Melt inclusions in emerald from the Habachtal/Austria after re-homogenization at 700°C and two kbar

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Abstract

With homogenization experiment (700°C, 2 kbar) on polished thin sections of emeralds from the Habachtal we demonstrate that the primary crystallization of emerald started at significantly

higher temperatures than previously assumed. This experiment confirms the prediction in the precursor publication on this subject. Supercritical conditions around 700°C and 5 kbar fix the start point for the emerald crystallization.

Keywords

Emerald, melt inclusions, homogenization under pressure, conditions of crystallization

Introduction

Thomas et al. (2020) demonstrated for the first time melt inclusions in the emerald of the Habachtal/Austria. In that paper, the authors used well-ordered graphite and extremely fluid-rich melt inclusions for an estimation of the trapping conditions. According to that study, we demonstrated that the emerald mineralization in the Habachtal was primarily from an extremely fluid-rich pegmatite-like aluminosilicate melt under supercritical conditions, at high temperatures and moderate pressures (~700°C, 5 kbar). These results contradict all previous work (e.g., Nwe and Grundmann, 1990).

Melt inclusions which show the characteristic phase composition are mostly small and rare and were not noticed by the previous scientists. By careful analyses of the melt inclusions, a preliminary pseudo-binary solvus could be deduced. For the solvus crest, a temperature of 698°C and a water concentration of 27.7 % was estimated. Furthermore, we could show that $MgCO_3$ in the melt inclusions correlate very well with the bulk water concentration of the corresponding melt inclusions. $MgCO_3$ vs. H_2O show an excellent Lorentzian distribution, which is a strong

proof for the supercritical conditions and show a significant water loss by counter diffusion (see Thomas et al. in preparation).

Sample and methods

For the study of melt inclusions in emerald we have used double-polished thick sections, about 300 µm thick, from a crystal (about 15 x 4 mm) in biotite schist from the gallery D of the Habachtal mine/Austria (Fig. 1 in Thomas et al. 2020).

Methods

Homogenization experiment

For the homogenization of the melt inclusions we used the hydrothermal rapid-quench pressure vessel technic (see Thomas et al. 2009). A double-polished plate of emerald were placed into an Au-capsule (5 x 30 mm) with a fixed amount of pure water. The inclusions were re-melted at 700°C and 2 kbar at a run time of 20 hours. The used temperature of 700°C was chosen from the estimated solvus temperature in Thomas et al. 2020.

Raman spectroscopy

Raman spectra were recorded with the En*S*pectr Raman microscope RamMics M532 in the spectral range of 80 - 4000 cm^{-1} using a 50 mW single mode 532 nm laser, an entrance aperture of 20 µm, a holographic grating of 1800 g/mm, and a spectral resolution of 4 - 6 cm^{-1}.

Results

In order to validate of our results presented in Thomas et al. 2020, we have performed a hydrothermal rapid quench experiment (700°C, 2 kbar). From this experiment result a critical temperature of 700°C and a water concentration of 31.6 ± 2.4 %. That is an excellent confirmation of our prediction. Figure 1 shows a typical water-rich melt inclusion in emerald from the Habachtal after re-homogenization and quenching. The phase composition of this melt inclusions is depicted for clarification (G – glass, L -solution, V – vapor).

Figure 2 show typical melt inclusions trapped near the solvus crest of about 700°C. According to Raman spectroscopy the inclusions contain an alkali carbonate-rich glass and a carbonate-rich fluid, as well as a vapor bubble (with traces of CO_2). Figures a) and b) represent near-critical melt inclusions and c) and d) are water-rich type-A and type-B melt inclusions, which were trapped at slightly lower temperatures.

In addition to the typical melt inclusions in emerald shown in Figs. 1 and 2 we have found several large glassy melt inclusions (Fig. 3) containing a water-bearing glass and a large vapor bubble. In these inclusions we found nahcolite crystals [$NaHCO_3$]. Given the relatively high concentration of nahcolite (about 6.5 % (vol/vol)), demonstrated by strong Raman bands at 225.4 and 1045, medium bands at 1266, and 1432 cm^{-1}) the trapped melt was originally alkali carbonate-rich, which we know from the $MgCO_3$-daughter crystals in the unheated melt inclusions at room-temperature. However, as already discussed in Thomas et al. 2020, additional $MgCO_3$ also formed as a secondary phase, because of the pervasive presence of Mg^{2+} ions.

The Raman spectra of the inclusion glass are difficult to interpret, because no relevant crystallized Be-mineral phase in the glass could be found. A very strong and polarizable Raman band at 568 cm^{-1} is cautiously interpreted as Na-Li-Be tetrafluoride in relatively high concentration in the glass. According to Quist et al. (1972) and Toth et al. (1973) the Raman band at 568 cm^{-1} can be assigned to $\nu_1(BeF_4^{2-})$ species. The bands at 354, 436, and 467 cm^{-1} represent $Be(OH)_2$ components. Strong and broad bands between 800 and 1000 cm^{-1} 977 cm^{-1} are possible evidence of the presence of boric acid (880 cm^{-1}) and alkali-borates. Figure 4 gives the Raman spectra of the inclusion glass in comparison with the inclusion host (emerald). The steeply rising background in the low frequency range is typical for all the studied glassy melt inclusions.

Between the glass-vapor phase boundary of some large melt inclusions we also detected small zircon crystals with clear indications that this crystals were grown in the melt and not trapped accidentally, showing that melt can solve compounds like zircons at about 700°C.

Discussion

The homogenization experiment on melt inclusions in emerald have confirmed our prediction regarding the genesis of the emerald from the Habachtal/Austria presented in Thomas et al. (2020). The crystallization started at about 700°C and 5 kbar. The proof of the solvus with the crest at 700°C and a water concentration of about 32 % demand therefore a general rethinking regarding the formation of this deposit.

References

Nwe YY, Grundmann G (1990) Evolution of metamorphic fluids in shear zones: the record from the emerald of Habachtal, Tauern window, Austria. Lithos 25:281-304

Quist AS, Bates JB, Boyd GE (1972) Raman spectra of tetrafluoroberyllate ion in molten sodium fluoride and lithium fluoride to 686°C. J Phys Chem. 76:78-83

Thomas R, Davidson P, Rericha A (2020) Emerald from the Habachtal: new observations. Miner Petrol. 114:161-173

Thomas R, Davidson P, Rhede D, Leh M (2009) The miarolitic pegmatites from Königshain: a contribution to understanding the genesis of pegmatites. Contrib Mineral Petrol. 157:505-523

Toth LM, Bates JB, Boyd GE (1973) Raman spectra of $Be_2F_7^{3-}$ and higher polymers of beryllium fluorides in the crystalline and molten state. J Phys Chem, 77/2, 216-221

Wolf, G.H., McMillan, P.F. (1995) Pressure effects on silicate melt structure and properties. In: Reviews in Mineralogy, Mineralogical Society of America, Vol. 32, 11: 505-561

Figure captions:

Figure 1 Near-critical melt inclusion in emerald from the Habachtal: G – glass, L – carbonate-rich solution, V – vapor phase

Figure 2 Typical melt inclusions in emerald trapped near the solvus crest of about 700°C. Figures a) and b) represent near-critical melt inclusions and c) and d) are water-rich type-A and type-B melt inclusions, which were trapped at slightly lower temperatures.

Figure 3 A large melt inclusion containing a water-rich glass (G), alkali carbonate-rich solution (L) and CO_2-poor vapor phase. The marked ellipse shows the poorly

visible nahcolite [$NaHCO_3$] crystal. It is possible that this type of inclusion lost water after re-homogenization via diffusion through micro-channels in the beryl.

Figure 4 Raman spectra of the melt inclusion glass of a re-homogenized melt inclusion of the type shown in Fig. 3. The spectrum of emerald (host) is shown for comparison. Note: all shown very water-rich melt inclusions cannot be quenched to a homogeneous glass. Brc – brucite, Brl – beryl, mul – mullite.

Fig. 1

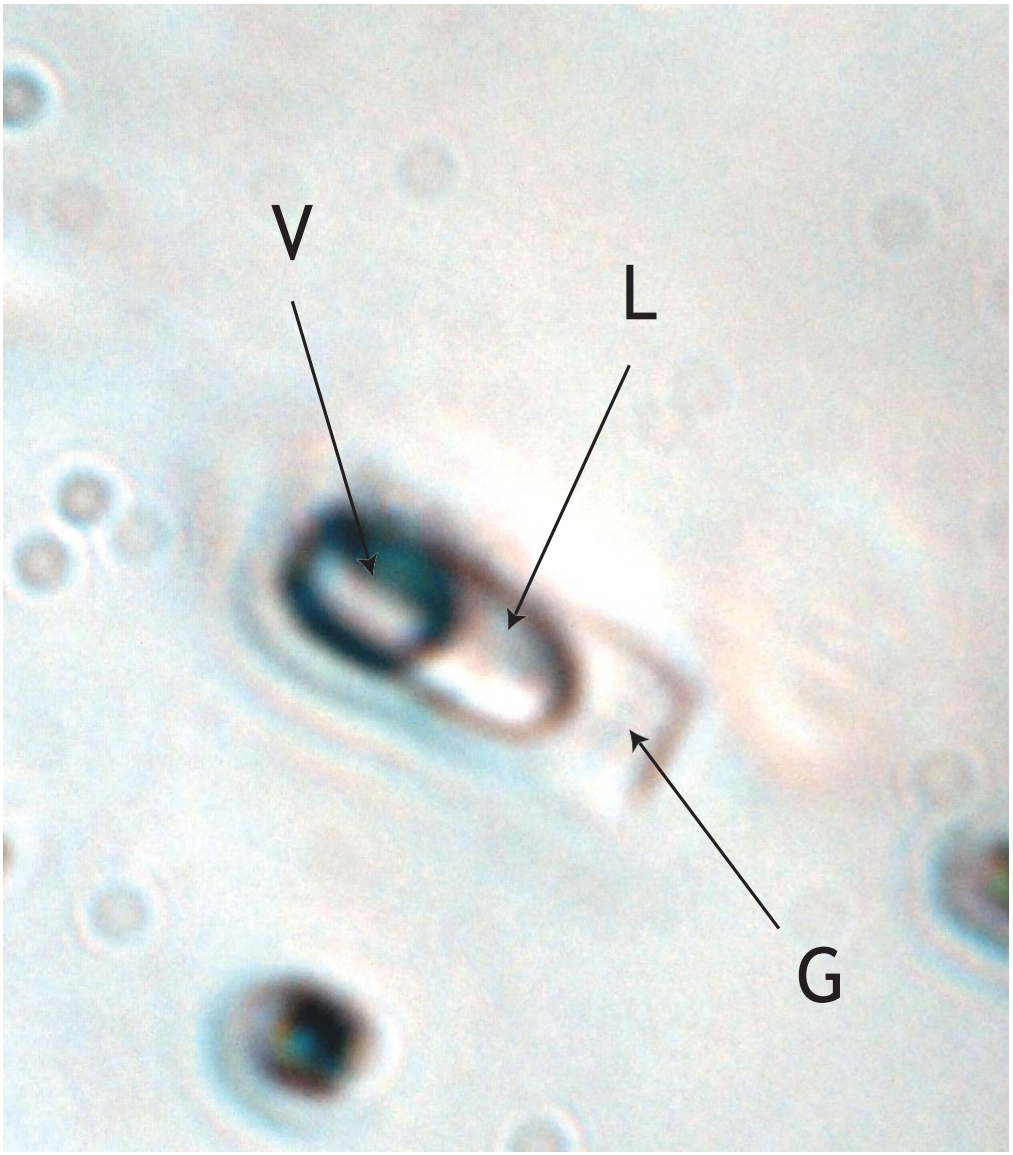


Fig. 2

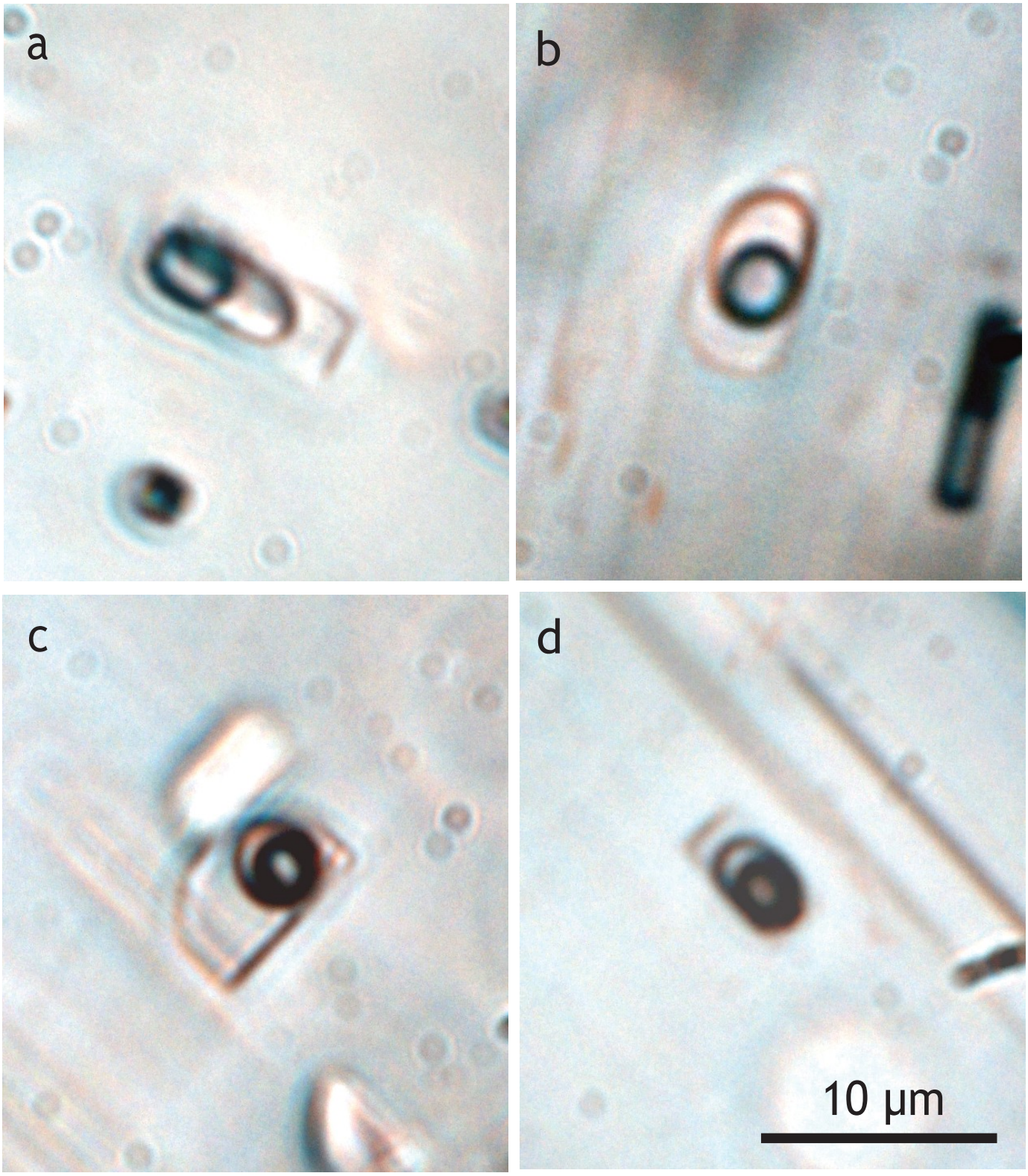


Fig. 3

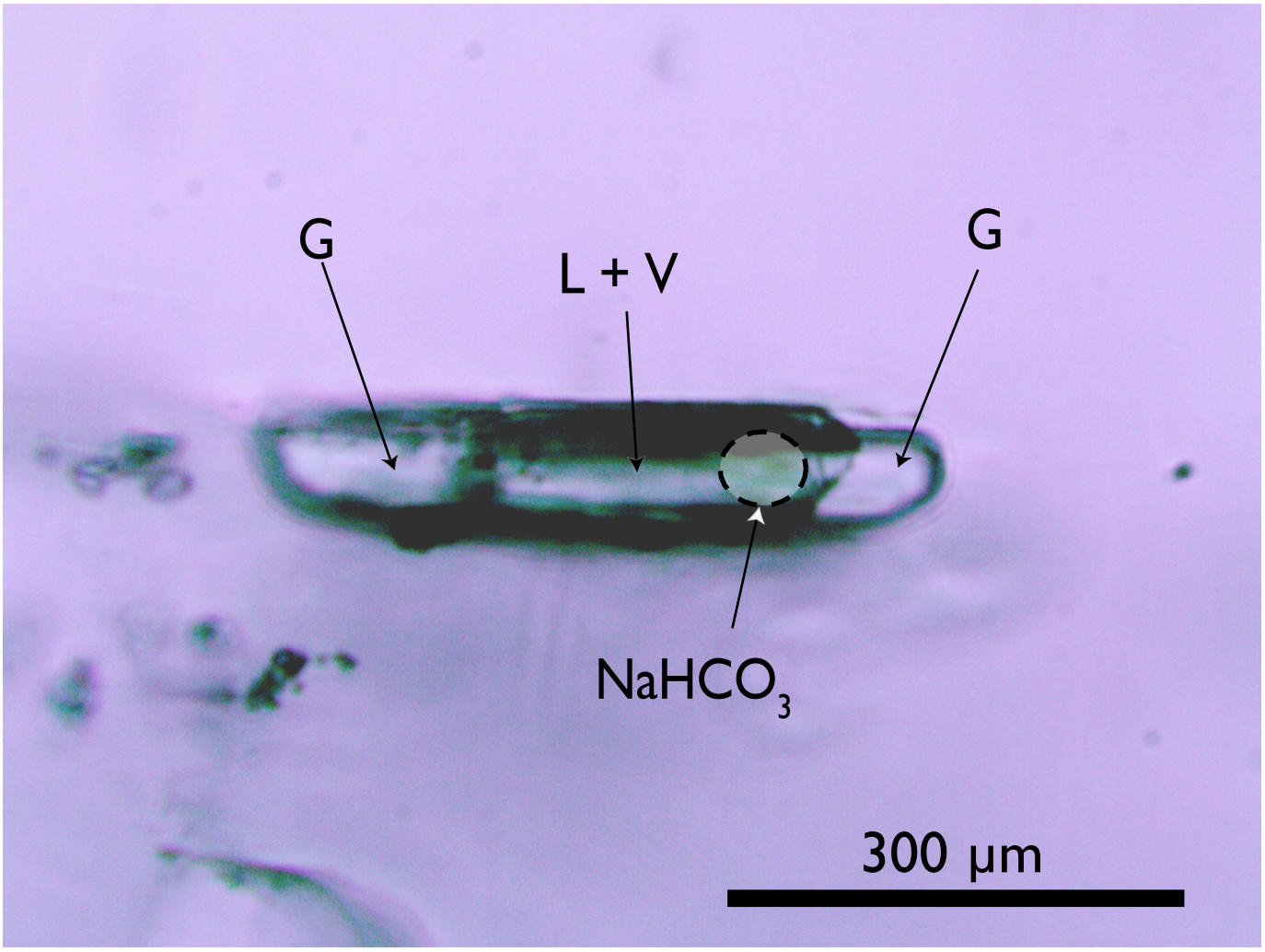


Fig. 4a

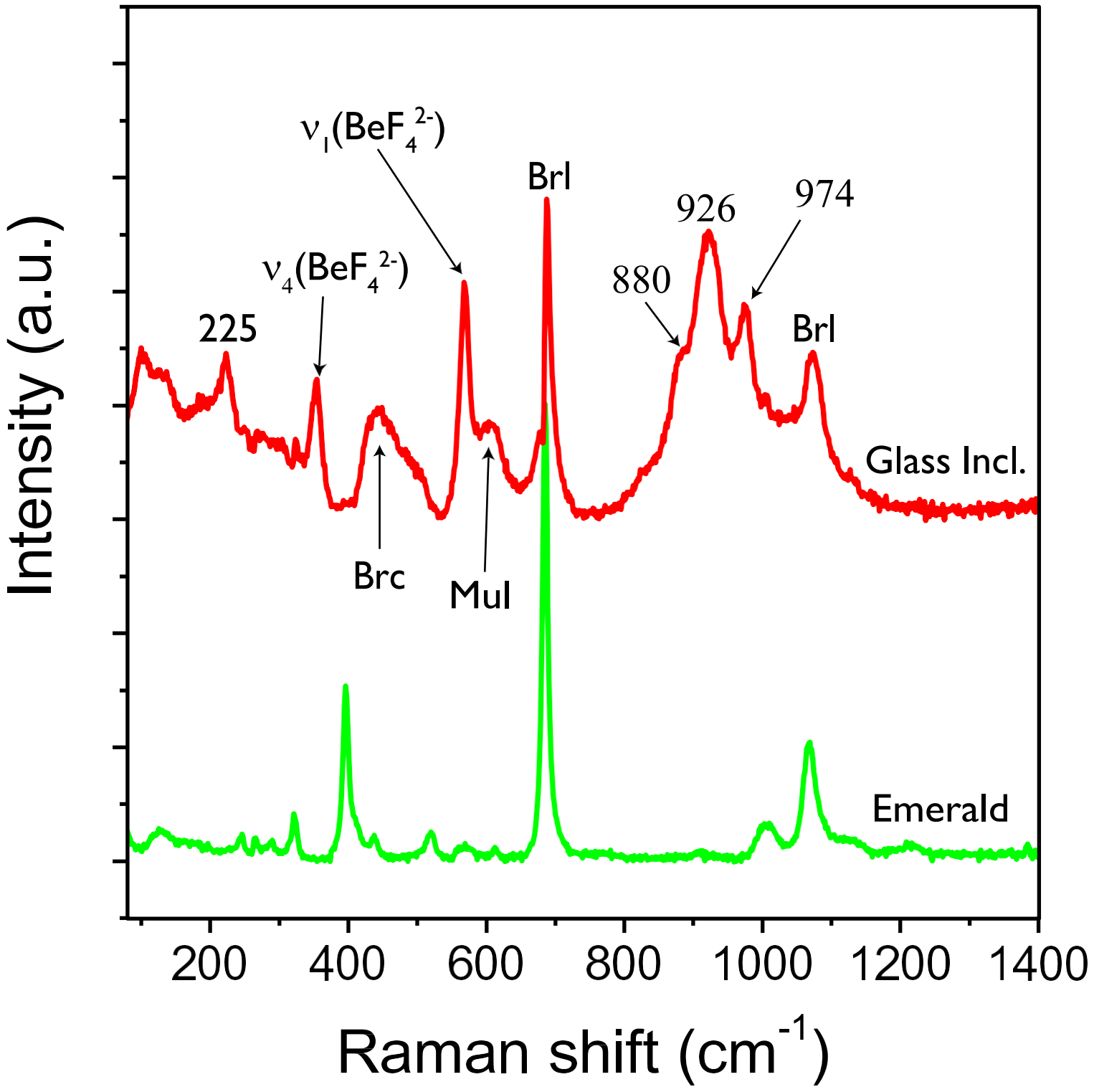
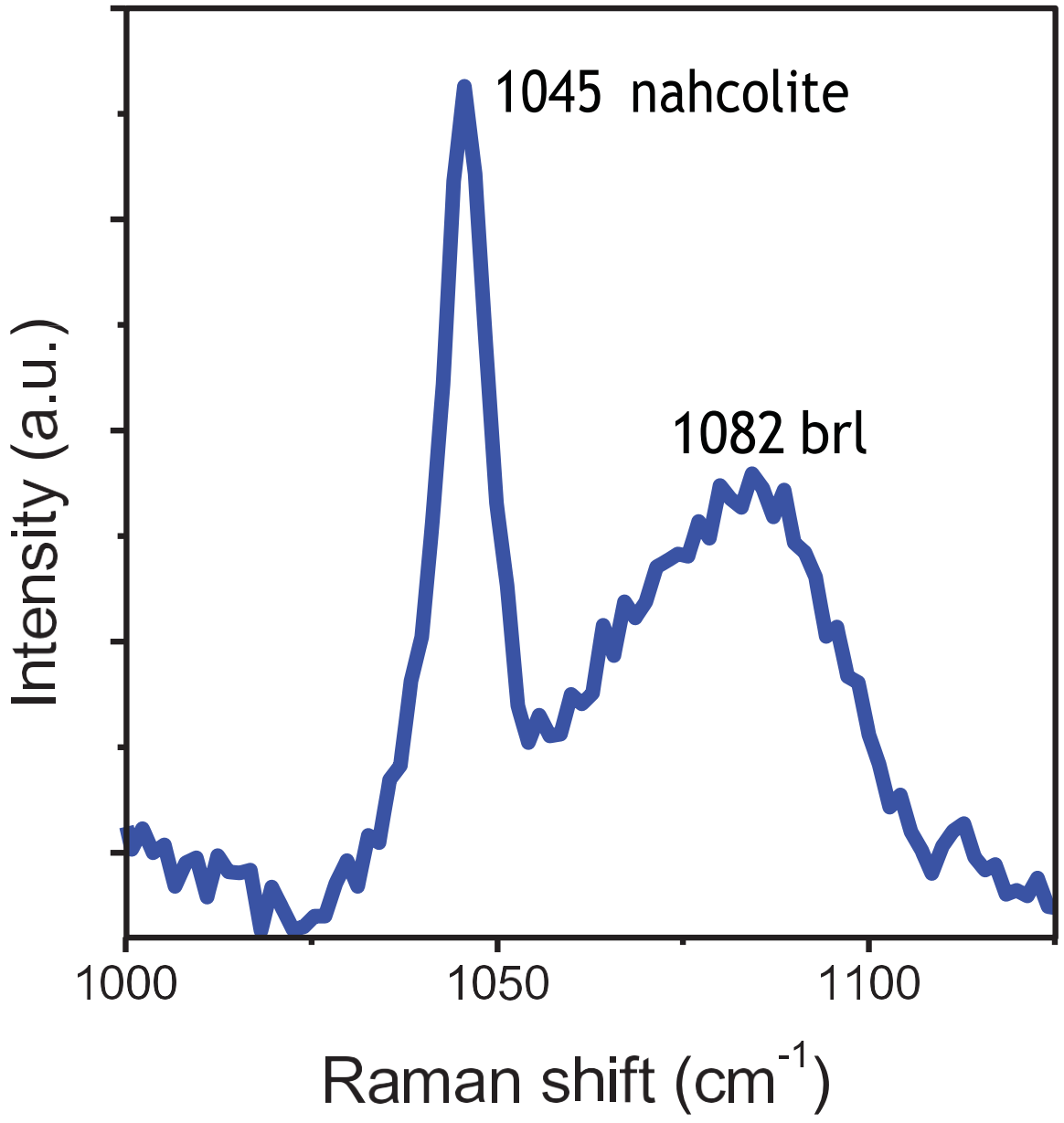

$\nu_1(BeF_4^{2-})$
$\nu_4(BeF_4^{2-})$
225
Brc
Mul
Brl
880
926
974
Brl
Glass Incl.
Emerald
Intensity (a.u.)
200
400
600
800
1000
1200
1400
Raman shift (cm^{-1})

Fig. 4b


1045 nahcolite
1082 brl
Intensity (a.u.)
1000
1050
1100
Raman shift (cm-1)