Cathodoluminescence Response of Barite at Room and Liquid Nitrogen Temperatures

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Rare earth element (REE) abundances in the Elk Creek carbonatite, Nebraska USA, is comparable to ore grade enrichment in carbonatite-hosted REE deposits [1]. Petrographic examination of textures documents a complex history of crystallization, brecciation, recrystallization, oxidation, and near surface alteration. Barite (BaSO₄) is present in most units, including REE-enriched zones, such that it may provide important constraints on processes that lead to ore-grade enrichment of carbonatites. Barite-containing samples from different temperature regimes within the deposit were chosen to determine if the cathodoluminescence (CL) response at room and liquid nitrogen (LN) temperatures provide clues as to the processes by which REEs were enriched within the deposit and possible contributions of REE to the CL response.

Room temperature (sample stage) CL analyses on petrographic thin sections were conducted at the Denver Microbeam Laboratory, U.S. Geological Survey (USGS) on a JEOL 8530F Plus. LN temperature (sample stage) CL analyses on an ~8 mm diameter polished plug from the matching billet of the thin section were conducted at the Microbeam Laboratory, CSIRO Minerals also on a JEOL 8530F Classic. Further details of the analytical parameters are summarized in Table 1. CL data collection and data reduction were performed with the xCLent Analysis software package [2]. Quantitative point analyses of barite (Ba, Sr, Ce, and S) were conducted at the USGS on the same instrument as the CL analyses operating at 15 kV accelerating voltage, 50 nA beam current, and 20 seconds on the peak and background.

Results of the LN and room temperature acquisitions are presented in Figure 1. Quartz optics from the room temperature analysis at USGS allow collection of signals beyond 4 eV whereas the glass optics used at CSIRO have a strong absorption starting around 3.54eV (350nm). The background of the room temperature spectrum is higher at lower energies than the LN spectrum and the position of the peak near 3 eV is different for the two temperatures. These changes are likely due to reduced thermal vibrations caused by the LN environment thus accentuating the main transitions. Similar intensity increases for quartz, especially poorly crystalline quartz, associated with low temperature formation have also been observed [3]. The effect of reducing the thermal vibrations results in more apparent detail visible in the peak intensity distributions from the LN acquisition than the room temperature acquisition (Figure 1). The increased detail reveals original barite cores displaying oscillatory zoning with subsequent dissolution and additional barite growth textures, similar to those found in zircons. The peak in barite at room temperature $\sim 3.9 \text{ eV}$ (318nm) may also be attributed to either an intrinsic (SO₄)²⁻ or the presence of Ti³⁺ [4]. The peak at ~2.25eV (550nm) is most likely associated with Mn²⁺originally attributed by Tarashchan [4] and subsequently confirmed by Gaft et al. [5]. The peak observed at ~ 3.02eV (410nm) in the LN CL spectra may be attributed to Ca replacement in the barite structure [5]. Attempts to correlate peak intensities to the measured trace element (Sr and Ce) abundances is currently unsuccessful [6].



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Table 1. Comparison of operating parameters for the liquid nitrogen and room temperature studies of barite cathodoluminescence.

Parameter	CSIRO	USGS
Stage temperature	Liquid nitrogen	Room
Spectrometer range (nm)	QEPro, 199-972	QEPro, 197-985
Spectrometer channels	1024	1024
Entrance aperture (um)	200	300
Sample Coating (nm)	Ir, ~2	C, ~10
Probe optics	Glass	Quartz
Accelerating voltage (kV)	20	10
Beam current (nA)	30.4	30
Dwell (ms)	40	30
Step size (um)	1.00 x 1.00	1.00 x 1.00

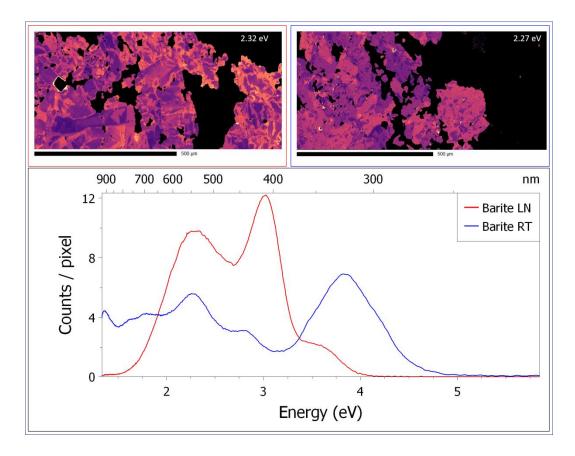


Figure 1. Intensity distribution of the 2.32 eV and 2.27 eV peaks from liquid nitrogen (LN) {top left} and room temperature (RT) analyses {top right}. The bottom pane displays the sum CL spectra of barite for the liquid nitrogen (red) and room temperature (blue) acquisitions.

References:

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- [4] AN Tarashchan, Naukova dumka (in Russian) (1978).
- [5] ML Gaft et al., Phys Chem Minerals 11 (1985), p. 255.
- [6] Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.