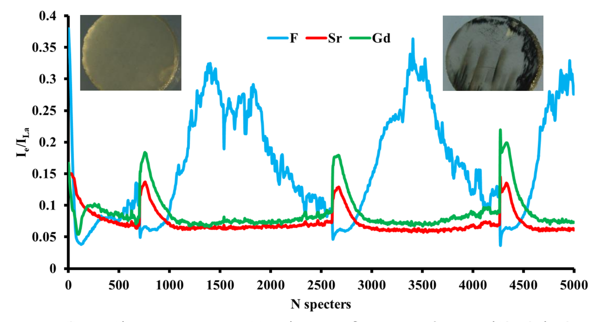
Element	Stoichiometric, mass%	GDMS, mass%	GFA, mass%	SEM EDX, mass%
K	20.10	19.3±1.3	*N.a.*	16.4±1.3
Ti	24.12	(24.12)[a]	*N.a.*	18.6±0.9
P	15.58	16.5±1.7	*N.a.*	15.1±0.7
O	40.20	40.0±1.8	38.6±2.9	50.0 ±2.8

a – Ti was used for internal standardisation

LaF_3SrF_2:Gd crystals

Powdering and pressing on aluminum foil tablete helps avoiding the signal instability

Sample	SrF_2, mass %		
	Putative	SEM EDX	GDMS
1	0.01	-	0.009±0.0002
2	3.0	2.53±0.23	2.64±0.19
3	10.0	6.04±0.25	6.33±0.23
4	16.0	8.21±0.16	8.42±0.26



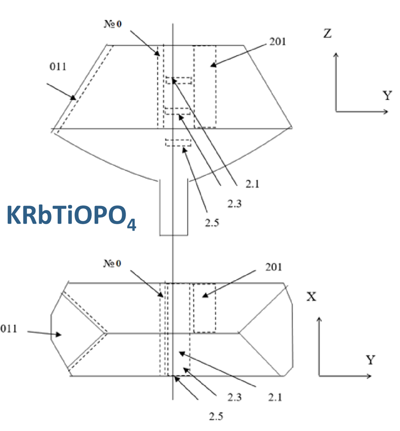
Continuous sputtering of samples with high fluorine content and ionic conductivity

RSF and LoD values for Ar and Ne discharges

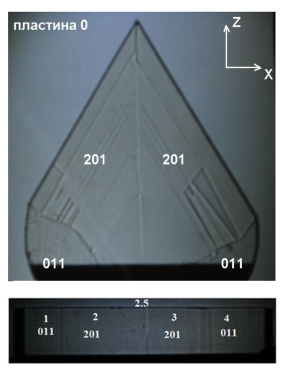
Element	Penning ionization	Electron ionization	
	Ne	**Ar**	**Ne**
Ti	1.80±0.13	1.00	0.20±0.04
K	0.40±0.03	0.46±0.08	0.06±0.03
P	0.45±0.04	0.13±0.04	0.017±0.002
O	0.010±0.001	0.0710±0.0009	**0.30±0.07**
F	0.0060±0.0004	0.22±0.05	**1.9±0.3**

Element	**LoD-Ar, mass %**	**LoD-Ne, mass %**
K	0.002	0.008
P	0.001	0.01
O	0.001	**0.0005**
F	0.01	**0.0002**

Stoichiometry study



KRTP crystal (K:Rb 99.8:0.2 at.%).



Diffraction shadow images of samples indicating different faces

K and Rb content (at. %) in adjacent crystal growth faces

Crystall	Growth Face	GD MS	SEM EDX	GD MS	SEM EDX
		Rb		K	
0.2% Rb 2.5. 1	(011)	0.022±0.001		11.20±0.11	11.26±0.20
0.2% Rb 2.5. 2	(201)	0.052±0.003		12.50±0.06	12.50±0.06
0.2% Rb 2.5. 3	(201)	0.067±0.004		13.12±0.07	13.04±0.12
0.2% Rb 2.5. 4	(011)	0.044±0.005	-	12.14±0.06	12.17±0.17
0.2% Rb 011	(011)	0.066±0.004		11.93±0.04	11.81±0.14
0.2% Rb 201	(201)	0.020±0.002		11.59±0.07	11.54±0.18
5% Rb 5	(100)	0.35±0.02	0.36±0.04	11.43±0.03	11.39±0.24
5% Rb 4	(201)	0.28±0.01	0.34±0.04	11.24±0.06	11.21±0.07

Electrical resistivity of KRTP samples with different Rb content

Crystall	Salt solvent	$C_{Rb/(Rb+K)}$	C_{Rb}, at.%	R, 10^{11} Ohm*cm (T=25°C)
97-05	K_3PO_4:KPO_3=1.5:1	-	-	-
31-11-07	$K_4P_2O_7$=K_3PO_4:KPO_3	-	-	-
31-34-14	K_3PO_4:KPO_3=1.5:1	0.2	0.03	0.6
31-36-14	K_3PO_4:KPO_3=1.5:1	1	0.13	0.8
9-06-17	$K_4P_2O_7$=K_3PO_4:KPO_3	5	0.63	3.0
H -01-19	$K_4P_2O_7$=K_3PO_4:KPO_3	5	0.63	3.3
31-71-97	$K_4P_2O_7$=K_3PO_4:KPO_3	10	1.25	7.8
31-72-97	$K_4P_2O_7$=K_3PO_4:KPO_3	20	2.50	7.9
31-73-97	$K_4P_2O_7$=K_3PO_4:KPO_3	25	3.00	7

Effect of growth speed

Crystal		5% H-01-19	5% 9-06-17
Growth mode		Fast (2.5 weeks)	Slow (5 weeks)
GD MS	C_{Rb}, at.%	0.45±0.02	0.35±0.03
SEM EDX		0.44±0.02	0.34±0.035
Putative		0.625	
GD MS	C_K, at.%	12.08±0.07	11.27±0.06
SEM EDX		12.02±0.09	11.21±0.07
Putative		11.72	

Effect of solvent. Pure KTP samples

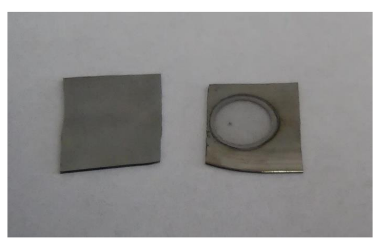
KTP crystal	Salt solvent	O	P	K
97-05	K_3PO_4:KPO_3=1.5:1	94.2±0.8	95.9±0.1	97.7±0.3
31-11-07	$K_4P_2O_7$=K_3PO_4:KPO_3	88.3±2.3	95.6±0.15	97.4±0.5

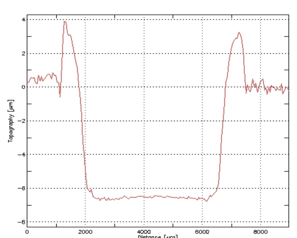
Growth conditions
Temperature, Growth speed, Solvent composition, Dopant content

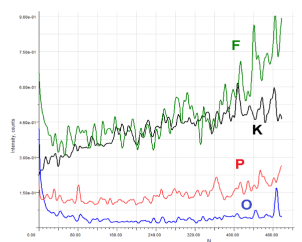
Composition
Distribution of main components and dopants, coefficients of inclusion from crystallization charge

Properties
Optical
Nonlinear optical
Electrochemical

Depth profiling


Before and after sputtering

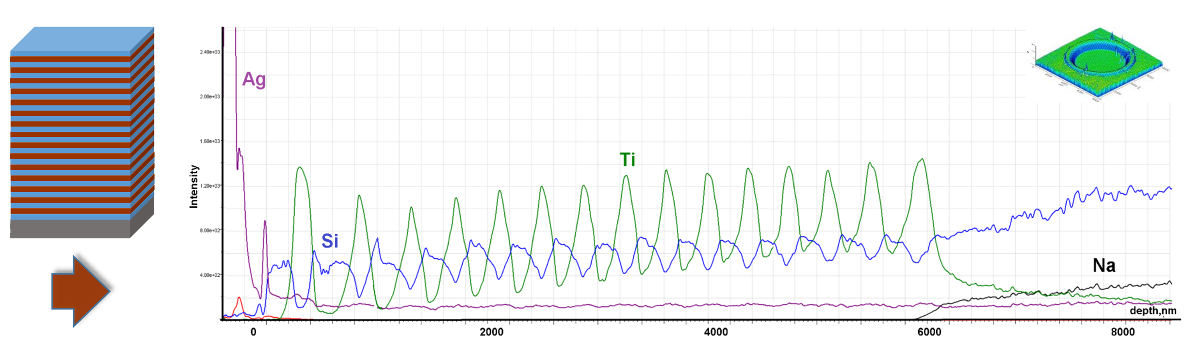

Crater profile



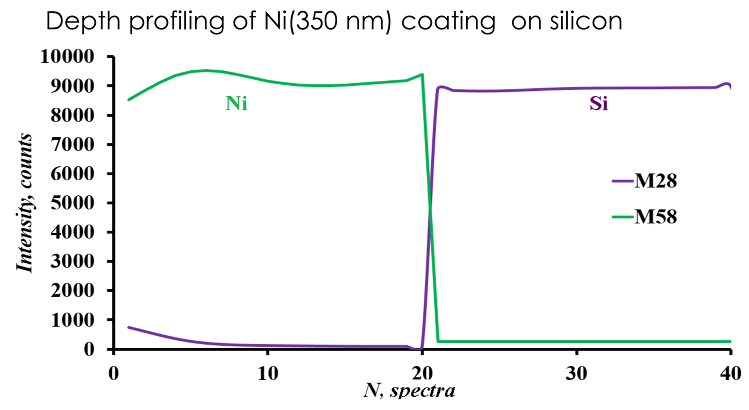
Distribution of components

- ✓ In-depth distribution of main components and dopants
- ✓ Analysis of multilayer mirror/antireflection coatings

Depth profiling of multilayer coating (mirror) 100 nm SiO_2-(200 nm TiO_2-200 nm SiO_2)x15 on glass



Depth profiling of Ni(350 nm) coating on silicon



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References

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