Pyroelectric X-ray Generator for XRF in Combination with Optical Microscopy

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Abstract. X-ray fluorescence spectroscopy (XRF) is a method for elemental analyses of materials. In comparison to other analysing methods such as energy dispersive X-Ray spectroscopy (EDS) within a scanning electron microscope (SEM) or optical emission spectroscopy (OES) there are several advantages. This paper contains experimental investigations to improve the emission behaviour of a pyroelectric X-ray source regarding X-ray energy and output intensity. Pyroelectric lithiumtantalate (LiTaO₃) was used to emit and accelerate electrons and to generate primary X-rays subsequently. Geometrical conditions were altered and the design of the X-ray source was optimized. All steps of optimization have been performed with respect to an application in a spectroscopic device in combination with an optical microscope (OM). Based on this purpose, the miniaturization of all applied components is of major importance. Different pure metals, alloys, and a coated specimen were analysed to demonstrate potential applications and current limitations of the designed system. Materials with a wide range of necessary excitation energy for chemical analyses of 1.5 to 10 keV for the Kα and Lα X-ray fluorescent lines were used to demonstrate the technical relevance of this type of application. As a result, a prototype of a spectrometer that combines XRF and OM was designed and tested.

1 Introduction

The pyroelectric effect is a well-known phenomenon by now. It is based on a change in polarization of pyroelectric crystals such as lithiumniobate (LiNbO₃) and lithiumtantalate (LiTaO₃) caused by a change of crystal temperature¹. Under atmospheric conditions this change in polarization does not cause an electrical field due a compensation of the polarization by surface charges ¹,². The compensation is suppressed by applying vacuum conditions and a strong electrical field of up to 1.35 · 10⁷ V/cm for LiNbO₃ can be measured³. The generated potential difference ΔU in dependence on the temperature change ΔT can be estimated by the following equation:

\[
\Delta U = \frac{p \cdot z}{\varepsilon_r \cdot \varepsilon_0} \cdot \Delta T \quad (1)
\]
$z$ is the dimension of the crystal in direction of polarization, $p$ is the pyroelectric coefficient of the used pyroelectric material, $\varepsilon_r$ is the relative permittivity of the crystal and $\varepsilon_0$ is the permittivity of the vacuum ($8.854 \times 10^{-12}$ As/Vm)$^4$.

The strength of the electrical field caused by the crystal under suitable conditions can be used to ionize residual gas molecules and emit electrons. These electrons are accelerated by the surface charges of the crystal subsequently. The direction of the acceleration depends on the direction of $\Delta T$, heating or cooling respectively$^6$. The energy and intensity of the accelerated electrons is sufficient high to generate X-rays, which was first described in 1992$^6$. In the following numerous possible applications were discussed and first commercial pyroelectric X-ray generators were produced ($Cool$-$X$, Amptek, Bedford MA, USA) and tested for potential X-ray fluorescence analyses (XRF)$^7,8$.

A significant increase of intensity and a controllable maximum output energy of a pyroelectric X-ray source could be reached by selectively optimizing working conditions$^9,10$. The existence of high intensities is fundamental for further applications of pyroelectric X-ray sources in $\mu$-XRF spectrometers$^{10}$. Aim of the studies described here is the transfer of the knowledge of possible optimization steps to miniaturize necessary components by providing basic requirements such as high intensities and adjustable energy in order to combine a pyroelectric X-ray source with an optical microscope for elemental analyses of materials.

2 Experimental

The experiments are divided in four major developing steps as shown in Figure 1.

![Figure 1. The stepwise development of a combined XRF and optical microscopy system.](image)

The pyroelectric X-ray source was optimized in terms of high output intensity. Results of previous experiments with regard to crystal type, geometrical parameters and optimized pressure were used$^9,10$. This is essential for the integration into an optical microscope because of the reduction of primary X-ray intensity due to the application of smaller crystals in a miniaturized device. After optimization and miniaturization, the X-ray source was integrated into an optical microscope to demonstrate a possible application for XRF during microscopic investigations. Finally, the developed system was tested with different samples. XRF and microstructural investigations were performed.

2.1 Optimization of X-ray output intensity

In the latest studies different possibilities of an optimization of output intensity were investigated. Different arrangements between crystal and target were compared regarding X-ray generation in remission and transmission respectively. The influence of the target material, target angle referring to the direction of the electrons, crystal size and crystal material were described as well$^9,10$. As a result of these improvements, an X-ray output intensity for primary X-rays of up to $1.0 \times 10^7$ counts in a period of 600 s for the Cu Kα peak has been achieved using a $5 \times 5 \times 6$ mm$^3$ LiTaO$_3$ crystal. A remission setup for crystal, target and window with a target angle of $12^\circ$ and a working pressure of $2 \times 10^{-4}$ mbar was identified as optimum. The maximum endpoint energies measured were up to 60-70 keV$^9$.

XRF with different materials was performed to evaluate potentials and limitations for an application as spectrometric tool in materials science. A vacuum test rig was used. An overlay of different spectra as results of XRF investigations is shown in Figure 2.
Figure 2. Results of XRF analyses with optimized pyroelectric X-ray source. Five sheets with different chemical composition were analyzed using the optimized X-ray source to determine the detection range. Distinct peaks of aluminum (Al), titanium (Ti), chromium (Cr), iron (Fe), copper (Cu) and zinc (Zn) are apparent.

An energy dispersive X-ray detector (Amptek X-123 silicon drift x-ray detector) was used to collect the X-ray spectra. The crystal was heated from room temperature up to 140 °C using a 5 Ω resistance heater. The spectra were collected for 4 to 9 heating-cooling-cycles of 600 s per cycle. The number of cycles was increased to reach evaluable intensities in the XRF spectra for elements with low atomic numbers such as aluminium (Al). Sheet metals of different composition with dimensions of 50 · 100 · 1.5 mm³ were used as specimens. Different characteristic X-ray fluorescent transitions from 1.48 keV for aluminium Kα to 9.56 keV for zinc Kβ were excited by the optimized X-ray source.

2.2 Transferring optimized conditions into a miniaturized X-ray source

For the combination of a pyroelectric X-ray source with an optical microscope the miniaturization of the arrangement described above is necessary. It had to be considered to reach sufficient output energy to excite fluorescence of all technical relevant materials and highest possible output intensity to lower the duration of the XRF analyses. The following setup was chosen:

- copper target in combination with a lithium tantalate crystal (9 · 9 · 5 mm³)
- target angle of 12 ° and a distance of 11 mm between target and crystal surface
- steel tube with a working pressure of 2 · 10⁻³ mbar and a 25 µm Kapton® X-ray window
- 5 Ω resistance heater
- Pt-1000 temperature sensor
- 3D-printed polymer mount for internal components
- external vacuum pump
- Amptek® X-123 silicon drift X-ray detector

To implement all conditions into the miniaturized X-ray source the polymer insert shown in Figure 3 was produced by additive manufacturing.
Figure 3. Schematic construction of the additive manufactured insert which implements the optimized parameters in the miniaturized pyroelectric X-ray source.

The shown device is inserted into a cylindrical stainless steel case. This case is connected to a mechanical rotary vacuum pump to evacuate the system. After evacuation, the system's pressure is about $2 \times 10^{-3}$ mbar. The case has a hole with a diameter of 3 mm which is covered by a polyimide film and used as an exit window for the primary X-rays. First XRF analysis of a brass sample was made using the developed X-ray source in combination with a silicon drift detector (SDD). The used arrangement is schematically shown in Figure 4.

The results show characteristic peaks for copper (Cu) and zinc (Zn). Additionally, a peak for iron (Fe) was measured which should not appear for the analysis of this type of brass sample. Obviously, the primary X-rays cause an emission of characteristic X-rays at the edge of the 3 mm hole of the steel case. To avoid the detection of this radiation a lead shielding was added. To prove the function of the shielding the brass sample was analysed again. The spectra were collected for 600 s with shielding and without using a lead shielding respectively. An overlay of both spectra is shown in Figure 5.
**Figure 5:** Spectra of XRF analyses of brass sheet. It verifies that the lead shielding is sufficient to prevent the detection of X-ray fluorescence emitted from the X-ray sources steel case during XRF analyses.

The copper $K_{\alpha}$ and $K_{\beta}$ lines as well as the zinc $K_{\alpha}$ and $K_{\beta}$ lines show similar intensities in both cases. The iron $K_{\alpha}$ line disappears when using the arrangement with a lead shielding. The lead shields the X-ray fluorescence of the steel case without decreasing the primary intensity and guarantees correct results.

### 2.3 Integration of the pyroelectric X-ray source into an optical microscope

A suitable geometrical arrangement was figured out for the optical microscope (Zeiss Stemi 305 with AxioCam ERC5s), the X-ray source and the SDD. It is necessary to ensure the sample to be in the focal point for both methods, optical microscopy and XRF respectively. This offers the possibility of microstructural investigations and XRF at the same time. For this reason an electrically movable stage was implemented. It allows to focus the sample surface for optical analyses as well as for chemical analyses without changing settings of the system itself. The arrangement is shown in Figure 6 A. Furthermore, the complete prototype system is shown in Figure 6 B.

**Figure 6.** A: Arrangement of pyroelectric X-ray source, SD detector and optical microscope. 

**B:** Developed prototype system for XRF and optical microscopy with its components.
2.4 Testing of combined analyses system

Different samples were analysed using the system described above. Three sheets made of titanium, stainless steel and brass were used. The spectra generated were collected within 900 s and are shown in Figure 7.

![Figure 7](image)

**Figure 7.** Spectra from XRF analyses of titanium, brass and stainless steel sheets with miniaturized pyroelectric X-ray source to proof that several elements can be detected with the developed arrangement.

Referring to the characteristic lines at 4.5 keV and 4.93 keV in the spectrum it is possible to identify the sheets as titanium and stainless steel with associated lines at 5.4 keV for chromium, 6.39 keV for iron and 7.47 keV for nickel. The copper and zinc lines at 8.04 keV and 8.63 keV in the spectrum belong to the brass sheet. As a consecutive step two parts of medical implants of unknown chemical composition were analysed. A microscopic characterization of the samples surface with a simultaneous chemical analysis was performed. Figure 8 A and B, are giving an overview. Figure 8 C and D are showing micrographs of each implant part applying a magnification of 25x.

![Image](image)

**Figure 8.** a: Overview of implant 1. b: Overview of implant 2. c: Micrograph of implant 1 at a magnification of 25x. d: Micrograph of implant 2 at a magnification of 25x. XRF analyses were applied on the red framed areas.
After the optical analysis an XRF analysis with the developed pyroelectric X-ray source was applied on both implant parts (red framed XRF area). The spectra were collected for about 900 s and are shown in Figure 9.

**Figure 9**: Spectra of XRF analyses with miniaturized pyroelectric X-ray source of implant 1 (red) and implant 2 (blue) to distinguish both samples with respect to their chemical composition.

The results of XRF show that implant 1 is made of a titanium vanadium alloy (lines at 4.5 keV for titanium and 4.94 keV for vanadium) and has a different chemical composition compared to implant 2, which is made of a cobalt chromium alloy (lines at 5.4 keV and 5.95 keV for chromium and 6.92 keV and 7.65 keV for cobalt). The lower part of implant 1 shows a different surface structure. An image was taken with the optical microscope and a chemical analysis was applied to this area. It shows a calcium (Ca) rich coating of this part of implant 1. The micrograph and spectrum are shown in Figure 10.

**Figure 10**: Spectrum from XRF analysis of hydroxyapatite coating on a TiAlV implant (top right corner) with miniaturized pyroelectric X-ray source. Distinct peaks of the substrate (Ti, V) and of the coating (Ca) can be separated.

Calcium Kα (3.7 keV) and Kβ (4.01 keV)-Lines were detected. Titanium and vanadium are also detected caused by the interaction with the substrate. By identifying calcium, the coating is assumed to
be hydroxyapatite being a common coating for prosthesis besides Ti(Nb)N, different ceramic alternatives and polymer coatings. Hydroxyapatite also contains phosphorus. This element could not be detected using this arrangement.

3 Summary and conclusion
A functional prototype combining an optimized pyroelectric X-ray source and an optical microscope was developed and tested. Different materials were characterized by XRF and optical microscopy. It was shown that a wide range of technically used metals and alloys can be analyzed due to their elemental composition. The developed system is a suitable tool for extending the opportunities of characterization of an optical microscope. During the analyses, limitations of detectable elements were determined. The detectable element with the lowest atomic number Z in this arrangement was Calcium. By a further increase of the primary X-ray intensity, a measuring time reduction for faster investigations might be achieved and the detection of characteristic X-rays of lower energy might be enabled as well. For local XRF (μXRF) the focusing of primary X-rays is conceivable. This might be accomplished by individually designed glass fiber capillary lenses.

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