

Cathodoluminescence color-zoning in the enstatite chondrite of Yamato 86004

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Enstatite is one of most important rock-forming minerals in the terrestrial and extraterrestrial materials. Luminescent enstatite has been found and investigated in enstatite chondrite (E-chondrite) and Aubrite, but in terrestrial materials. Yamato 86004 (Y-86004) belongs to E-chondrite, of which luminescent features have been scarcely investigated so far. In this study, we have conducted to evaluate the temperate history of Y-86004 during heating when the meteorite entered into the atmosphere by using cathodoluminescence (CL) of the enstatite as main constituent mineral.

The sample of Y-86004 provided by the National Institute of Polar Research (NIPR), Japan has a spherical form of ca. 4.5 mm with a thin surface of fusion crust. The polished thin sections were used for CL measurements. Color CL imaging was carried out using a cold-cathode type Luminoscope with a cooled-CCD camera. CL spectroscopy was made by a SEM-CL system, which is comprised of SEM (JEOL: JSM-5410LV) combined with a grating monochromator (OXFORD: Mono CL2), where all CL spectra were corrected for total instrumental response.

Y-86004 contains near-end-member enstatite, opaque minerals, plagioclase with albite composition and silica mineral of tridymite and glassy materials mostly in the fusion crust. Orthoenstatite (Oen) is predominant phase, which occurs as euhedral lath-shape grains, which usually protrude into or enclosed in opaque minerals. Plagioclase and silica mineral are commonly found as interstitial materials in the Oen grains. Y-86004 has no impact-shock textures (e.g., planar fractures, clinoenstatite lamellae, and mosaicism) in the constituent minerals. Detailed petrological descriptions can be found in Lin and Kimura (1998).

A color-CL imaging revealed that several CL phases are discriminated as arranged in a concentric pattern, from within outward blue CL (zone 1), light blue CL (zone 2), red CL (zone 3), where the outer rim shows no CL due to a fusion crust (zone 4). Average width of each band in the zonation is ~1.50 mm for zone 1, ~700 μm for zone 2, ~100 μm for zone 3 and ~80 μm for zone 4. Zone 1 and 2 consist of blue and light blue enstatite, dark blue tridymite, reddish-brown plagioclase, and non-CL grains of opaque minerals. These zones have similar petrographic texture, however, the distribution ratio of light-blue-CL enstatite in zone 2 is higher than that of zone 1. Zone 3 is characterized by red-CL enstatite with opaque minerals, but no tridymite. Zone 4 composed of glassy materials including blebs and opaque minerals exhibits no emission. Concentric CL zoning has been found in the meteorites for the first time.

Most enstatite with CL has similar chemical composition (e.g. FeO <1 wt.%), suggesting almost none of quenching effect by Fe²⁺ ion. The CL spectra of these enstatite show a broad emission band around 400 nm in a blue region related to a defect center (intrinsic defect center) derived during crystal growth, and a broad emission band at around 670 nm in a red region assigned to impurity centers of activated ions substituted for Mg. A spectral deconvolution of the CL in energy units using a Gaussian curve fitting specifies the emission components related to impurity centers of Cr³⁺ at 1.71 eV and Mn²⁺ at 1.86–1.91 eV in a red region, and to defect centers at 2.73, 3.13–3.15 and 3.77 eV in a blue region.

Color CL image shows four CL zones arranged in a concentric pattern. As demonstrated by Zhang et al. (1996), the CL of the enstatite in E-chondrite reflects a petrographic type and a peak temperature during thermal metamorphism in space. Y-86004 experienced a melting on the surface of a parent body possibly related to a heavy shock event (Lin and Kimura, 1998) and a rapid cooling from the melt. It is supported by the presence of tridymite, which emerges by a quenching from high temperature (867 < T < 1470 °C) (Swamy et al., 1994; Kimura et al., 2005). Therefore, all of the enstatite in Y-86004 were formed in a quenching process near surface of the parent body, suggesting that original enstatite in Y-86004 should have been Oen with a blue CL emission.

The result of polarization microscopy and Raman spectroscopy deduce two types of enstatite with blue and light-blue CL in zone 2, former of which is virtually identical to Oen with a blue emission in zone 1. The light-blue enstatite has two defect centers of Defect I and Defect II, whereas the enstatite is identified as Oen. It is characterized by the Defect II not detected in the blue enstatite. In as much as the meteorite experienced a flash heating above the melting point of the enstatite, the heating and cooling process during a falling through the atmosphere might affect a creation of defect center (Defect II) and alteration of existing defect (Defect I). Therefore, according to Gasparik (1990), some portion of the enstatite in zone 2 probably might have experienced a phase transition from Oen to protoenstatite (Pen) during a flash heating, which occurs at near 1273 K. In this case, the enstatite with blue CL considerably survived from the original enstatite the same to one in zone 1, suggesting the

temperature at around 1273 K. When Pen is rapidly cooled, the phase transition involves physical stress, which might create defect center (Defect II) in the structure.

The enstatite in zone 3 is identified as low-temperature-clinoenstatite (LT-Cen) by a Raman spectroscopy. This result is also supported by the peak energy of the emission component related to Mn^{2+} impurity. According to Ohgo et al. (2015), CL feature of red emission is useful to distinguish between Oen and LT-Cen phases. In the terrestrial enstatite, Oen has an emission component of impurity Mn^{2+} ion at 1.85 eV, but at 1.90 eV for LT-Cen. The enstatite in zone 3 has a corresponding component at 1.92 eV, suggesting identification of LT-Cen. According to Gasparik (1990), when the Oen experienced high temperature at a temperature near the melting point of enstatite, it transfers from Oen and Pen to high-temperature-clinoenstatite (HT-Cen), which is stable near the melting point at 1831 K. Therefore, red-CL enstatite in zone 3 might be formed by a rapid quenching from HT-Cen at around 1831 K due to structural similarity between LT-Cen and HT-Cen. The enstatite in zone 3 has almost none of blue emission related to the defects centers, implying the elimination of lattice defect by the elevated temperature near the melting point without structural stress in the transition between HT-Cen and Oen.

Y-86004 suffered a heavy ablation on its surface, which took away melting materials from the meteorite body in a short period. Zone 4 was formed during such ablation with amorphousization of enstatite-rich materials at the surface of the meteorite. Therefore, the surface of the meteorite has been exposed at and above the temperature of a melting point (>1831 K) of the enstatite.

Y-86004 was abruptly heated for a short time when it entered the earth's atmosphere, and rapidly quenched in the Antarctic ice immediately after its falling. In this study, the enstatite with a background of previous phases corresponding to the elevated temperatures can be characterized by CL imaging and spectroscopy, which reveals a mechanism of CL-color zonation found in Y-86004.

The result of CL examination suggests that zone 2 in the range of the depth from surface between ~ 200 and ~ 900 μm might be heated at around 1273 K, which corresponds to the transition temperature from Oen to Pen. Zone 1 was not heated up to 1273 K due to the presence of only Oen with a blue CL. Zone 3 between ~ 100 and ~ 200 μm might be expected to be heated up to the melting point of the enstatite at 1831 K due to the presence of HT-Cen supposed by the CL spectroscopy. The elevated temperatures in the zones estimated from the result of CL analysis might be consistent with the temperatures in corresponding depth from the surface calculated from the duration of 20 second, which is able to be adapted due to allowable values compared to previously obtained ones.

Conclusively, an abrupt heating of the spherical meteorite during atmospheric entry might cause the difference in peak temperatures depending on the depth from the surface due to a sudden increase in the temperature during a short time, which should eliminate the defect centers for a blue emission in response to the depth from the surface, resulting in the CL zoning in the section of the meteorite.