Atomic Absorption Spectrometric Studies for the Analysis of Optical Single Crystals

Summary of Doctoral (Ph.D.) Thesis

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2013

Introduction

Industrial application of optical single crystals depends on their optical properties (e.g. photorefractivity, frequency doubling). These optical properties are determined by the structure and the chemical composition of the crystals. Incorporation of a dopant element (or an impurity, in an unfavourable case) into the crystal bulk can be decisive. Its effect is determined by the crystal type, the element itself and the concentration of the element. Moreover, it is an important question that how effectively the dopant element incorporates into the crystal bulk during the growth process and what kind of concentration profile of it develops along the growth axis. Incorporation of dopants along the growth axis is often not even, but it can be of very different degree, depending on the element and the crystal type. For the understanding of the optical properties and for the optimization of the growth parameters, the concentration of dopants in the studied crystals or in their different parts (top, bottom) and in the growth residue is important information to learn. In our laboratory we determine the concentrations of dopants and impurities of optical crystals by flame atomic absorption spectrometry (FAAS) and, in the case of lower analyte concentrations, by means of graphite furnace atomic absorption spectrometry (GFAAS).

In atomic absorption spectrometry solution sampling methods are generally used. The use and the study of solid sampling methods are infrequent, they can be considered as rarity. GFAAS is the only atomic absorption technique, which is suitable for solid sampling analysis directly, without technical modifications. Solid sampling analysis has several advantages over solution sampling GFAAS: better detection power, shorter total analysis time, less probability of sample contamination and the freedom from solvent-induced interferences. However, the sample amount in solid sampling analysis can be some orders of magnitude higher than that of using solution sampling, and because of this, significant spectral and non-spectral interferences can occur.

Our aim was to elaborate a reliable solid sampling GFAAS method for the analysis of iron- and manganese-doped $LiNbO_3$ (lithium niobate) single crystals.

The GFAAS determination of rare earth elements using an end-heated tube is usually hampered by memory effect and carry-over. The literature describes several methods in order to eliminate or at least to reduce memory signals. One of them is the halogenation of refractory sample components. However, most of the published halogenation procedures require the modification of the gas supply system of the GFAAS spectrometer.

Our aim was to reduce the memory effect occurring in the GFAAS analysis of erbium- and neodymium-doped $LiNbO_3$ and Bi_2TeO_5 (bismuth tellurite) crystals using a novel halogenation method, which does not require the modification of the gas supply system of the GFAAS spectrometer.

Applied Methods

Sample preparation and other procedures

Samples were taken from different parts of the crystal bulk, cut by a diamond-edge disc perpendicularly to the growth axis. These crystal slices, weighing up to 1-2 g, were washed in ethanol and acetone-ethanol mixture and after drying they were ground in an agate mortar. In order to avoid cross-contaminations, each crystal type was ground in its own mortar, which served for grinding exclusively $LiNbO_3$ or Bi_2TeO_5. For solid sampling analysis further sample preparation was not done. For solution sampling analysis, the crystal samples were digested. For this purpose, samples were weighed on a calibrated electronic analytical balance.

For solid sampling GFAAS experiments, powdered samples were weighed on a calibrated microbalance onto curved graphite platforms. Before weighing, 10-20 μL aliquots of blank or standard solutions were pipetted onto the platforms and the platforms were dried in an electric hotplate. Platforms were inserted to the graphite furnace via tube ends using plastic tweezers, after the optical windows were removed. Platforms were positioned in the middle of the furnace by thin, yellow plastic micropipette tips with pre-marked distance scales. After positioning a platform, the ends of the furnace were sealed by the optical windows, the heating programme was run and the atomic absorption measurement was performed.

Halogenation was done using 20 μL aliquots of CCl_4, which were pipetted into the graphite furnace. After dispensing, CCl_4 was partially evaporated and the remaining part of it halogenated the sample components, by using a heating programme elaborated for this purpose.

Instrumentation and measurement conditions

All GFAAS measurements were performed at Wigner RCP of HAS on a Carl Zeiss AAS-3 (Jena, Germany) atomic absorption spectrometer, equipped with an end-heated Carl Zeiss EA-3 graphite tube electrothermal atomizer. An MPE type autosampler pipetted the 20 μL aliquots of

solutions or CCl_4 into pyrolytically coated graphite tubes. For continuum source background correction, deuterium and tungsten halogenide lamps were used in the UV and the visible spectral range, respectively. As primary sources, hollow cathode lamps (Cathodeon, Cambridge, England) of the analyte elements were applied. High purity argon (4N5) was applied as a furnace purge gas with an external flow rate of 1000 cm^3/min.

For the temperature calibration of the graphite furnace, an automatic optical pyrometer was focused onto the inner wall of the graphite atomizer via the sample dosing hole. This pyrometer follows the wall temperature in the range of 20-2800 ^{o}C by detecting the IR radiation at 2.5 μm. NiCr-Ni and PtRh-Pt thermocouples were used to determine the emissivity of the tube wall relative to that of the black body radiation and to calibrate the pyrometer.

The reliability of the elaborated analytical methods was checked applying several independent analytical methods: X-ray fluorescence spectrometry (XRF), flame atomic absorption spectrometry (FAAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS).

Energy dispersive XRF analysis was performed by László Bencs and Katleen van Meel at University of Antwerp, Belgium, using an Epsilon 5 (PANalytical, Almelo, The Netherlands) model high-energy spectrometer, equipped with a 600 W Gd-anode and a high purity Ge-detector. Measurements were done under vacuum and by rotating the samples, using an acquisition time of 1000 s.

FAAS measurements were done at Wigner RCP of HAS using a Varian AA-20 spectrometer. An air-acetylene flame was applied with a burner of 10 cm slit. As primary sources, the same hollow cathode lamps were used like in GFAAS experiments.

The ICP-OES analysis was performed at Eötvös Loránd University, Faculty of Science, Institute of Chemistry, by Imre Péter Varga, using a Labtam 8440 Plasmalab type spectrometer equipped with a polichromator and also a monochromator.

ICP-MS measurements were performed at Centre for Energy Research of HAS with the participation of Zsolt Stefánka, Éva Széles and Kornél Fél. A high resolution, double focusing magnetic sector field mass spectrometer, equipped with a single electron multiplier was applied.

For the interpretation of my results I utilized the EPMA (electron-probe X-ray microanalysis) measurements of Bálint Alföldy, which were performed at Centre for Energy Research of HAS using a PHILIPS 505 type scanning electron microscope equipped with Link Si(Li) detector. I also utilized the XANES (X-ray near-edge absorption structure) analysis of János Osán, which was performed at the microfluorescence-beamline L of the DORIS III synchrotron ring of HASYLAB, Hamburg, Germany.

New Scientific Results

1.) I have elaborated a novel, solid sampling (SS-) GFAAS method for the determination of Fe and Mn dopants in $LiNbO_3$ optical single crystals. For the optimization of the measurement conditions I applied the Welz-type pyrolysis and atomization curves recorded by solution-based GFAAS. I performed the calibration by the „Three-Point Estimation Standard Additional Method". The reliability of this SS-GFAAS method was checked by numerous independent analytical techniques. The new SS-GFAAS method can be an alternative solution for the occurrence of strong non-spectral interferences, for instance, in the presence of a refractory matrix. The method is very flexible and because of this it is suitable for determinations over a wide analyte concentration range, either it can achieve a detection power commensurable to that of the ICP-MS technique.

2.) I have developed a new calculation method for the estimation of the limit of detection (LOD) in SS-GFAAS using the Three-Point Estimation Standard Additional Method. Accordingly, the measured concentration in the sample was multiplied by the ratio of the sample mass used for the calculation of the points of the addition curve and the maximum sample mass, which could be weighed onto the platform. Since the measurement conditions can be adjusted flexibly to the concentration of the sample, the LODs calculated in this manner reflect the detection power only under the given circumstances and not the real limits of the method.

3.) I have elaborated a novel procedure for the estimation of the best attainable LOD using the Three-Point Estimation Standard Additional Method. The principle of this is that the characteristic masses reflect the sensitivity of measurement conditions numerically. Because of this, the sensitivity and the characteristic mass of the actual SS-GFAAS determination are compared to the most sensitive conditions and to the corresponding characteristic mass as a reference value. The best attainable, „theoretical" LOD can be estimated as the SS-GFAAS LOD is divided by the ratio of the characteristic masses belonging to the SS-GFAAS and to the most sensitive, „solution-based" GFAAS conditions. In the case of Mn, the analysis under the most sensitive analytical conditions was not performed, so only the best attainable LOD at the utilized analytical line could be estimated. On the basis of the theoretical LOD of Fe, with the application of the new SS-GFAAS method, a detection power commensurable to that of the ICP-MS technique can be achieved.

4.) I have applied a novel halogenating procedure to reduce the memory effects of refractory sample components occurring in the graphite furnace. In this procedure, liquid CCl_4 is pipetted into the graphite furnace, then it is partially evaporated and the CCl_4 remaining in the furnace was

employed to halogenate the refractory sample components. This procedure is simpler and cheaper than most of the methods published in the literature, since in contrast to them, it does not require any modification of the GFAAS spectrometer's gas supply system. This halogenation procedure is appropriate for the cleaning of used, contaminated graphite tubes and platforms and for the regeneration of their pyrolytic graphite coating.

I have shown that the novel halogenation method using CCl_4 efficiently reduces the memory effects of Er and Nd in the graphite furnace. However, chloride residues in the furnace may reduce the absorbance signal during subsequent analytical cycles. These are valid in the presence of digested Bi_2TeO_5 and $LiNbO_3$ matrices and in a media containing no matrices. The efficiency of the halogenation procedure presumably can be further improved both in the case of Er and Nd by the further optimization of the procedure.

5.) Using this CCl_4-assisted halogenation, I have elaborated and applied a novel GFAAS method for the determination of Er and Nd dopants in Bi_2TeO_5 optical single crystals. The main point of it is that the cleaning step of the conventional GFAAS heating programme was replaced by this halogenation procedure. This modified programme was applied at the end of every measurement series (3-5 measurements). After that it was proven to be useful to run a furnace blank to get rid of the chloride residues. Calibration could be performed by simple aqueous standards. The achieved LODs of this new GFAAS method for the solid crystal samples are 0.18 µg/g and 2.5 µg/g for Er and Nd, respectively. The reliability of this GFAAS method was checked by means of XRF spectrometry.

Publications

Articles on the Subject of the Thesis

1.) László Bencs, Krisztina György, Márta Kardos, János Osán, Bálint Alföldy, Imre Varga, Zsolt Ajtony, Norbert Szoboszlai, Zsolt Stefánka, Éva Széles, László Kovács, *Determination of trace elements in lithium niobate crystals by solid sampling and solution-based spectrometry methods*, **Analytica Chimica Acta**, 726 1-8 (2012).

2.) Krisztina György, Zsolt Ajtony, Katleen Van Meel, René Van Grieken, Aladár Czitrovszky, László Bencs, *Fast heating induced impulsed halogenation of refractory sample components in electrothermal atomic absorption spectrometry by direct injection of a liquid halogenating agent*, **Talanta**, 85 1253-1259 (2011).

Conference Poster and Oral Contribution on the Subject of the Thesis

3.) György Krisztina, Ajtony Zsolt, Bencs László, *Nehezen párolgó mintakomponensek halogénezése grafitkemencés atomabszorpciós meghatározáshoz*; **56. Magyar Spektrokémiai Vándorgyűlés**, Veszprém, Hungary, 2013. July 1-3, (poster, in Hungarian).

4.) György Krisztina, Ajtony Zsolt, Varga Imre, Széles Éva, Stefánka Zsolt, Bencs László, *Lítium-niobát kristályok adalékelemeinek szilárdmintás és oldatos grafitkemencés atomabszorpciós meghatározása*, **56. Magyar Spektrokémiai Vándorgyűlés**, Veszprém, Hungary, 2013. July 2, (oral contribution, in Hungarian).

Articles on Other Research Subjects

5.) Zsolt Ajtony, Norbert Szoboszlai, Emőke Klaudia Suskó, Pál Mezei, Krisztina György, László Bencs, *Direct sample introduction of wines in graphite furnace atomic absorption spectrometry for the simultaneous determination of arsenic, cadmium, copper and lead content*, **Talanta**, 76 627-634 (2008).

6.) Krisztina György, László Bencs, Pál Mezei, Tamás Cserfalvi, *Novel application of the electrolyte cathode atmospheric glow discharge: Atomic absorption spectrometry studies*, **Spectrochimica Acta Part B,** 77 52-57 (2012).

Conference Posters on Other Research Subjects

7.) Mezei Pál, Cserfalvi Tamás, Bencs László, György Krisztina: *Elektrolitkatódos atmoszférikus kisülés vizsgálata atomabszorpciós spektroszkópiával*; **Kvantumelektronika 2008**, VI. szimpózium a hazai kvantumelektronikai kutatások eredményeiről, Budapest, Hungary, 2008. Oct. 17. (in Hungarian).

8.) Pál Mezei, Tamás Cserfalvi, László Bencs, Krisztina György: *Investigation of the metal distributions in the plasma of the Electrolyte Cathode Atmospheric Glow Discharge*; **Colloquium Spectroscopicum Internationale XXXVI**, Budapest, Hungary, 2009. Sept. 2.