



Direct determination of oxygen and other elements in non-conducting crystal materials by pulsed glow discharge time-of-flight mass spectrometry with potassium titanyl phosphate as an example



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ABSTRACT

Direct quantification of oxygen in dielectric materials using non-destructive or nearly non-destructive techniques still remains a nontrivial task. Simultaneous assessment of oxygen with other elements in a single analytical procedure is even more challenging. In the current study, a method of direct determination of oxygen and other matrix elements in solid samples, based on time-of-flight mass spectrometry with pulsed glow discharge in combined hollow cathode (CHC) is designed and tested. The possibility to effectively ionise oxygen owing to the electron impact mechanism under short repelling pulse delays has been shown. Stable sputtering and ionisation of dielectric samples were obtained via sample coating with thin conducting layer of silver. The parameters of oxygen quantification were optimised: duration and voltage of the discharge pulse, cell pressure, repelling pulse delay and material of the auxiliary cathode. The calibrations of oxygen, phosphorus and potassium are presented. The intensity of $^{16}\text{O}^+$ was shown to be highly dependent on discharge cell pressure. The limits of detection were 0.001, 0.001, and 0.002 mass% for oxygen, phosphorus and potassium respectively. The designed approach enables direct, fast and accurate quantitative and in depth analysis of oxygen-containing samples.

1. Introduction

Oxygen is an omnipresent element and its quantitative determination, both as necessary constituent and admixture, in various natural and technological materials claims high requirement to the analytical techniques employed [1–4]. Currently, the determination of oxygen in gaseous phase or that of dissolved oxygen usually does not pose a serious challenge. Recent review by Wang et al. [5] comprehensively describe the use of spectroscopic techniques in the determination of oxygen. The established methodology includes CNO-analysers [6], Winkler's titration [7,8], electrochemical [9] and optical methods [5]. Nevertheless, for the analysis of solids more problems arise, since the majority of methods applicable for oxygen quantification requires sample dissolution or analyte transfer into gaseous phase [10]. That causes high analytical uncertainty owing to analyte loss and contamination risks. Thus, simple direct techniques are needed in order to fulfil the high requirements to the material testing methods.

The crystals of potassium titanyl phosphate KTiOPO_4 (KTP) and solid solutions containing it are well-known nonlinear optical materials

[11,12]. The properties of KTP-containing materials are highly dependent on the growth method and conditions as well as on concentration and distribution of alloying ions and admixtures in the crystal [13–16]. However, owing to the complexity of the analysis and calibration, there are no reliable direct methods for the quantification of all constituting elements in KTP. Amongst these, oxygen is the most complicated analyte, owing to its pronounced non-metal properties, volatility and omnipresence in the environment.

The following techniques may be applicable for the determination of oxygen in solids: micro-FTIR [17], nuclear techniques (neutron activation analysis and proton induced gamma ray) [18,19], laser-induced breakdown spectroscopy (LIBS) [20], glow discharge optical emission spectrometry (GDOES) [21,22], X-ray techniques (X-ray fluorescence – XRF, energy dispersive X-ray scanning electron microscopy – EDX SEM) [23] and mass spectrometry [21]. X-ray based approaches usually have relatively high limits of detection (LoDs), which are mostly related to the high matrix effects for the light elements [24]. Such LoDs are usually unacceptable for the determination of oxygen at admixture level. Nuclear techniques are capable to quantify oxygen

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both in thin films and bulk samples [19,23]. However, high instrumental and maintenance costs, low availability of the methods and spectral interferences are limiting the use of these techniques. The applicability of micro-FTIR [17,25], LIBS [20] and GDOES [21] is mainly limited by relatively high detection limit and interferences. Concerning all the mentioned techniques, one should notice that oxygen quantification needs special approaches and becomes much more complicated if simultaneous assessment of other elements in a single analytical procedure is required. This is, for example, the case of crystal non-stoichiometry study.

Glow discharge mass spectrometry (GDMS) is a highly sensitive technique capable to quantify such elements as oxygen. Recent studies on GDMS assessment of oxygen in conducting materials showed good calibration linearity and relatively low LoD [21,26]. GDMS does not require laborious sample pre-treatment and is capable to perform a multielement analysis of dielectrics [27] and in depth analysis [28–30]. In the studies devoted to the determination of light non-metals (oxygen, chlorine, nitrogen etc.) [21,31–33], the following approaches have been proposed for the effective ionisation [31,32]: helium addition into the discharge cell [32] or electron impact ionisation under short repelling pulse delay [31]. To the best of our knowledge, GDMS oxygen quantification was previously reported for the conducting materials only [21,26]. The GDMS analysis of dielectrics requires special means: the use of radiofrequency power supply or the formation of surface conductivity for direct current glow discharge. Surface conductivity formation may be achieved by pressing into the conducting matrix [34–36], pouring into metallic indium [37], the use of secondary [38] or auxiliary hollow cathode [27,39].

The current study reports a GDMS-based approach for the effective ionisation and quantification of oxygen and other matrix elements of the dielectric sample. The direct analysis of pure KTP crystal and comparison to reference techniques were used for the quality control.

2. Materials and methods

2.1. Instrumentation

A time-of-flight mass spectrometer Lumas-30 (Lumex, St. Petersburg, Russia) with pulsed glow discharge was used for the measurements. The discharge cell consists of a combined hollow cathode (CHC), including the sample under study and a metallic cylinder (inner diameter of 6 mm), produced of high purity tantalum (99.99%) or aluminium (99.999%). The instrument provides elemental analysis of solids in mass range up to 350 u with mass resolution $m/\Delta m \approx 800$. The technical characteristics of the instrument and its applications are described elsewhere [36,40–42]. High purity argon (99.9999%, LindeGaz Rus, St. Petersburg, Russia) was used to maintain the glow discharge. The working parameters are presented in Table 1. The intensity of isotope components was obtained by integrating the mass spectrum using an integration window of ± 0.15 u from a peak centre.

As an alternative quantification approach, SEM EDX, using a scanning electron microscope Zeiss Merlin (Carl Zeiss AG, Oberkochen,

Germany) with an EDX detector INCAx-act (Oxford Instruments, Abingdon, UK) and accelerating voltage of 20 kV, was used. The scanning area was $100 \times 100 \mu\text{m}$. Prior to analysis, 2 mm carbon layer was deposited onto the sample. The measurements were performed in 4 replicates ($n = 4$).

Also, gas fusion analysis (GFA), using oxygen analyser in inorganic samples TC-500 (LECO Corporation, St. Joseph, MI, USA) was used as a reference approach of oxygen assessment in KTP. Since the approach is designed for low oxygen content (up to 5%), powdered KTP sample was preliminary mixed with iron powder (1:10). Fusion was performed in helium atmosphere; oxygen was detected in the form of carbon dioxide with IR sensor. The measurements were performed in 5 replicates ($n = 5$).

2.2. Materials and chemicals

KTP crystals were grown using modified Czochralski method from phosphate melt solution (KH_2PO_4 , K_2CO_3 , TiO_2) at the JSC “Research and Production Corporation S.I. Vavilova”. For the analysis, the crystals were polished and cut into the specimens with dimensions of $20 \times 10 \times 2$ mm.

For quantification, relative sensitivity factors (RSF) [43,44] were used. Titanium was used for normalisation due to its constant and stable content in KTP (ca. 24.12 mass%). Two types of calibrants were prepared for the RSF assessment (Tables 2 and 3). The first type (specimens C1–C5) was produced from aluminium powder (99.9%), titanium oxide (99.5%) and lanthanum fluoride (99.99%) – Table 2. All chemicals were purchased from Sigma Aldrich (Merck KGaA, Darmstadt, Germany). The second type (C6–C8) consisted of the same components (Al, TiO_2 and LaF_3) with the addition of KH_2PO_4 (Shvabe Holding, Moscow, Russia) – Table 3. To produce the calibrants (C1–C8), all materials were grinded in an agate mortar for at least 30 min. Afterwards, the mixtures were pressed into the tablets (diameter 10 mm, thickness 2 mm), using a hydraulic press PRG-400 (ROST, Moscow, Russia).

2.3. Sample preparation

A thin layer (ca. $5 \mu\text{m}$) of metallic silver was coated on the whole sample surface to maintain surface conductivity. For this purpose, silver suspension in 2-propanol (Kontaktol-Radio (Elast), Moscow, Russia) was used. All test and calibration samples were preliminary dried with a technical fan (150°C , 2 min) to reduce the effect of absorbed moisture. The samples were installed into the mass spectrometer and purged by argon flow for additional 20 min.

2.4. Statistics

For the determination of the RSF, 10 replicate measurements of the calibrants were used ($n = 10$). The data obtained are presented as mean \pm confidence interval ($n = 10$, $P = 0.95$). For the normalisation element (Ti) the RSF value was taken as 1.00 with a standard deviation of 0.00. Quantification data were also calculated from 10 replicate measurements ($n = 10$) and are presented as mean \pm confidence interval ($n = 10$, $P = 0.95$).

3. Results and discussion

3.1. Effective sputtering of KTP

The important feature of the KTP crystals to be kept in mind is their non-conductive nature. The effective sputtering requires the formation of surface conductivity. We used the silver coating (section 2.3) for the purpose [45]. The use of silver suspension in 2-propanol with concomitant drying at 150°C is rather simple and cheap approach to maintain surface conductivity. This approach allows for effective

Table 1
Mass spectrum acquisition parameters.

Parameter	Value
Sampler aperture diameter	1.5 mm
Skimmer aperture diameter	1.5 mm
Auxiliary cathode material	Ta or Al
Discharge pulse voltage, V	–900 to –1600
Discharge current	up to 3A
Pulse duration, μs	3–5
Discharge frequency, kHz	1–4
Pressure, Pa	37–45
Repelling pulse delay, μs	1–300

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