MICROANALYSIS OF RARE-EARTH ELEMENTS USING AN ELECTRON BEAM FROM A PYROELECTRIC CRYSTAL

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ABSTRACT
We report two methods to analyze rare-earth elements in a small area with an electron beam generated using a pyroelectric crystal. We utilized characteristic X-rays and visible lights emitted from rare-earth elements for the analysis. Only characteristic X-rays of rare-earth elements contained in a sample was detected by focusing the electron beam on an area with a diameter of 300 μm. The electron beam was focused by producing an electric field between a metal needle tip set on the pyroelectric crystal and the sample. We also analyzed rare-earth elements by utilizing visible light emitted from rare-earth elements by bombardment with non-focused electron beam on a sample (Cathodoluminescence (CL) phenomenon). We succeeded in an elemental mapping of rare-earth elements by capturing a CL image of the sample.

INTRODUCTION
Brownridge (1992) first reported that X-rays were emitted by changing the temperature of a pyroelectric crystal in vacuum. He detected Au L lines using the pyroelectric crystal of cesium nitrate (CsNO₃) and a gold foil target at 5 × 10⁻⁵ Torr. Since his discovery, pyroelectric crystals were used for researches on the miniaturization of X-ray generator (Brownridge, 2004; Geuther et al., 2005; Imashuku et al., 2012), electron beam generator (Brownridge et al., 2001; 2005), X-ray fluorescence measurement setup (Kawai et al., 2005), neutron generator (Tornow et al., 2008; Gillich et al., 2009), and mass spectrometer setup (Neidholdt et al., 2007). We also used the pyroelectric crystal for electron source and realized a portable apparatus to analyze characteristic X-rays emitted from samples (Imashuku et al., 2011). When silver and titanium plates were measured with the portable apparatus, characteristic X-rays of silver and titanium were detected as shown in Figure 1. In addition, characteristic X-rays of chromium, iron, nickel, copper, and zinc were detected. These elements came from stainless steel of the chamber wall (Cr, Fe, Ni) and brass sample holder (Cu and Zn). Thus, the electron beam bombarded on areas other than the sample. Therefore, it is difficult to carry out elemental analysis in a micrometer-sized area with the apparatus. In the present study, we tried to focus the electron beam on a sample containing rare-earth elements to prevent the detection of the elements of stainless steel and brass.
We also realized a portable cathodeluminescence (CL) spectrometer using the pyroelectric crystal (Fuyuno et al., 2012). Rare-earth elements in fluoride compounds were detected with the CL spectrometer. A spot size of the electron beam in the CL spectrometer was several millimeters. Thus, it is difficult for the CL spectrometer to determine positions of rare-earth elements in a sample owing to using an optical spectrometer and optical fiber. In the present study, we tried to carry out an elemental mapping of rare-earth elements by equipping the CL spectrometer with a CCD camera.
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EXPERIMENTAL
The details of the setup used in the present study were reported in our previous paper (Imashuku et al., 2013). A metal needle was tightened into a hole in a needle holder. A gold wire with a diameter of 0.2 mm and silver black were used as the metal needle and needle holder, respectively. The needle holder was attached on the \( z \) plane of \( \text{LiTaO}_3 \) crystal with silver paste. The surface of the needle holder was covered with high-vacuum grease. A mixture of lanthanum fluoride (LaF\(_3\)), neodymium fluoride (NdF\(_3\)), gadolinium fluoride (GdF\(_3\)), and thulium fluoride (TmF\(_3\)) powders was used for X-ray spectrum measurement. We also used a fluorescent screen (Ag-doped (Zn,Cd)S) to check an area bombarded with an electron beam. A spot size of the electron beam was evaluated from a photograph of an illuminated area of the fluorescent screen using a CCD camera as shown in Figure 2(a).
As for a CL spectrometer, the CCD camera was used instead of an optical fiber and optical spectrometer equipped with the CL spectrometer we previously reported (Fuyuno et al., 2012). The CCD camera was introduced into the sample chamber with T shape ISO quick release coupling and detachable vacuum joints as shown in Figure 2(b). Terbium fluoride (TbF\(_3\)) and GdF\(_3\) powders were used for the measurement.
In all the measurements, the LiTaO\(_3\) crystal was heated to 100 °C for 120 s using a Peltier device at 1.0 Pa before the measurements. Then, the LiTaO\(_3\) crystal was cooled to 5 °C during the measurements. X-ray spectra were measured for 120 s.

RESULTS AND DISCUSSION
Figure 3 shows energy dispersive X-ray (EDX) spectra of the mixture of LaF\(_3\), NdF\(_3\), GdF\(_3\), and TmF\(_3\) powders with and without the needle and high-vacuum grease. Without the needle on the LiTaO\(_3\) crystal, Cr, Fe, and Ni K lines from the stainless steel of the chamber and Cu K line from the brass sample holder were detected in addition to La, Nd, Gd, and Tm L lines from the sample. On the other hand, only L lines from the sample were detected by setting the needle on the LiTaO\(_3\) crystal and covering the needle holder with high-vacuum grease. This is because an electric field was produced between the needle tip and the sample holder, and the electron beam was focused on the sample. The needle tip was electrically charged faster than the surface of high

![Figure 1. EDX spectrum of Ag and Ti plates with a portable apparatus to analyze characteristic X-rays we previously realized.](image-url)
vacuum-grease because electric conductivity and dielectric constant of high-vacuum grease are lower than those of LiTaO₃. When the needle was set on the LiTaO₃ crystal without high-vacuum grease, Cr, Fe, Ni, and Cu K lines were detected in addition to L lines of the sample in the same manner without the needle on the LiTaO₃ crystal. This result indicates that an electric field was produced between the surface of the needle holder and the area including the sample holder and the wall of the chamber. Thus, it is not sufficient to set a metal needle on a pyroelectric crystal for focusing the electron beam. Prevention of electrical charging of material supporting the metal needle is also an important process.

Figure 3. EDX spectra of the mixture of LaF₃, NdF₃, GdF₃, and TmF₃ powders with and without setting the metal needle on the LiTaO₃ crystal and covering the needle holder with high-vacuum grease.
We evaluated the spot size of the electron beam by using a fluorescent screen. Figures 4(a) and (b) show photographs of the fluorescent screen during the bombardment of the electron beam with and without the needle and high-vacuum grease. Without the needle on the LiTaO₃ crystal, the whole fluorescent screen was illuminated. This result also supports that the electron beam bombarded on areas other than the sample. On the other hand, the electron beam was focused on the fluorescent screen by setting the needle on the LiTaO₃ crystal and covering the needle holder with high-vacuum grease. The distribution of brightness in Figure 4(b) is shown in Figure 4(c). The plotted data showed Gaussian distribution and the spot size of the electron beam was calculated to be 300 μm from full-width at half-maximum (FWHM).

![Image](image-url)

Figure 4. Photographs of a fluorescent screen by bombardment with the electron beam. (a) Metal needle not on the LiTaO₃ crystal. (b) Metal needle on the LiTaO₃ crystal and the needle holder covered with high-vacuum grease. (c) Distribution of brightness of the illuminated area in Figure 4(b).

We then performed an elemental mapping by utilizing CL phenomenon of rare-earth elements. Figure 5(a) and (b) show photographs of TbF₃ and GdF₃ powders using the pyroelectric CL spectrometer equipped with a CCD camera before and during bombardment with the electron beam. It was observed that TbF₃ and GdF₃ illuminated green and orange, respectively. Colors of TbF₃ and GdF₃ in Figure 5(a) corresponded with those at the strongest peaks of their CL spectra in Figure 5(c) (542 nm for TbF₃ and 595 nm for GdF₃). The whole area of TbF₃ was illuminated green. On the other hand, a part of GdF₃ was illuminated orange. This is because the luminescence intensity of GdF₃ was 10 times lower than that of TbF₃ as shown in Figure 5(c).

![Image](image-url)

Figure 5. Photographs of TbF₃ and GdF₃ powders (a) before and (b) during bombardment with the electron beam using the pyroelectric CL spectrometer equipped with a CCD camera. (c) CL spectra of TbF₃ and GdF₃ powders using the pyroelectric CL spectrometer equipped with an optical fiber and optical spectrometer.
CONCLUSIONS
We carried out two kinds of analysis of rare-earth elements by bombarding a pyroelectric crystal with an electron beam. The results obtained in the present study are summarized as follows:

1. We only detected characteristic X-rays of rare-earth elements in a sample by setting a metal needle tip set on a pyroelectric crystal and covering the surface of the needle holder with high-vacuum grease. Electric field was applied between the metal needle and the sample, and then the electron beam was focused on the sample.
2. The spot size of the focused electron beam was calculated to be 300 μm from an illuminated area of a fluorescent screen.
3. We also analyzed rare-earth elements by utilizing CL phenomenon. By capturing a CL image with a CCD camera, we determined positions of TbF₃ and GdF₃ from their colors.

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REFERENCES