

Determination of channel CO₂ contents in random cordierite crystals using Raman spectroscopy

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Cordierite is a common metamorphic mineral, which entraps volatiles such as CO₂, H₂O in its channel, consisting of six-membered rings of (Al, Si) O₄. Carbon dioxide is orientated linearly along the *a*-axis in cordierite channel, and therefore the peak intensity of CO₂ at 1383cm⁻¹ obtained from Raman spectroscopy varies considerably depending on the crystal orientation of cordierite. Kaindl et al. (2006) has shown that the Raman spectral intensity of CO₂ band in crystallographically oriented cordierite grains can be used to estimate the CO₂ contents. These previous studies suggested the importance of applying a correction on the effect of crystal orientation for the determination of intrinsic contents of CO₂ in randomly oriented cordierite crystals. The purpose of this study is to reveal the relationship between Raman spectral patterns and crystal orientation of cordierite, and to construct a new method for the determination of CO₂ content in cordierite using Raman spectroscopy.

For the identification of crystal orientation of cordierite, euhedral cordierite crystals, from the volcanic ash deposit in the Takiga swamp, Gunma Prefecture, Japan were used to prepare crystallographically oriented thin sections, and examined in detail using micro-Raman spectroscopy. In addition, to examine the effect of crystal orientation to the intensity of CO₂ for its determination, two cordierite samples were analyzed. One is cordierite crystal from a pelitic cordierite-bearing from gneisses in the Kerala Khondalite Belt (KKB), southern India, and the other is a standard cordierite with known CO₂ contents (SH). Since Raman spectral intensity also depends on polarization of the incident laser, Raman spectra were obtained by rotating the sample at an interval of 10°. The crystal orientation of cordierite was cross-checked by using 5-axis universal stage and conoscopic figures.

Raman spectral patterns obtained for (001), (100) and (010) crystallographic planes change cyclically with the polarization of incident laser. We selected six peaks of cordierite (1: 554 cm⁻¹, 2: 575 cm⁻¹, 3: 670 cm⁻¹, 4: 970 cm⁻¹, 5: 1010 cm⁻¹, 6: 1180 cm⁻¹) for a detailed analysis. The intensity of peak-5 and peak-6 changed systematically when compared with other peaks, and so these peaks were used for the identification of crystal orientation. The intensity of peak-3 did not change and we used it as a normalizing peak for instrumental intensity variations. The intensity ratio of peak-5/ peak-3 versus intensity ratio of peak-6/ peak-3 (I_5/I_3 vs. I_6/I_3) in (001), (100) and (010) plane showed a linear relation. The value of other oriented cordierite crystals and random ones fell within this range. Therefore, it is possible to identify the crystal orientation of cordierite using the relation of I_5/I_3 vs. I_6/I_3 . The cyclic patterns can be expressed mathematically using a combination of sine curves, where it is possible to determine the crystal orientation. Furthermore, the peak intensity of CO₂ for SH cordierite with known CO₂ contents also showed cyclic variations, similar to the periodicity of the peak-6 in the crystallographically oriented crystals. Accordingly, using the mathematical expression we could retrieve the maximum peak intensity of CO₂ at 1383cm⁻¹ from a random crystal, which was then used for determining the CO₂ contents of unknown cordierite crystals.

References

Kaindl, R., Tropper, P. and Deibl, I (2006) A semi-quantitative technique for determination of CO₂

in cordierite by Raman spectroscopy in thin sections. *European Journal of Mineralogy*, 18, 331-335

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