Palm-top size X-ray microanalyzer using a pyroelectric focused electron beam with 100-micro-meter diameter

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Palm-top size X-ray microanalyzer using a pyroelectric focused electron beam with 100-micro-meter diameter

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Abstract. We have developed a palm-top size EPMA (electron probe X-ray microanalyzer), operated by 3 V electric battery except for a rotary vacuum pump. The electron beam was generated by a pyroelectric single crystal, $LiTaO_3$. A needle was used to make a focused electron beam. The smallest beam size was 100 μm on the sample surface. The X-ray spectra were measured through a Kapton window by a Si-PIN detector for a model specimen containing TiO_2 and MnO_2 particles, which was an aerosol model specimen, where TiO_2 and MnO_2 particles of size about 100-200 μm were separated by a few hundreds micrometers. By moving the sample stage manually, the X-ray spectra were measured for 300 s each by 300 μm e-beam, and the measured X-ray intensities were strong enough for identification of the major element in individual 100-200 μm size aerosol particles.

1. Introduction

Brownridge found X-ray emission effect from a pyroelectric single crystal when it was placed in a vacuum and it was heated or cooled [1]. The conditions of the pyroelectric X-ray emission were extensively studied by Brownridge and Reboy [2] and by Brownridge [3]. An X-ray source using the principle found by Brounridge is commercially available from Amptek Ink. as COOL-X [4]. Applications of COOL-X for X-ray fluorescence analysis and even X-ray absorption spectroscopy were summarized by Kawai *et al.* [5]. Kawai *et al.*[6] also published methods how to make such an X-ray source using a cheap and easily obtainable electric, mechanical, and vacuum parts in a chapter of an open access book.

Geuther and Sanon [7] showed a series connection of two pyroelectric crystals in an electric circuit produced twice the higher energy X-rays; one crystal produced 100 keV X-rays, and two crystals could produce X-rays up to 200 keV. Hiro *et al.* [8] put a small specimen piece on the top of one pyroelectric single crystal ($LiTaO_3$ of 3×3 mm^2 cross-section and 10 mm length) during a similar experiment as Geuther and Danon, and observed strong characteristic X-rays from the small piece specimen. This was the first experiment of the “palmtop EPMA”. The palmtop EPMA has been improved step by step by using quick coupling nipples and T-shape pipes [9-11]. Carbon rod sample holder could avoid the X-rays from the sample stage. And finally by using a needle on the top of the pytoelectric crystal, we have succeeded to make an electron beam of the size of 100 μm diameter [12].

When the temperature of the pyroelectric single crystal increased from room temperature to *e.g.* 100 °C by a small Peltier device, the top surface of the pyroelectric crystal accumulated electric charge and consequently the electric potential becomes about -40 kV. A floating residual electron in the vacuum was accelerated toward to the grounded sample on the carbon rod, hitting the sample surface.

Once the sample was bombarded by the electron, then the secondary electrons will be produced, and again the secondary electrons were accelerated by the electric potential to hit the target again and again, exciting the characteristic X-rays. The X-rays continued for a few minutes and stopped by neutralized the electric charge on the ptroelectric crystal. Then the temperature of the pyrpelectric crystal should be decreased down to room temperature by changing the polarity of the 3 V electric battery of the Peltier device. Then again the temperature was increased, we could repeat the X-ray emission. If a needle was put on the top surface of the pyroelectric single crystal, and high electric potential surfaces other than the needle was shielded by vacuum silicone grease, the electron beam could be focused to 100 μm on the sample surface. In the present paper, we describe how to find the focusing of the electron beam during the experiment, and present an example of practical single particle model specimen analyzed by a 300-μm electron beam excited X-ray emission, where the X-ray intensity was 9 times stronger than 100-μm diameter e-beam.

2. Experimental

A photo of the pyroelectric crystal used for the palmtop EPMA (electron probe X-ray microanalyzer) was shown in Figure 3 of Ref.[10], a previous proceedings paper of this series of international conference (ICXOM 2011). As a first experiment after ICXOM2011, we installed a metal needle (Figure 1) on the top of the pyroelectric single crystal. However, the electron beam was not focused, and was radiated in all directions observed by a fluorescent screen and a CCD camera [13]. This experiment was set in a dark vacuum chamber evacuated by a rotary pump (1 Pa).

Then the next step of experiment, we buttered vacuum silicone grease on the surface of the pyroelectric crystal and the metal base (Figure 1) of the needle, just like buttering a bread. Since the vacuum was a low vacuum, evacuated by a rotary pump (1 Pa), and the vacuum chamber was made of quick couplings, this buttering was quite easily finished within a few minutes. Then we were surprised that the electron beam was focused on the fluorescent screen as a tiny spot as shown in Figure 2. The place of the beam spot on the fluorescent screen was always the nearest place from the tip of the needle.

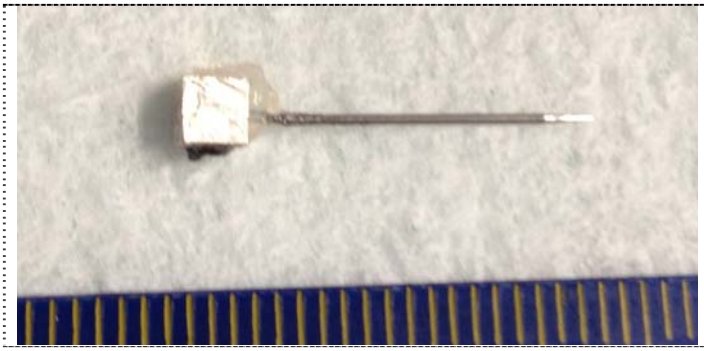

Figure 1. Photo of a needle. The base is metallic cube (3 × 3 × 3 cm^3). This photo was taken after the vacuum silicone grease was buttered. The needle length is 16 mm. The smallest scale is 1 mm.

We have tried to make much smaller the spot size, and finally the size became 100 μm diameter [12], by reducing the emission current, changing the distance between the target and the tip, length of the needle, and kind of metal (Fe, Cu, W or Au) and sharpness of the needle. The emission current could be controlled by changing the temperature gradient of the pyroelectric crystal. The emission current was most effective for the beam size. We are now making an effort to make much smaller the beam size.

The beam size was determined by the brightness read from the CCD data, as shown in Figure 3. The measured brightness was plotted, and was fitted by a Gaussian function. The full width at half maximum (FWHM) of the Gaussian function was used as the electron beam size.

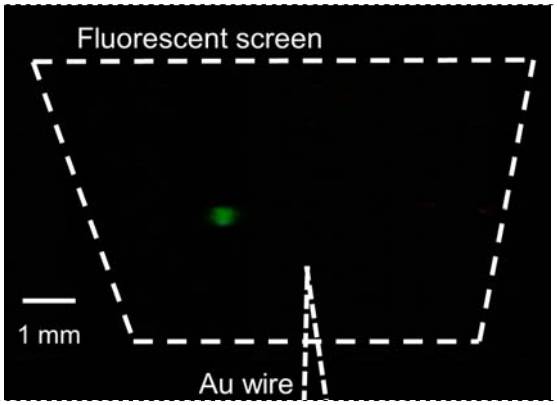

Figure 2. The beam spot observed by a fluorescent screen and by a CCD camera.

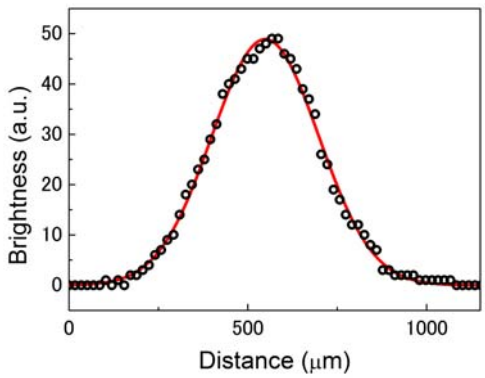

Figure 3. The recorded beam spot brightness of Figure 2, and Gaussian fitted curve. The FWHM is about 300 μm.

3. Results and discussion

The practical size of the electron beam at present is now 300 μm. However even such a relatively large spot size compared with genuine EPMA or SEM (scanning electron microscope), we can demonstrate some usage of our palmtop EPMA. Figure 4 shows a model specimen we tried. TiO_2 and MnO_2 particles of size about 100-200 μm were put on a double-sided adhesive carbon tape, but separated about a few hundreds micrometers as shown in Figure 4, which is a SEM image (JEOL JSM-5610LVS, Tokyo) of the model specimen. We placed TiO_2 particle at the beam position of our palm-top EPMA in order to measure the X-ray spectrum, and then placed the MnO_2 particle, by moving the sample stage manually. The X-ray spectra were measured through the Kapton window for 300 s each by using a Si-PIN X-ray detector (Figures 5 and 6). The X-ray intensities were strong enough for identification of the major element in 100-200 μm size particles. The present model specimen can be regarded as aerosol particles collected by an impactor though still the particle sizes were still too large.

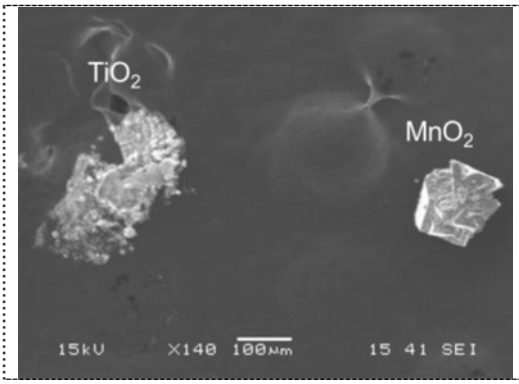

Figure 4. A secondary electron image of an SEM for two different particles in order to demonstrate the microarea analysis by the present palmtop EPMA.

By comparing Figures 5 and 6, we can find that the Ti Kα is about 60 counts while Mn Kα is 400 counts. The particle size of TiO_2 in Figure 4 was about twice as large as that of MnO_2. Therefore the electron beam when TiO_2 was measured was a little bit away from the centre of the particle. The MnO_2 spectrum was strong enough and thus the continuum X-ray spectrum was also observable. The maximum intensity of the continuum X-rays was about 4 keV, and thus the effective electron beam acceleration voltage to excite the sample X-rays was quite similar to those of the conventional EPMA or SEM-EDX, *i.e.* 15-25 kV acceleration voltage. The duration time was 300 s for each of the sample

particle, and thus the heating and cooling cycle of the Peltier device was more than one cycle to measure one X-ray spectrum.

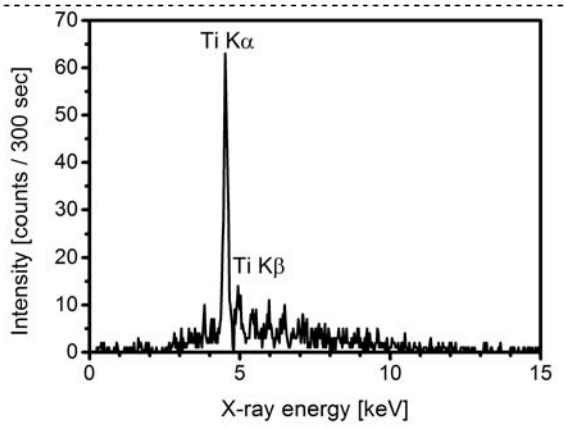

Figure 5. Measured X-ray spectrum at the beam position of TiO_2 particle in Figure 4.

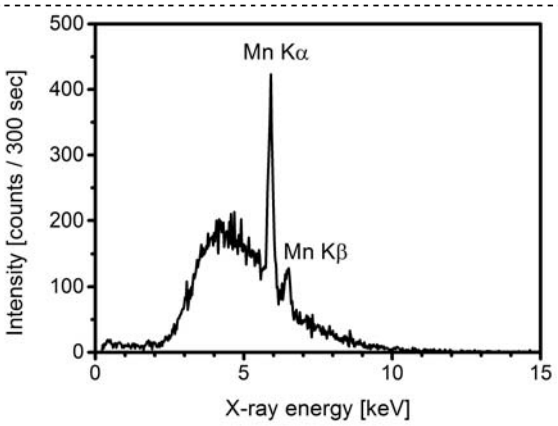

Figure 6. Measured X-ray spectrum at the beam position of MnO_2 particle in Figure 4.

4. Conclusions

We have described how easily we discovered a method of focusing an electron beam using a pyroelectric single crystal and a needle. The buttering of vacuum grease was the key but it was quite easily achieved because we have used quick-coupling vacuum components. We also demonstrated that even a palmtop size EPMA operated by 3 V electric battery except for a rotary vacuum pump, could measure X-ray spectra of a few hundreds μm size single particle within 5 minutes, but the intensities of which were from 60 to 400 counts for 5 minutes. The electron beam was generated by a metal needle buttered by vacuum silicone grease attached to a pyroelectric $LiTaO_3$ single crystal. The smallest beam size was 100 μm on the sample surface at present, but practically 300 μm diameter was easy to produce and the X-ray intensity was not too weak.

Acknowledgement

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